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Application of 3-D fluorescence

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Application of 3-D Fluorescence: Characterization of Natural Organic Matter in Natural Water and Water Purification Systems

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ABSTRACT

Natural organic matter (NOM) found in water sources is broadly defined as a mixture of polyfunctional organic molecules, characterized by its complex structure and paramount influence on water quality. Because the inevitable release of pollutants into aquatic environments due to an ineffective control of industrial and agricultural pollution, the interaction evaluations of NOM with heavy metals, nanoparticles, organic pollutants and other pollutants in the aquatic environment, are rapidly increased. The three-dimension (3-D) fluorescence has a potential to reveal the interaction mechanisms between NOM and pollutants as well as the source of NOM pollution. In water purification engineering system, the 3-D fluorescence can indicate the variations of NOM composition and gives an effective prediction of water quality as well as the underline water purification mechanisms. Inadequately treated NOM is a cause of precursors of disinfection byproducts (DBPs), posing a potential threat to human health. Effective control and measurement/evaluation of NOM have long been an important factor in prevention of water pollution. Overall, 3-D fluorescence allows for a rapid identification of organic components thus indicating possible sources of water pollution, mechanisms of pollutant interactions, and possible DBPs formed during conventional treatment of this water. This article reviews the 3-D fluorescence characteristics of NOM in natural water and typical water purification systems. The 3-D fluorescence was effective for indicateing the variabilities in NOM composition and chemistry thus providing a better understanding of NOM in natural water system and water engineering system.

1. Introduction

Natural organic matter (NOM) is an essential component of aquatic environments. The chemical nature and composition of NOM, as well as its efficient removal are a major factor influencing the design and operation of water treatment plants. There is an urgent need for rapid assessment of quality of the water environment, meeting the needs of engineering system design. Three-dimension fluorescence (denoted as 3-D fluorescence) monitoring of NOM (denoted as 3-DFMM) using fluorescence excitation-emission matrix spectroscopy as a monitoring method has been widely used in water treatment processes (WTPs) to assess NOM chemical structure [1,2]. The NOM is a heterogeneous mixture of the organic molecules, originating from a range of sources [3]. Analyzing its chemical nature by the conventional methods, such as high performance size exclusion chromatography, Fourier transform infrared spectroscopy and nuclear magnetic resonance, is not cost-effective and is time consuming, which can be an issue for online monitoring at WTPs. However, using a 3-D fluorescence method to characterize NOM can provide a rapid, sensitive and simple approach with lower cost and simple sample preparation, and is potentially suitable for online monitoring of NOM [4-6]. In addition to the advantage of its low cost and simple operation, the 3-D fluorescence method has the advantage of separation of different fractions of NOM, which is beneficial to the understanding of their physico-chemical, and biological behaviors in the aquatic environments. For example, these fractions can often be identified and used to establish the source of organic pollution in the aquatic environments [7-9], and for quantifying NOM and associated products resulting from the reaction of NOM and disinfectants [10,11]. Because NOM originates from soil, plant and animal residues, and human activities, its chemical composition and molecular structure is complex and site-specific, thus its chemical properties vary not only from one site to another, but there are also seasonal changes in the same water source. The NOM has been known to produce a significant fluorescence signal while generating many kinds of characteristic peaks, which correspond to specific organic material sources. Among them, typical fluorescence peaks (e.g., corresponding to humic, fulvic and protein-like molecules) have been identified [12]. It is noteworthy that some NOM fractions correlate well with generic water quality parameters such as Total Organic Carbon (TOC). While TOC is considered as a parameter providing quantitative information about NOM content, it does not provide any information about its chemical characteristics. The 3-D fluorescence method may develop as a critical indicator for assessing the chemical nature of organic matter, with full potential to improve the efficiency of water treatment plants [13].

Organic compounds may be released into aquatic environment (and drinking water) by four major sources [14]: as natural organic matter (NOM), compounds originating from human activities, compounds formed by chemical reactions occurring during disinfection, and compounds formed or added during the treatment and transmission of water. Human activities are becoming increasingly important as a source of organic compounds and include organic chemicals from direct industrial, agricultural and municipal effluents. Both groundwater and surface water may be contaminated . The major sources of organic pollutants are industries utilizing large quantities of chemicals in the manufacturing process. Usually the organic compounds used in industry are synthetic organic compounds (SOCs) which are commonly found in water bodies at low concentrations. However, even at low concentrations they are of significant health concern. Common examples of SOCs found in water are: Benzene, Dichlorobenzenes, Methyl tert-butyl ether (MTBE), Toluene, Xylenes. Agricultural pesticides form an important class of organic pollutants and are widely dispersed in the environment. Some examples of herbicides typically of concern in WTPs : Atrazine, Cyanzine, Metribuzin. Despite the effectiveness of secondary treatment an increasing range of new organic compounds are detected in the effluents from treatment plants, these 'emerging organic compounds', originate from veterinary and human antibiotics, human drugs (prescription and nonprescription), and industrial and household wastewater products [14].

In order to improve water treatment efficiency and to investigate relevant mechanisms involved, fundamental research onon colloidal particles and the distribution and transformation of organics in the aquatic environments is critical for explaining the characteristics and the corresponding variation in quality in water bodies [15]. The NOM found in aquatic systems contains abroad spectrum of organic compounds, such as humic substances, proteins, polysaccharides and other substances. The resulting profile is closely related to the design of WTPs as well as other factors such as the efficiency of water treatment and the formation of disinfection byproducts (DBPs) [16]. The observation of molecular fluorescence can be used to reveal their chemical characteristics. Analyzing the correlation between NOM fractions and the DBPs can be a useful tool in understanding the transformation of organic molecules in WTPs. In the last decade, 3-D fluorescence have been extensively studied in the assessment of WTPs, but there is lack of understanding of it's the fundamental properties of , 3-D fluorescence response and the characterization of NOM.

Analyzing chemical nature of NOM via 3-D fluorescence offers an opportunity to improve the efficiency of monitoring and control of WTPs. This short review deals with the characteristics of the 3-D fluorescence of NOM and a specific environmental application of 3-DFMM in monitoring natural organic matter in WTPs

operations, which include the chemical/biological oxidation, coagulation-flocculation process and membrane/biological treatment process.

2. Analytical process and environmental influence

2.1. 3-D fluorescence spectra

The 3-D fluorescence spectra of NOM from a variety of sources, provides information about its chemical characteristics, which could be used for optimizing the performance of water treatment plants. The 3-D fluorescence is a three-dimensional contour plot, which can be obtained from a fixed scanning speed and varying excitation (EX) and emission wavelength (EM) at a fixed interval step. For analysis of data from 3-D fluorescence, although the collection of data is a simple operational process, there are some common interference resulting from the environmental conditions or instruments, which distort the actual fluorescence intensity. Therefore, spectrum correction is required to eliminate the interference. For instance, due to characteristics of instrumental components (e.g., excitation light source, monochromator and detector), the spectra are likely to be distorted. Using Rhodamine B as a quantum counter to correct spectroscopy intensity within the specific wavelength range of an excitation and emission wavelength can be a way of mitigating this interference [5]. The 3-D fluorescence include Rayleigh and Raman scattering (see Figure 1), which affects the analysis of 3-D fluorescence, especially modeling the 3-D fluorescence data. As seen from the Figure 1, larger Rayleigh scattering signal occurs, and the peak positions change with their excitation wavelength. These fluorescence data require some form of normalization because if they are modeled with parallel factor analysis (PARAFAC) to obtain fluorescence components, a new factor would be needed for each excitation wavelength [17]. Subtracting the background fluorescence of a pure water blank from emission spectrum of an observed sample is an important step in the pretreatment of 3-D fluorescence data in order to remove the majority of Raman scattering bands. The potential method for removing the interference of the scattering including both Rayleigh and Raman scattering can be completed using interpolation in the areas affected by the Rayleigh and Raman scatter, a method developed by Bahram, et al. [18].
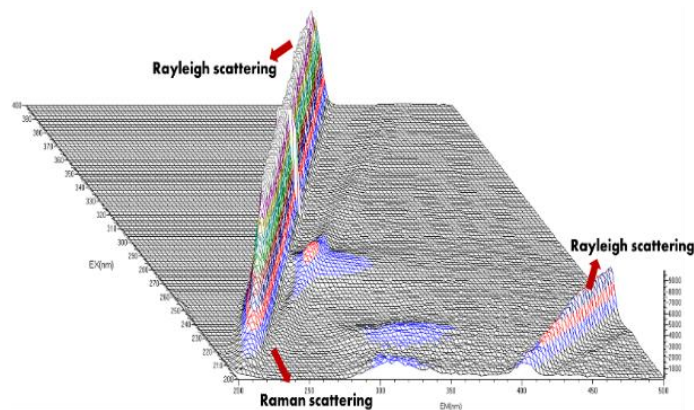
Figure 1 3-D fluorescence of dissolved organic matter of artificial lake (Artificial lake was located on the Hunan University of Science and Technology campus, named as Yuhu Lake) (Self-scanned in the laboratory).
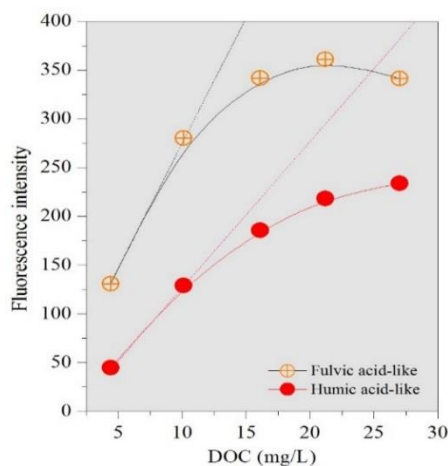
Figure 2 Fluorescence intensity inner filter effect on two components: fulvic acid-like and humic acid-like (the components were extracted from Aldrich humic acids) (Self-plotted in the laboratory).

In addition, during analysis of Dissolved Organic Matter (DOM) fluorescence, Dissolved Organic Carbon (DOC) is proportional to fluorescence intensities of several specific fluorescent fractions. However, with the increase of DOC concentration, the fluorescence intensities of components potentially deviates from a linear relationship (see Figure 2). This kind of optical phenomenon involves a significant decrease in emission quantum yield as a result of the absorption of excited and emitted radiation by a sample matrix, which is known as the "inner filter effect". In water treatment engineering system, 3-DFMM analysis is susceptible to inner filter effect. Some samples such as surface water and sewage samples have to been pretreated if we want to obtain actual fluorescence intensity[19]. Therefore, the deviation of the fluorescence intensity during the analysis of NOM fluorescence components cannot be neglected. The inner filter effect

often has no significant influence for samples with low absorbance or concentration, thus there are two methods for reducing the influence of inner filter effect. The first method is to dilute the solution in order to decrease the absorbance (optical density) or concentration of a given sample. Absorbance can be used as an indicator for determination of the need for dilution. For example, Green, et al. [20] diluted the solution to a degree at optical density of 0.02 at 300 nm to avoid inner filtering of light within the sample in a 1 cm wide square quartz cell. Based on absorbance profile of sample, another classical model [21] can be used for the correction of modified fluorescence intensity, given as follows:

$$F_{corr} = F_{obs} \text{ antilog } ((OD_{ex} + OD_{em})/2) \hspace{2cm} （1）$$

where OD_{ex} and OD_{em} stand for the optical density of one sample at both excitation and emission wavelengths, respectively.

2.2. Typical NOM characteristics and fluorescence fractions

The NOM found in aquatic environments is composed of biological matter (carbohydrates, lipids, amino acids, nucleic acids) and the products of biotic and abiotic chemical reactions between NOM molecules or between NOM and inorganic constituents of water. The chemical properties of NOM vary significantly from one water body to another, where soil, climate and hydrologic conditions are different. Traditionally, NOM can be divided into three main groups based on their solubility in acid and alkali [14,22]: humic acid- soluble in dilute alkaline solutions but can be precipitated by acidification; molecular weights of HA are up to 200,000 g/mol, fulvic acid (FA) – remains in solution at low pH, molecular weights of FA are in the range of 200-1000 g/mol, humin – not soluble in water at any pH. NOM is much too complex to measure its individual components, so it is usually quantified by using bulk parameters such as Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC), and UV254 absorbance. However, the above mentioned measurements do not provide any information about the nature of organic matter and its origins. For more specific purposes NOM can be also separated into fractions based on such properties as hydrophobicity, polarity or molecular weight [14].

Characteristics of different NOM fractions are presented in Table 1. It has been reported in the literature, that the main fraction of NOM present in surface waters contains humic substances, which are responsible for the color of natural waters. Presence of NOM in drinking water supplies is undesirable due to its reactivity with oxidants and disinfectants, which leads to a decrease in efficiency of these processes. Also, it may lead to formation of inorganic and organic disinfection by-products (DBPs), which cause health

concerns [23]. Another disadvantage of presence of NOM is the fact that the oxidized NOM is a nutrient for microbes in water distribution systems[24], so it promotes microbial growth in distribution systems[25].

Although there are many NOM fractions, the data provided by the 3-D fluorescence method can distinguish and be used to source multiple NOM fractions. Examples of several typical NOM fractions that are isolated from different aquatic environments, as well as their possible sources, are shown in Table 2.

Table 1 Characteristics of different NOM fractions.[26]

Fraction	Characteristics
Hydrophobic fraction	Mostly representing hydrophobic acids: higher molecular weight (MW) humic acids, fulvic acid components and weak alkyl mono and dicarboxylic acids: - complex, aromatic structure and high MW subunits; - anionic polyelectrolytes with acidic functional groups such as carboxylic acid, methoxyl, carbonyl and phenolic groups; Few groups of neutral compounds with relatively low MW and a degree of condensed aromatic moieties: aromatic and aliphatic amines and amino acids.
Intermediate or transphilic fraction	Mostly relatively hydrophilic aliphatic acids.
Hydrophylic fraction	Mostly representing hydrophilic neutrals and some bases: - aliphatic linear molecular structure; - lesser electron rich sites than in the hydrophobic fraction; - few groups of acids and bases with relatively low MW and a degree of condensed aromatic moieties; - lignin derived constituents with relatively low MW; - hydroxyl and sugar acids; - non-humic, aliphatic and low MW components, aromatic and aliphatic amines, amino acids; - polysaccharides and proteins;

Table 2 Characteristics of 3-D fluorescence fractions of NOM investigated in different water environments, and their potential source.

Aquatic environment	Dominant fluorescence	Excitation/Emission (Ex/Em) wavelength	Source	Reference

	components	(nm)		
Algal suspensions through culture collection of algae	Protein-like materials	280/340 or 230/340	Blue-green algae (M. aeruginosa) : extracellular organic matter (EOM) and intracellular organic matter (IOM) and algal cell	[27]
Impacted water along the Zhejiang coasts in China	Humic acid-like or protein-like materials	275/310 (tyrosine-like) and 275/340 (tryptophan-like) 342/442 (humic-like)	Submarine groundwater discharge, terrestrial inputs, land-based pollution, and local biological activities in combination	[28]
Tributaries: Las Vegas Wash (LVW); upper Colorado River (UCR); lower Colorado River (LCR) (USA); Muddy River (MR); Virgin River (VR). They are located around Lake Mead reservoir between Arizona and Nevada in the USA.	Aromatic proteins, microbial by-products (for LVW, UCR and LCR); Fulvic acid-like, humic acid-like (for MR and VR)	220-250/280-332 (Aromatic proteins I), 220–250/ 332–380 (Aromatic proteins II), 250–470/280-380 (Microbial by-products) for LVW, UCR and LCR; 220–250/380–580 (Fulvic acid-like), 250–470/380–580 (humic acid-like) for MR and VR	Microbial activity or wastewater influence or autochthonous processes for LVW, UCR and LCR; limited microbial influence for MR and VR	[29]
Nanming River in China	Fulvic acid-like substance (upstream); protein-like or tryptophan-like substance, and fulvic acid-like substances (downstream)	300–310/423–448 and 235–240/427–444 (fulvic acid-like, upstream); 275–280/337–351 and 225–230/340–347 (protein-like materials, downstream), 300–310/428–447 and 235–255/425–447 (fulvic –like materials, downstream)	Untreated sewerage effluents	[30]
Kishon River in Israel	component I corresponding to humic-like matter; component II	345/438 (Component I); 280/364 (Component II)	Component I was linked to seawater tidal intrusion; Component II was associated with the location of major inputs of the industrial effluents	[31]

			associated with biological productivity	
Planktonic bacteria Urban River Tame, Birmingham, UK	Amino acid-like materials (tryptophan and tyrosine-like substances)	(220,280)/320-37 (Tryptophan-like);: approximately 220/around 240 (Tyrosine-like)	Bacterial activity (e.g., Pseudomonas aeruginosa)	[32]
Downstream samples on both the River Team and the Twizell Burn from Northeastern England, UK	Fulvic-like and tryptophan fluorescence (outfall, downstream);	276-281/340-370 (Tryptophan-like materials); 326-339/410-422 (Fulvic-like materials)	Sewage treatment works (STW) discharges	[33]

Although the NOM fluorescence fractions found in aquatic environments are different from the individual fluorescent compounds, their fluorescence are very similar. As the molecular structures of humic acid and fulvic acid are complex, they have no specific molecular formula, only the hypothetical structures as reviewed in Table 2. In previous research, International Humic Substances Society (IHSS) samples (Suwannee River humic acid standard used in this study) were applied as the standards for the humic and fulvic fractions [34]. Table 3 shows their similar fluorescence characteristics. In natural water system or water engineering system, these similar fluorescence fractions are called humic-like acid or fulvic-like acid components. The 3-D fluorescence spectra of the pure chemicals include tryptophan, tyrosine, and phenylalanin, which can be purchased and scanned in the laboratory are also presented in Table 3. Similar fluorescence characteristics are found for other components, such as protein-like materials. Overall, they are often used as standards to identify the category of DOM fractions. The fluorescence characteristics of typical Suwannee River NOM including humic acid and fulvic acid organic matter have been found in a range of water environments. A possible change to the positions of fluorescence peaks occurs due to the change of the aquatic environments.

In cases when an aquatic environment is affected by microorganisms (such as algae) the amount of abundant protein-like materials will be higher. The presence of this kind of organic matter has a significant impact on the overall composition of organic matter originating from this type of aquatic environment. The protein-like materials have similar characteristics to materials presented in Table 3, such as Tryptophan,

Tyrosine and Phenylalanin. At present, many identified fluorescence fractions (e.g., humic-like acid, fulvic-like acid, amino acid-like materials including proteins and peptides), share some similar compositions. Several kinds of commonly identified PARAFAC-based components have been widely distributed in aquatic environments [5,35]. Table 4 shows the typical PARAFAC-based components and their possible sources of water.

These fractions have become an important part of the chemical nature of NOM for specific water environments. Their chemical species derive from variety of sources, such as the humic-like acid and fulvic-like materials, potentially derived from decomposition of plants by biological and chemical processes [3], while the protein-like materials (mainly includes tryptophan-like and tyrosine-like) potentially originate from industrial and agricultural activity, or higher biological activity [32,27].

Table 3 Structure and 3-D fluorescence spectra of tryptophan, tyrosine, phenylalanine.
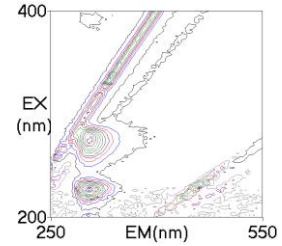
Name	Molecular formula	3-D fluorescence spectra
Theoretical humic acid model [36]		 Suwannee River humic acid standard [37]
Theoretical fulvic acid model [38]		 Suwannee River fulvic acid standard [37]
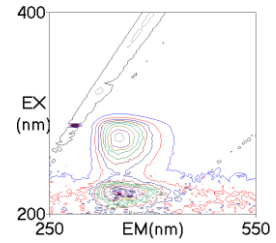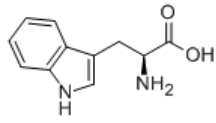
Tryptophan		Self-scanned in the laboratory
Tyrosine		Self-scanned in the laboratory
Phenylalanin		Self-scanned in the laboratory
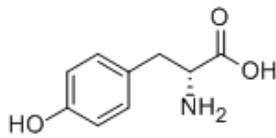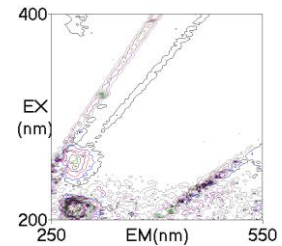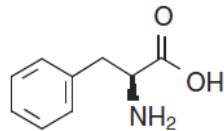
Table 4 PARAFAC modeled fractions of DOM and possible sources of water.

Component	Excitation(nm)/Emission(nm)	Description
Humic acid-like substances	250/452	The component was terrestrially-derived component, which is common in various estuarine, marine and oceanic environments, such as river water[5], industrial wastewaters[40], drinking water [41], danish streams[42], freshwater ecosystem[43], natural water [44], water from trans-oceanic cruises in the Pacific and Atlantic oceans [45], water from Ise Bay, Japan[46], water from the South Atlantic bight[39].

[39]
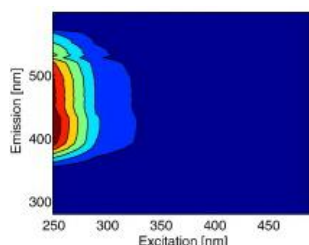
Humic acid-like substances [39]

250/420

The component was terrestrially-derived component, which is common in various estuarine, marine and oceanic environments, such as landfill leachate[47], industrial wastewaters[40], Danish estuary[7], ebinur lake watershed[48], water of typical agriculture, watershed of three Gorges reservoir areas[49], municipal solid waste leachate[50].
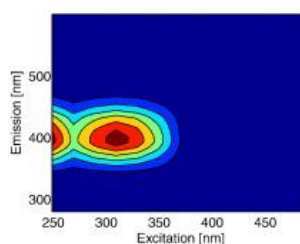
Marine humic substances[39]

(250,310)/400

The component was considered as marine humic substances resulting from microbial reprocessing. It was also identified as marine humic acid-like component or biological and microbial origin DOM [51], which has been found in several aquatic environments such as missouri river water[5], industrial wastewaters[40], landfill leachate[52], red wines[53], freshwater ecosystem [43], marine bacteria[54], coastal environments[55], the North Pacific Ocean, Bering, chukchi and Beaufort Seas [56], the South Atlantic Bight[39], Barataria Basin[57], coastal Canadian Arctic surface waters[58].
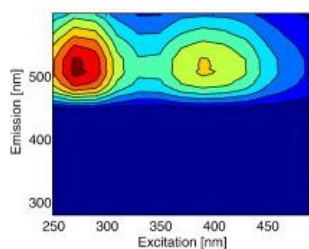
Terrestrial organic matter[39]

(270, 390)/508

The component was considered as terrestrial organic matter composed of high molecular weight and aromatic organic compounds. The component was also found in other aquatic environments such as synthetic DOM solution[59], Alpine lake catchments[60], Ballast water[61], water from the Baltic Sea [62].
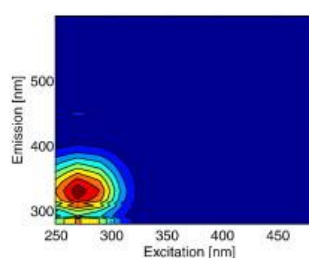
Tyrosine-like substances [39]

270/332

The component was considered as tyrosine-like substance belonging to protein-like materials. The component was also found in other aquatic environments such as high-strength nitrogenous wastewater[63], lake water[64], submerged membrane bioreactor [65].
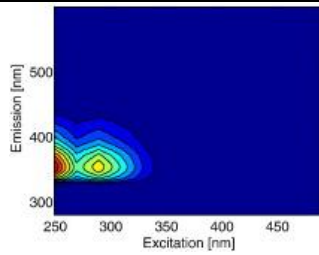
(250,290)/356

The component was considered as tryptophan-like substance belonging protein-like materials. The component was also found in other aquatic environments such as natural water [44], pools of a subtropical dryland river [66], lake water[64], freshwater ecosystems [43].

Tryptophan-like substances [39]
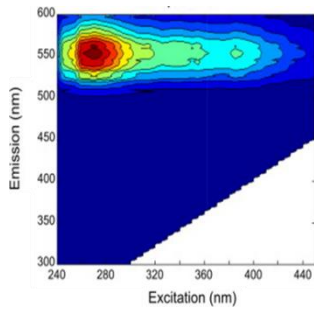
270/550

The componnet was considered as humic-like substances, correlated with anomeric, acetal andketal carbon.

Humic-like substances[67]

2.3. Comparison of fluorescence fractions

Analysis of the chemical nature of NOM via 3-D fluorescence data includes both the qualitative and quantitative infomration. The qualitative analysis focuses on component identification. The identification process often involves search of the characteristic peaks over a wide range, followed by peak position matching with the previous findings or data from standard samples including both excitation wavelength and emission wavelength. An excitation and emission wavelength boundaries (lines) for different component regions can be used as references [68]. Subsequently, the type of component can be identified and classified. The analysis of 3-D fluorescence data containing additional information such as the relative content of a component can be interpreted by fluorescence intensity (FI), fluorescence index or other derived expressions. For instances, Bugden, et al. [69], used the slope ratio and the intensity ratios to interpret 3-D fluorescence data based on specific peak FI value in order to fingerprint oil and chemically dispersed oil in seawater. Chen, et al. [70] employed the fluorescence regional integration method for quantifying spectra for NOM in which the normalized fluorescence volume was used. This method was also present in the literature as a reference [71]. Whether it is qualitative or quantitative, using these fluorescence parameters is very effective. However, the main drawback of this method is that some fluorescence fractions could not be identified because of overlapping of the fluorescence signatures of individual compounds [5]. Therefore, 3-D fluorescence can be also coupled with PARAFAC to characterize NOM in natural water and give more

comprehensive results[2,72]. The PARAFAC model is effective for fractionation of the 3-D fluorescence data into the underlying fluorescence components based on an alternating least-squares algorithm, which extends the usefulness of this kind of spectroscopy [2]. The fractionations of 3-D fluorescence data into several independent fluorescent components by PARAFAC model is unique, which overcomes the problem of missing fractions [5]. In the practical engineering application, the variations in the intensity of fluorescence fractions can define the water quality. While the actual intensity of the fluorophore cannot be obtained through PARAFAC simulation, the fluorescence intensity at the maximum can be derived for each component so that the relative changes and the ratios between fluorescence components can illustrate the quantitative and qualitative difference between samples [39,17]. A complete PARAFAC simulation process is present in a previous literature as presented in Figure 3.
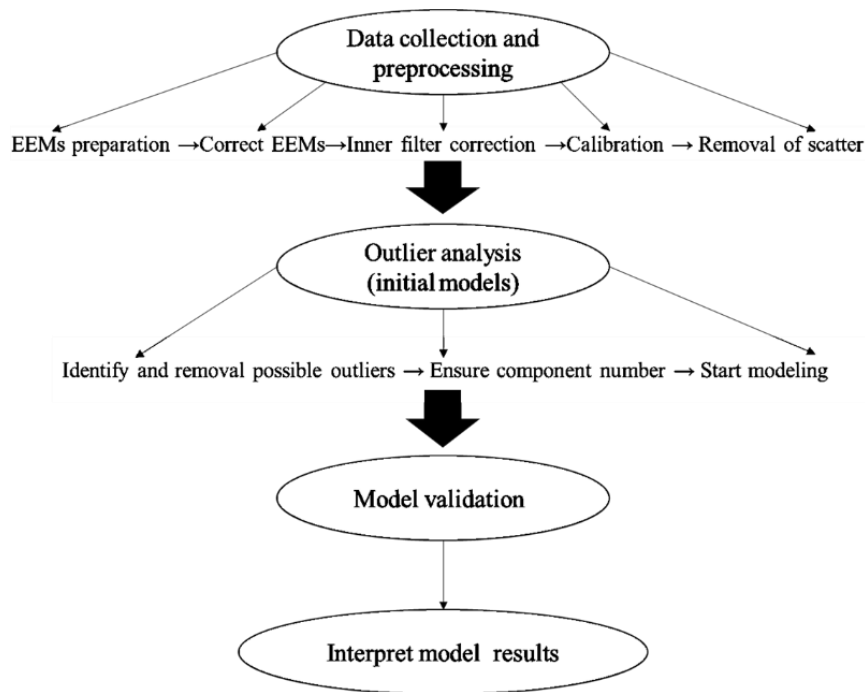
Figure 3 Fluorescence-based PARAFAC model analysis. [17]

In WTPs, a comparison between the PARAFAC-based components in the raw water and those in the treated water is needed. Only when the PARAFAC-based components have similar, high fluorescence characteristics including the components' contour plots and their excitation and emission loadings, their fluorescence intensity can be used to quantitatively analyze the degree of change, highlighting the differences in water quality before and after treatment. Similarity of these components can be quantitatively analyzed using Uncorrected Matrix Correlation(UMC)[73]. The UMC value between 0 and 1 is used to

measure the degree of spectral overlapping between two components. The 0 and 1 values for matrices indicate null and complete spectral overlapping, respectively. At present, the UMC have been used to compare the difference between the two components in nature water and water engineering system[74].

2.4．Background water matrix influence on the measurement

Various environmental factors have negative effects on analysis of 3-DFMM, including pH, metal ions, temperature, and photodegradation[75,3,13]. The pH and presence of metal ions effects have been widely studied, showing 3-D fluorescence to be applicable in a wider pH range of 2 to 12. The influence degree of pH in the 3-DFMM is dependent on specific fluorophores present in the water samples [3]. For example, Sorrentino et al. [76] indicated that the FI of two fluorescence fractions of river water increased with the increase of pH in the range of 2 to 10, with different responses to pH variation. For most natural water systems with the pH range normally from 5 to 9, less influence in 3-DFMM occurred [3]. Murphy, et al., [77] suggested that the pH influence in the spectral shape could be precluded because the pH and the treatment process stage were confounded variables; their results indicated that under such conditions PARAFAC model for fitting 3-D fluorescence data was successful.

In aquatic environments, various metal ions can be found, depending on the background water matrix and possible sources of pollution. The metal ions commonly present in water sources are: iron, aluminum, copper, mercury, chromium, cadmium, lead, nickel, zinc and vanadium, et al. [78]. Metal ions such as Cu^{2+}, Fe^{3+}, Hg^{2+}, Mg^{2+} and Cd^{2+} have been reported to quench the fluorescence of NOM, , et al., while the degree of fluorescence quenching was dependent on the fluorophore, metal ion concentration and speciation and pH conditions [13,3]. The modification effects of four kinds of metal ions, Hg, Cu, Fe and Al on the fluorescence of three fluorescence components of NOM in natural water system were compared [2]. It indicated that their effects on fluorescence modification of the identified components were not uniform and dependent on some specific factors. Hg, Cu and Fe had quenching effects on fluorescence of all components tested but Al had a quenching and enhancement effects on component 3, which had a greater quenching effect on component 2, followed by component 1. The metal ions concentration limitation that induces the quenching or enhancement of NOM was not clearly presented in this literature. Hudson, et al. [3], summarized the previous researches, which showed that the quenching effect of fulvic acids is obtained when using excess Cu, Fe and Al ions by varying their concentration as low as 0.1 mg/L. In the water treatment system, an accurate investigation of the effect of concentration of metal ions on fluorescence quenching of NOM still needs to study. In water treatment systems, the strict control of the output of the metal ions is important, which could reduce the influence of metal ions on the fluorescence analysis. In the

water treatment system, some researchers also reported no effects on wastewater fluorescence in the presence of metal ions[79,13]. With the wide use of nanomaterials, these materials will be inevitably released into the aquatic environments. The concerns on their long-term safety to human and inherent toxicity to aquatic organisms still remain. The nanomaterials treatment have become one of the issues of concern in WTPs [80]. During the transfer of nanomaterials in the aquatic environments, the NOM has been a identified as an important carrier. The metal nanomaterials may result in a modification in their optical properties such as fluorescence quenching and enhancement. The fluorescence quenching or enhancement effects possibly indicate the interaction between NOM and metals. For example, the gold nanoparticles were coated with two different stabilizers, β-D-glucose and citrate, forming two products denoted as BG-GNPs and CT-GNPs[81] (see Figure 4). Their interactions with humic acid were expected as follows and the results of fluorescence quenching and enhancement by the nanoparticles were also shown in the figure.
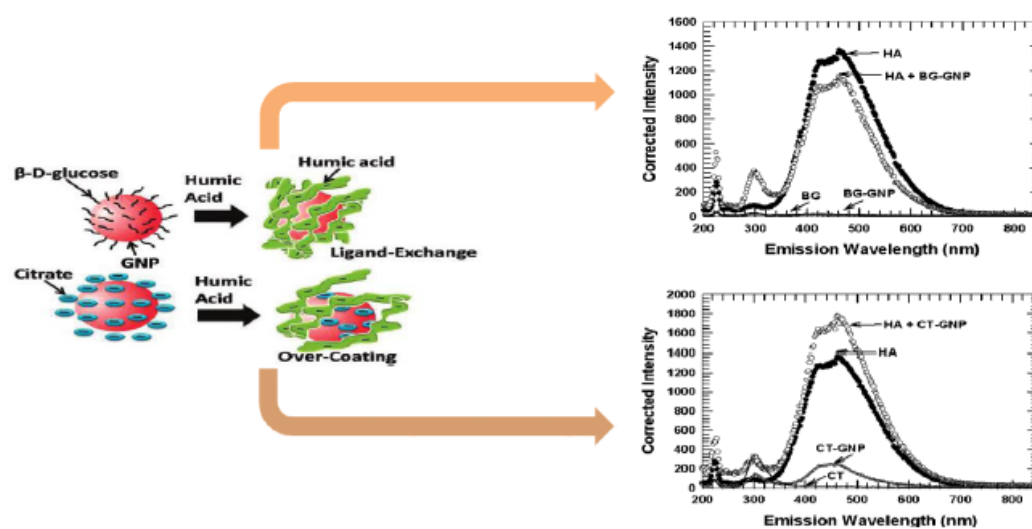
Figure 4 Schematic of interactions between humic acid and BG-GNPs and CT-GNPs suggested by Vasantal, Pallem[81], and their fluorescence results of interactions. [81]

As seen from Figure 4, the interaction of humic acid with BG-GNPs resulted in a fluorescence quenching of humic acid but the CT-GNPs caused an enhancement of fluorescence intensity of humic acid[81]. The main reason for the enhancement was the overcoating effect of HA molecules on the citrate lay on GNPs[81]. In an observation tested in the lab, we can see a significant fluorescence quenching effect of DOM by the metal silver nanoparticles with time (see Figure 5). A near field electro dynamical environment of the metal nanoparticles would influence the fluorescence behaviors of humic acid[82,83]. The included electrolytes in model solution also influenced the fluorescence intensity of humic acid in which the calcium nitrate had a larger quenching effect[83]. Other interactions of nanoparticles and NOM, such as suwannee

River fulvic acid and iron oxide nanoparticles[84], which was demonstrated that different mechanisms of NP:SRFA binding with pH could be indicated by fluorescence quenching.
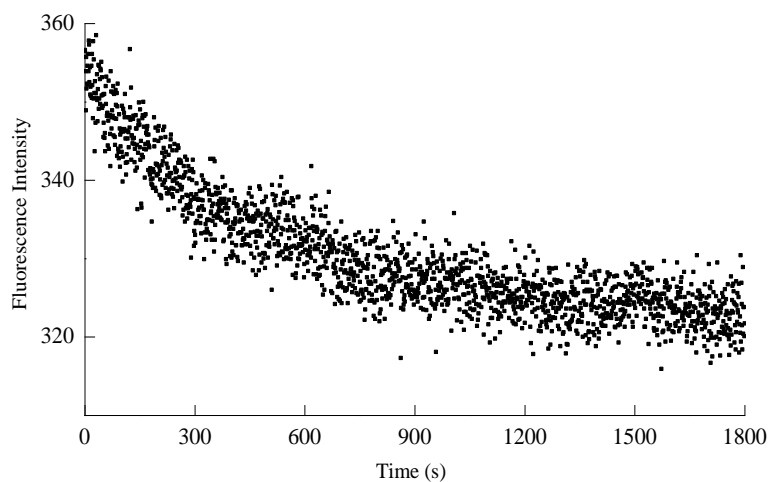
Figure 5 Fluorescence intensity quenching of Aldrich humic acids by silver nanoparticles with time at Ex (nm)/Em (nm) of 269/490 (tested in the laboratory).

Other factors such as photodegradation and temperature during 3-DFMM measurement may also affect the fluorescence of NOM [3]. In brief, in water treatment system, photodegradation can change NOM structure and character thus influencing the fluorescence intensity [85]; the degradation of NOM and the disinfection by UV exposure potentially impact NOM fluorescence analysis. Temperature has a significant impact on NOM fluorescence; however, using constant temperature may avoid any interference from thermal quenching during fluorescence analysis [3].

2.5. Environmental correlation

The aquatic NOM plays an important role in transmission or transformation of carbon, nitrogen and phosphorus, and of the toxic and hazardous substances, which poses a potential threat to human health. NOM structure has been extensively studied for many years while employing various methods to analyze the relationship between NOM and the water quality parameters. The organic matter has been known to interact with ultraviolet light, particular at 254 nm-wavelength adsorption (UV_{254}), which is more indicative of aromatic organic content. The aromatic organic materials are rich in carbon compounds, mainly originating from humic acid and fulvic acid materials, and the UV_{254} has been recognized to have a linear correlation with DOC, potential as a candidate for the latter to indicate water quality. Carbon and nitrogen are the primary elements of NOM, but NOM is most accounted of by carbon compounds. Therefore, the organic carbon compounds content is often calculated as the NOM concentration. 3-D fluorescence is able to yield

important information on the chemical nature of NOM [65], especially the aromatic organic materials. The aromatic carbon compounds can yield the carbonaceous DBPs, such as trihalomethanes (THMs), trichloroacetic acid and other (C-DBPs) [86]. Fulvic acid also has a significant impact on the formation of THMs, haloacetic acids, and aldehydes, while 2,3,5-tribromopyrrole can be produced from humic acid [87]. These imply that there should be a relationship between the fluorescence fractions and TOC or DBPs. Humic-like fluorescence was correlated well with DOC in marine DOM [88]. The squared correlation coefficient (R^2) between fluorescence intensity and DOC was up to 0.87. The cumulative normalized 3-D fluorescence volumes at some specific regions could correlate linearly with the dichloroacetic acid ($R^2=0.60$), chloroform ($R^2=0.42$), dichloroacetonitrile ($R^2=0.53$)[71]. F. Nakajima, et al. [89], suggested that the fluorescence intensity of DOM in a river system could present a good correlation with trihalomethane formation potential, and the fluorescence mainly originated from the THMs precursors. These demonstrate that the fluorescence fractions have a potential correlation with the yield of DBPs.

Besides aromatic carbon compounds, organic nitrogen compounds can also excite the fluorescence and generate the DBPs, and a significant correlation exists between the nitrogen compounds and the nitrogenous disinfection by-products (N-DBPs) as well as the organic nitrogen-related fluorescence fractions. The nitrogen-related fluorophores correlated with the protein and peptides materials are often present in three kinds of fluorescent amino acids, including tryptophan, tyrosine and phenylalanine [3]. The amino acids have been known to account for a significant portion of DON pool in natural lakes and streams and to generate N-DBPs [90]. Among them the tryptophan [91], tyrosine [92,93] and phenylalanine [94] have been reported to be the important components responsible for production of N-DBPs. In addition, for samples with higher concentrations, such as sewage, it showed a correlation between COD and protein-like fluorescence intensities [95]. The protein-like fluorescence intensity has been shown a possible tool for determining river water quality in earlier study[96], showing the statistically significant correltions of tryptophan-like fluorescence intensity at Ex/Em=280nm/350nm with nitrate, phosphate, amonia, and biochemical oxygen demand at Ex/Em=220nm/350nm in River Tyne catchment (England), except for three polluted sites. The dissolved oxygen was then found not a good indicator of water quality. The effectiveness of the correlations was found to exist only when treated sewage, sewerage overflows or cross connections, or agricultural organic pollutants dominate water quality. In a landfill leachate solution, the leachate fluorescence intensity had a strong correlation with ammonia, TOC and biochemical oxygen demand[97]. The impacted river by leaking landfill leachate with high amonia concentration affected the relationship,

where humic acid-like and fulvic acid-like materials were dominant fluoresent DOM[96]. When the sewerage sources of DOM are important, the use of tryptophan-like fluorescence intensity was suggested as a proxy for BOD, nitrate eand phosphate[96]. Overall, it is likely to find a significant correlation between the fluorescence fractions and the corresponding N-DBPs; however, a warning needs to concern that cross contamination between water is likely to lead to a deterioration in fluorescence assessment of quantitative water quality parameters.

3. Application in water purification systems

3.1. Surface and groundwater treatment processes

The ultimate objective of water treatment processes is the removal of different pollutants from the water supply in order to ensure that the treated water quality meets with the appropriate standards. Depending on the water source, different constituents have to be removed during water treatment in order to meet specific water quality standards. As an example, different constituents, which can be found in ground and surface water, and which have to be removed in the water treatment train are presented in Table 5 [14]. To discuss in detail all the processes used for water treatment as beyond the scope of this review, so we will focus on chemical oxidation, coagulation/flocculation and biological/MBR processes.

Table 5 Typical constituents found in ground and surface water that may need to be removed in order to meet water quality objectives [14].

Class	Typical constituents found in:	
	Groundwater	Surface water
Floating and suspended materials	None;	Branches, leaves, algal compounds, soil particles;
Colloidal constituents	Microorganisms, trace organic and inorganic constituents;	Clay, silt, organic materials, pathogenic organisms, algea, other microorganisms;
Dissolved constituents	Iron and manganese, hardness ions, inorganic salts, trace organic compounds, radionuclides;	Organic compounds, tannic acids, hardness ions, inorganic salts, radionuclides;
Dissolved gases	Carbon dioxide, hydrogen sulfide;	-

Immiscible liquids - Oils and greases;

3.2. Chemical Oxidation Processes

The WTPs use different treatment steps such as physical, chemical or physical-chemical, and biological processes. In these processes, the study of the fate and the structure of NOM is helpful in assessment of the environmental quality and the design of the water treatment engineering systems, thus it has received a wide attention. The 3-D fluorescence, assessment methodology allows frequent and informative monitoring of NOM [2], which favors the need of the increase in rapid assessment of WTPs.

Chemical oxidation and reduction methods are typically used in water treatment for the removal of specific inorganic and organic compounds from the treated water. Many different types of oxidation processes have been developed depending on their application, but there are three main types of oxidation processes used ion water treatment that may be distinguished: Conventional oxidation processes; Oxidation processes at elevated temperatures and/or pressures; Advanced Oxidation Processes (AOPs); Chemical oxidation can be used as a pretreatment processes, as well as for the disinfection processes. The application of chemical oxidation as a pretreatment processes is usually needed when some chemically or biologically recalcitrant pollutants are present in the water to be treated. They are helpful in the improvement of the performance for the post-treatment processes. The performance of oxidation processes in removing contaminates can be enhanced using appropriate operation. The disinfection process is an essential operational unit used for killing bacteria and viruses using strong oxidants, such as chlorine, ozone and chlorine dioxide during chemical/biological oxidation processes. These oxidants have been found effective for those organic compounds as the precursors of the DBPs. The typical DBPs such as THMs, haloacetic acids (HAAs) and N- nitrosodimethylamine (NDMA) could form through the interactions of organic matters with the oxidants. Figure 6a shows the transformation of the organic matters including phenolates, olefins, and amines under oxidation conditions to DBPs such as HAAs and THMs, of the data was collected from the references [98]. The source of the organic matters can result from the NOM. The contained dimethylamine (DMA) or related compounds in surface and wastewaters could be transformed to NDMA (see Figure 6b). Other DBPs can also form through the interactions of NOM (such as algal organic matter) with the oxidants (see Figure 6c). The organic compounds are not completely mineralized, which are converted from large molecules into small molecules, and under different environmental conditions, it is feasible to produce organic 3-D fluorescence while the correlation between the fluorescence intensity and the DBPs potential is also expected.
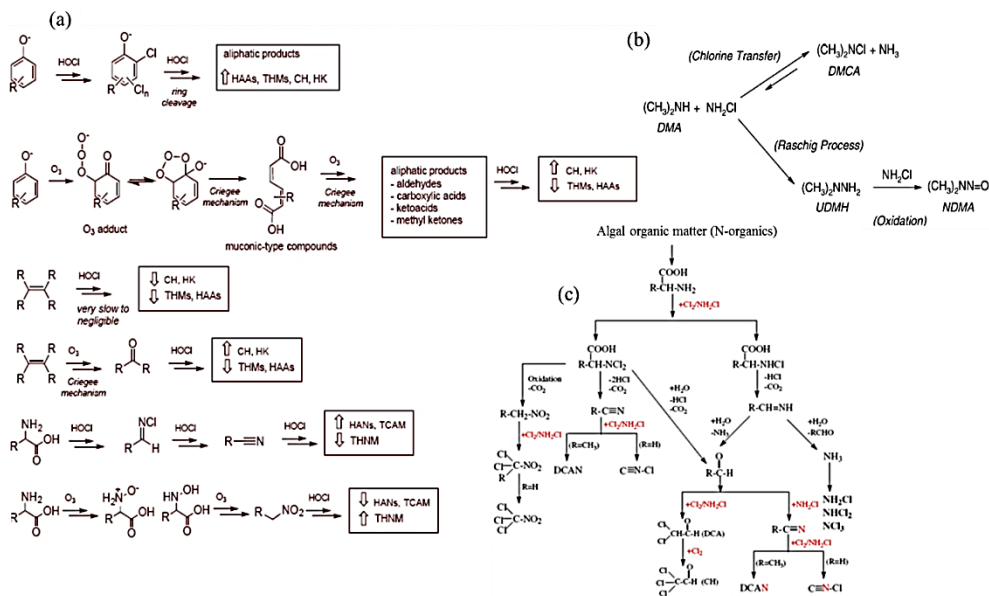
Figure 6 Impact of chlorination, ozonation on DBPs formation [98](a), NDMA formation pathways [99](b), and the transformation of algal organic matter to DBPs [27](c).

During the oxidation process, 3-D fluorescence has been used to characterize the organic compounds and the formation of DBPs [95]. The reported changes in the 3-D fluorescence of NOM during water treatment processes could be explained by potential partial NOM reacting with the oxidants to form the DBPs [100-103]. The oxidants found in reducing fluorophores in all 3-D fluorescence regions played an important role [100]. The species in investigated regions were primarily identified as organic materials including humic-like, protein-like, and fulvic-like [100,103]. Among them the humic-like and protein-like had higher reactivity than the fulvic-like species [100]. Ozone and chlorine dioxide presented relatively higher reactivity of reacting with NOM fractions [103]. Better relationship between the specific DBPs formation potential and the fluorescence fractions was observed [104,100,101,105,102]. For example, the total THMs were found to be correlated strongly with the humic-like component [5]. NDMA has a moderate and significant correlation with the tryptophan-like component [105]; the production of thechloral hydrate and cyanogen chloride correlated well with the decrease in protein/tryptophan-like and humic-like fractions, respectively, during UV radiation in combination with chlorination/chloramination [104].

Although fluorescent DOM is only a subfraction of DOM and accurately assessing how much of the total DOM pool is represented by fluorescence is difficult, 3-D fluorescence is feasible for tracing the dynamics of DOM in natural ecosystems[106]. The changes in fluorescence fractions during the chemical/biodegradable oxidation also had a potentials of assessing the formation potentials of DBPs.

In addition to the NOM, the release of organic matter were often produced from the metabolism of microorganisms, which include the release of organic matter by bacterial metabolic activity in activated sludge, and of the algal organic matter (AOM). These organic matters usually consist of extracellular organic matter (EOM) and intracellular organic matter (IOM) predominantly from the metabolic activity of algae or the cell decay [107,108], The nature of this kind of organic matter is different from NOM [108], thus they are often investigated sperately [27]. However, for their long-term release into the aquatic environments they have become an important components of NOM, significantly affecting the export of NOM. In addition, the presence of AOM, EOM and IOM in the drinking water system after the oxidation processes also have higher potential to generate the DBPs. With the frequent occurrence of algal blooms in drinking water reservoirs [27], it has posed a potential threat to water suply. Therefore, removal and characteristic analysis of AOM, EOM and IOM have been given a major consideration.

The observation of the nature of AOM indicates that the tryptophan-like (protein-like) rather than humic/fulvic acid-like dominates in the 3-D fluorescence of algae [108,109]. The peak positions found in the observation were centered at Ex/Em (nm/nm) wavelength pairs of 305/340 nm and 240/305 nm [108]. This implies that AOM is organic matter rich in nitrogen, with similar results previously described [27]. The 3-D fluorescence showed three fluorescence components (protein-like or organic nitrogen compounds, humic-like and fulvic-lik that were accounted for by organic carbon compounds). Their fluorescence peaks corresponding to the organic nitrogen compounds was centered at the Ex/Em (nm/nm) wavelength pairs of 280/340, and 230/340, and those to the organic carbon compounds at 350/450 and 275/450[27]. Higher portion of organic nitrogen compounds in AOM could generate more N-DBPs and haloaldehydes rather than the C-DBPs. EOM have relatively higher reactivity of generating DBPs except for trichloronitromethane in chlorination and chloramination than IOM as well as algal cells [27]. It also indicated that the chlorination of those algal cells including higher organic nitrogen content can generated more N-DBPs than the chlorination of NOM [110]. Therefore, the alga organic matter has become an important contribution to N-DBPs formation [111]. From above analysis, the 3-D fluorescence is able to provide a reliable information on analyzing chemical nature of AOM as well as the associated yields of DBPs. Because the N-DBPs have been considered more toxic than the most commonly regulated DBPs [112-114]. The correlation between N-DBPs formation potential and fluorescence fractions need to be studied further in order to effectively monitor and control the N-DBPs formation in WTPs.

In a more complex oxidation system including the introduction of photocatalysts in AOPs, 3-D fluorescence is also applied in a rapidly growing number of studies on catalytic and non-catalytic degradation of NOM, especially on the photodegradation of NOM [115-120]. For example, Phong, et al., [117] reported photocatalytic degradation of DOM using TiO_2 as a catalyst under various experimental settings. TiO_2 is a kind of various photocatalysts used widely in degradation of NOM (Figure 7a). It revealed that the DOM changes in fluorescence could be described by the combinations of four dissimilar components including one protein-like, two humic-like, and one terrestrial humic-like components, each degradation of which followed well the pseudo-first order model. The number of fluorescence components was determined based on split-half validation [121]. As a result, the protein-like component was preferentially removed by photocatalytic degradation probably due to its direct and preferable oxidation by hydroxyl radicals in solution. In addition to photocatalytic degradation, 3-D fluorescence was also applied in a non-catalytic photodegradation process for identifying components from NOM samples. For instance, Wada et al. [116] tested photoreactivity of the DOM from macroalgae using artificial sunlight and 3-D fluorescence analysis could showed generation of degradation products. First, 3-D fluorescence could indicated the fractions of macroalgae DOM (see Figure 7a) which shows two fluorescence peaks, and were identified as humic acid-like and tryptophan-like substances. However, fluorescence peaks of phenolic compounds were overlapped. Coupled with PARAFAC model, 3-D fluorescence extracted the phenolic fraction denoted as C3 (see Figure 7c). In the photo-degradation prcoess, C3 had a different variation from C1 and C2 with time under artificial sunlight. Furthermore, the decrease in C3 reflected the degradation of phenols. The increase in C2 implies that partial macroalgae DOM fractions had been transformed into lower molecular weight compounds, and subsequently accumulated as photo-degradation products. From the results of 3-D fluorescence analysis, photodecomposition has been found to be effective for phenolic compounds and the degradation products mostly contained the small molecules by low aromaticity. Overall, the 3-D fluorescence in investigating degradation of NOM have provided valuable information about the chemical composition and behaviors of DOM. These studies have profound implications for optimizing drinking water and wastewater treatments and for ensuring treated water quality and safety [122].
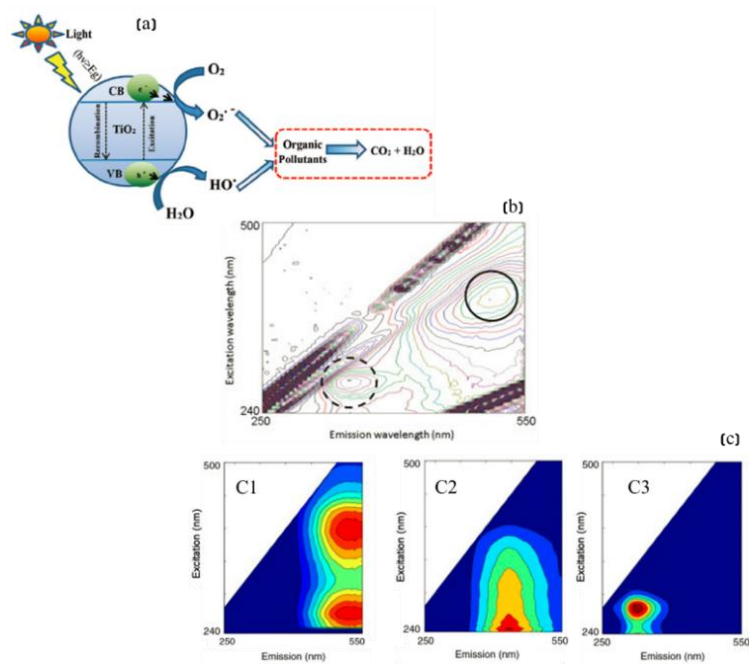
Figure 7 (a) Mechanism of TiO$_2$ photocatalysis process. [123]; (b) 3-D fluorescence of the macroalgal DOM which is collected on 0 h on the start of photodecomposition experiment, and the contour line means intensity of emission with an interval of 0.01 RU. Solid and dashed circles mean peaks 1 and 2, respectively [116]; and (c) components of macroalgal DOM was identified by PARAFAC model and the components are denoted as C1, C2 and C3.

3.3. Coagulation-flocculation Processes

Coagulation-flocculation process is widely used for the water and wastewater treatment. It is a very effective method for removal of colloids and suspended substances from the aquatic environments [124,125], along with other substances like organic matter and some metal ions. In addition to colloids and suspended substances, the coagulation-flocculation processes have been suggested to be a major treatment option for a better control of NOM and the associated DBPs [126]. To deeper understand the behaviors of the coagulation-flocculation for NOM and the associated DBPs, the characterization of NOM chemical nature is essential. A simple schematic of coagulation-flocculation for NOM and the introduction of 3-DFMM as shown in Figure 8.
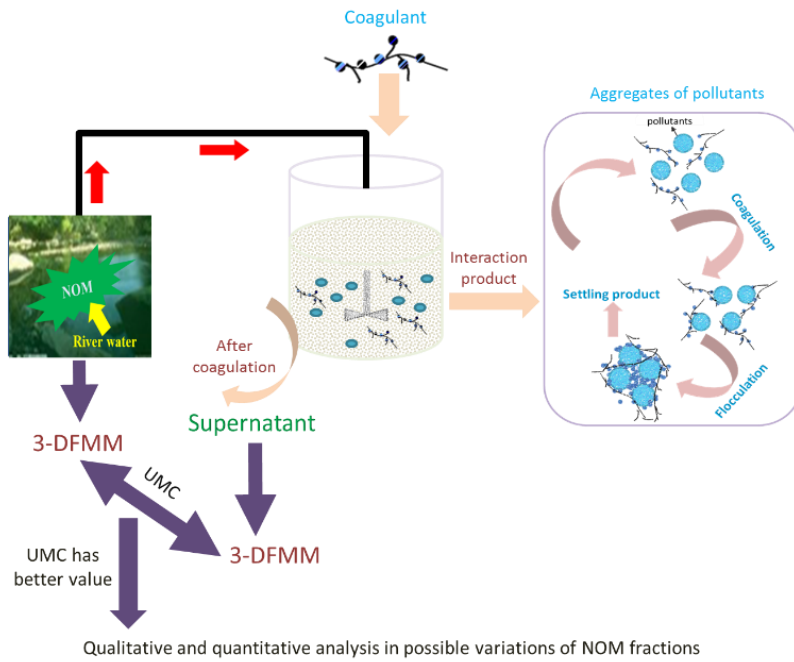
Figure 8 Schematic diagram of coagulation-flocculation for NOM.

NOM in the aquatic environments often varies with the water environments, either in concentration or in species. Therefore, the chemical nature of NOM resulting from different environments is often different. Their removal is usually affected by their physical/chemical nature in the aquatic environments. In addition, they are also influenced by coagulant dosage and type, the mixing conditions as well as the ambient conditions [27,127]. The molecule size or molecule weights of NOM are important, of which the characterization is helpful in better understanding NOM removal behaviors.

The pH influence on the fluorescence intensity of organic matters has been considered[128]. With pH 4-7.5 and variation of residual aluminium, Gone et al.[129] plotted fluorescence intensity versus DOC for both raw and treated Agbo reservoir surface waters by coagulation-flocculation, it indicated a significant shift between representative water point for pH 4 and the other samples while with the optimum optimal dose of alum and the approcate pH range of 4.5-7.5, the pH, residual aluminium and inner-filtering influences on fluorescence could be negligible. The significant high correlation between DOC removal and the fluorescence intensities of humic acid-like substances, fulvic acid-like substances and tryptophan-like also showed the 3-D fluorescence to evaluate the DOC removal to be feasible. Coagulation mechanisms could also be studied using fluorescence-quenching method [130]. The fluorescence quenching effect led to the residual humic acid TOC concentration to be higher than that measured by 3-D fluorescence. At both low and middle pH range, the major coagulation mechanism of coagulating humic acid by a polyferric sulfate was attributed to charge neutralization [130].

In an inorganic coagulation system, it had been demonstrated that the NOM fractions of raw water and the treated samples could be compared through a validation of UMC[72,2]. Missouri river water by the coagulation-flocculation process revealed three fluorescence fractions (humic acid-like, fulvic acid-like, and protein-like) [5]. The result showed that fluorescence fractions removals had a good correlation with DOC and DBPs reduction. The above study was mostly agree well with the previous findings [129]. The relatively straight forward removal of fluorescence components both indicated that it was effective for reducing humic acid-like and fulvic acid-like materials, while the protein-like fraction was relatively hard to treat [129,5]. The possible reason for the ease of component removal was largely attributed to the component nature such as molecular weight and solubility. Larger molecular weight compounds and the hydrophobic substances were easy to treat [131,132]. Further illustration describing 3-D fluorescence application in water treatment engineering system showed a long-term assessment of NOM in a multi-coagulant drinking water treatment scheme [72] in which two humic moieties (humic-like materials) and a protein-like structures similar to tryptophan were identified [72]. This research also indicated that humic-like materials were easy to treat, whereas the protein-like fraction was hard to reduce. Other further treatment technologies of NOM tend to use the combination model of 3-D fluorescence with other characterization methods. For example, Wassink et al. [133] used the 3-D fluorescence and the liquid chromatography–organic carbon detection to assess the removal of NOM and DBPs by enhanced coagulation, which could enable the quantitative detection of hydrophobic and hydrophilic DOC, thus it could provide better measurement of DBP precursors.

From the above findings, 3-D fluorescence is an effective tool for characterizing the NOM in coagulation-flocculation process in which the correlation is significant between some specific components and the water quality parameters such as DOC and DBPs. However, it was difficult to deal with organic nitrogen materials regardless of using aluminum and iron coagulants and composite coagulant. The fluorescence species, protein-like materials, including more organic nitrogen compounds, which were refractory to the coagulation-flocculation process [5,129]. This was not beneficial to the elimination of the N-DBPs. The protein-like materials would be considered as an indicator of the degree of reduction of N-DBPs. In addition to the coagulation-flocculation process, the adsorption and advanced oxidation were also found to have difficulties in reduction of organic nitrogen compounds [132]. In the aquatic environments, the organic nitrogen materials are less abundant, harder in detection and easy to create harmful nitrogen disinfection by-products, and are closely related to the design of WTPs as well as others such as water

treatment efficiency and the formation of N-DBPs. Therefore, the future rapid monitoring and control of the WTPs are necessary using 3-D fluorescence.

The precursors of N-DBPs are mainly composed of nitrogen organic compounds. For example, the precursors of halogen acetonitrile (HANs) formation are possibly free amino acids, nucleic acids, proteins, humic acid and small molecule amine reacting with chlorine and chloramines; the amino acids and humic acid are the precursors of chloropicrin in drinking water. Among them, the dissolved organic nitrogen (DON) can react with the disinfectant to generate N-DBPs [134,135]. The DON is a complex mixture consisting of less portion of DOM, which is composed of the materials such as amino acids, amides, amino sugars and peptides [92]. Some materials have fluorescence nature such as the typical amino acids including tryptophan, tyrosine and phenylalanine, which have been considered as indicative of proteins and peptides [3]. Therefore, the findings in the correlation between the fluorescence components and DON as well as the associated N-DBPs would be helpful in the understanding of formation of the N-DBPs. At present, the DON has posed a potential threat to human health and the removal of DON has been given more concern. Although 3-D fluorescence has been commonly used in WTPs, the fundamental research and its application involved in DON compounds and N-DBPs formation need to be investigated further.

Finally, because coagulation system often uses different coagulants according to water environment conditions, the 3-D fluorescence signal may be affected due to the fluorescence signal of external input or interference of external materials, especially the organic coagulants. The organic coagulants (e.g., polyacrylamide and polydimethyldiallylammonium chloride) can help inorganic coagulants to enhance their water treatment efficiency, accelerating floc aggregation, improving the settling rate, so it has become one of important methods to improve water purification in WTPs. However, these organic coagulants are a kind of macromolecular organic compounds which could excite a strong fluorescence signal (see Figure 9), possibly leading to a biased analysis in inherent fluorescence of NOM. With the rapid development of organic-inorganic composite coagulant, the organic coagulant influence in fluorescence of NOM has to be considered in the hope of providing technical support of eliminating interference of 3-D fluorescence.

(a) Polyacrylamide

(b) Polydimethyldiallylammonium chloride
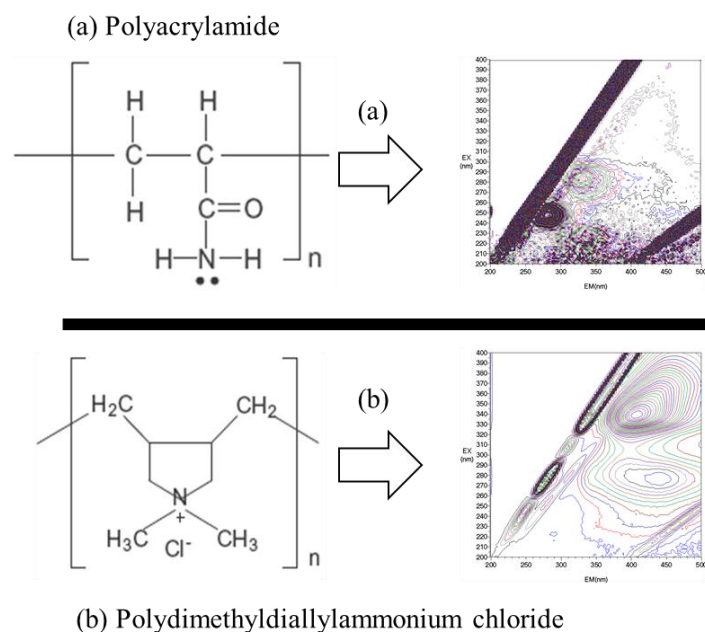
Figure 9 3-D fluorescence of polyacrylamide (a), polydimethyldiallylammonium chloride (b). (polyacrylamide and polydimethyldiallylammonium chloride were the commercial cationic polymers (cationic degree=40%), which were perchased from China).

3.4. Biological/Membrane BioreactorTreatment Processes

The performance of NOM removal in WTPs is largely improved by introducing the post-processes containing the biofilm process [136], activated sludge process [137], and membrane bioreactor treatment process [138]. Research on membrane fouling mechanisms via 3-D fluorescence has been developed rapidly in the recent years. For the short-term or long-term operation of the biofilm process and the activated sludge process, the types of biomasses resulting from these processes would have a major impact on the membrane performance, inevitably leading to membrane fouling. Membrane fouling refers to the process of membrane filtration in which the particles and the macromolecular species in the feed often interact with the membrane through deposition, reaction, precipitation, and/or microbiological process [139]. In the presence of the interaction, the particles and macromolecular solutes are possibly deposited or adhered to the membrane pores, or membrane surface (see Figure 10a). This would narrow or block the membrane pores, leading to the flux decline and needs for membrane cleaning and replacement.

Four classic filtration models can be used to analyze the flux decline of low-pressure membrane filtration in dead-end mode under constant pressure [140]. The schematic diagram of four filtration models is present in Figure 10b. According to the foulants distribution, the membrane fouling can be examined by analyzing

fluorescence fractions of those organic matters from the feed water, the membrane foulants, the membrane permeate, and others containing the sludge supernatant, extracellular polymeric substance in membrane filtration or bioreactor system [141,142].
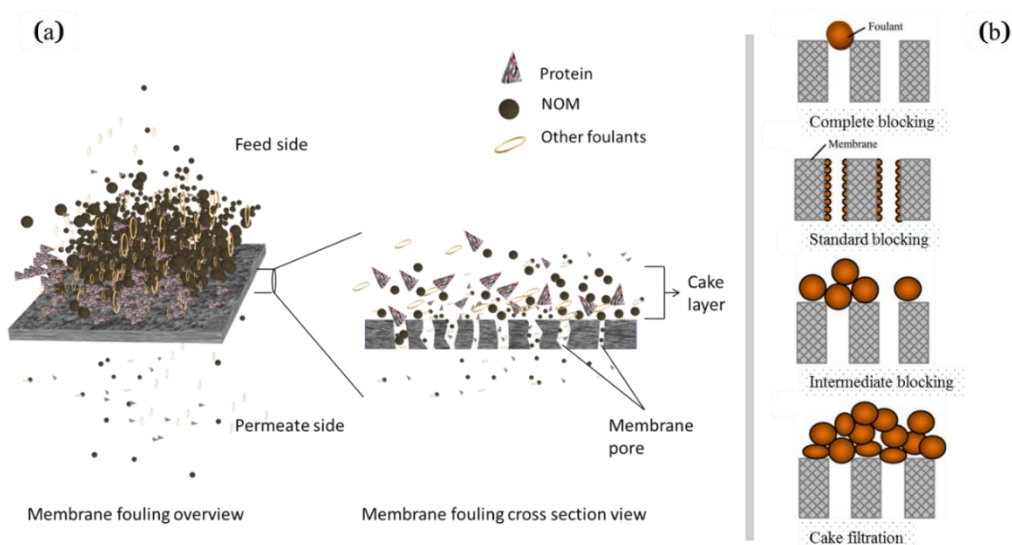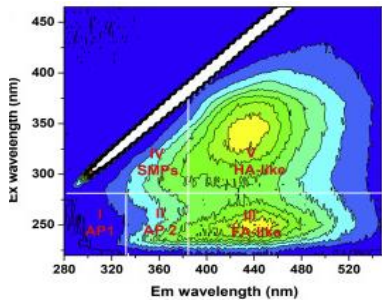

Figure 10 (a) Schematic diagrams of membrane fouling overview and membrane fouling cross section view, (b) Schematic diagrams of four filtration models. [140].

Membrane bioreactor (MBR) was used in WTPs and the membrane fouling characteristics were investigated [143,144]. The fouling mechanism was dominated by the cake layer formation [141]. Considering the initial fouling nature of an aerobic submerged MBR [143], the dominant fluorescence foulants were considered to be protein-like substances [144,143]. Protein-like substances had been retained at the membrane surface [143]. Although their removal efficiency was greater, a significant increase of transmembrane pressure was recorded. For long-term operation of membrane bioreactor in a lab-scale MBR, the fluorescence aromatic and tryptophan proteins, the polysaccharides, lipids and fatty acids, originating from the sludge supernatant, were reported to be more easily contained by the fouling layer rather than humic-like and fulvic-like acids, in which aromatic proteins have higher fouling propensity than tryptophan proteins due to a higher hydrophobic nature [141]. Overall, protein-like fluorescence fractions have a significant contribution in membrane fouling processes. The pre-ozonation has a potential to reduce the protein-like substances resulting from both extracellular polymeric substance, which is helpful to reduce external and internal fouling [138]. In addition, ultrafiltration membrane pore size and surface hydrophobicity was found a significant influence in the transportation of protein-like substances but less importance for humic-like substances [140].

In addition to the significant contribution to membrane fouling in MBR systems, protein based materials were also the prominent components in the membrane fouling layer in the ultrafiltration (UF) system in which some humic-like materials, soluble microbial products and protein-like extracellular material could be removed efficiently while the fulvic-like matter was hard to reject [145]. In the ultrafiltration and nanofiltration membrane systems, another study suggested that the humic substances, protein-like and particulate/colloidal-like matter were the key membrane foulants[146-148]. However, for the submerged hollow fibre membrane bioreactor at a shorter hydraulic retention time, the humic-like and fulvic-like acid materials were the dominant foulants of membrane fouling formed on membrane surface, whereas at a longer hydraulic retention time, the foulants contained also a significant amount of biopolymers [149]. For different kinds of membranes used in water treatment system, their fluorescence fractions foulants may be varied (see Table 6), and the ambient conditions and molecular sizes as well as other factors would have a prominent influence on the membrane fouling.

Table 6 Identified membrane foulants in membrane treatment system using 3-D fluorescence.

Membrane process	Feed	3-D fluorescence of organic matter	Organic foulants	References
Microfiltration	Biologically treated secondary effluent	(3-D Fluorescence of feed water (AP = aromatic protein, FA = fulvic acid-like, SMPs = soluble microbial products(e.g., proteins and polysaccharide-like materials), HA=humic acid-like))	High molecular weight humic substances	[150]
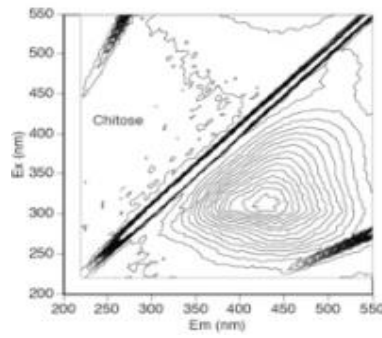
Microfiltration	Chitose River water in Japan	 (3-D Fluorescence of chitose River water)	Biopolymers and protein-like substances	[151]
Nanofiltration	Synthetic water samples with NOM derived from algogenic organic matter	 (3-D Fluorescence of feed water)	Protein-like and polysaccharide-like substances	[152]
Ultrafiltration	Chitose river water in Japan	 (3-D Fluorescence of feed water)	Polysaccharide-like organic matter	[153]
Forward Osmosis	Secondary wastewater effluent	 (3-D Fluorescence of feed water)	Biopolymers and protein-like substances	[154]
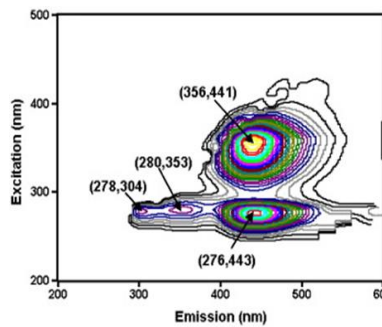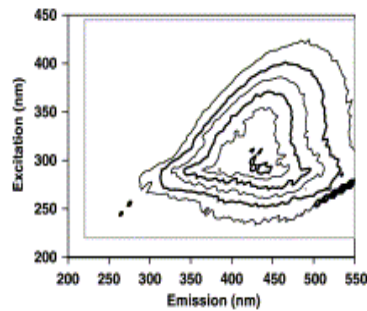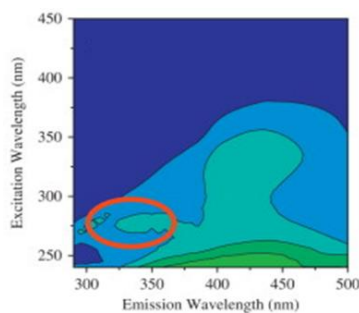
| Reverse Osmosis | Secondary treated municipal wastewater | | Protein-like material | [155] |
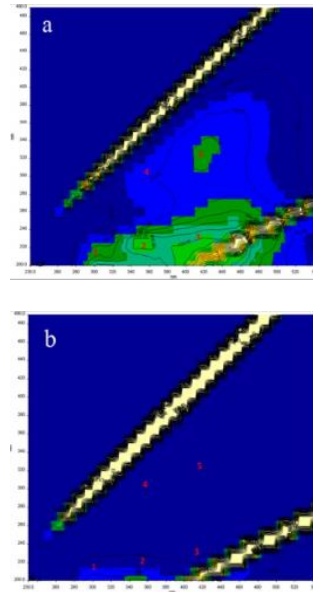
(3-D Fluorescence of (a) RO feed water, and (b) extraction from fouled membrane sample. RO feed water included higher content of humic and fulvic acids, and protein but only modest amounts of protein-like material could be found in the extraction of fouled membrane samples.)

The biological WTPs are largely affected by the bacterial metabolic activity [156,157]. 3-D fluorescence is able to provide some specific information on those metabolites resulting from bacterial metabolic activity[158]. The monitoring of activated sludge in WTPs system is closely correlated with extracellular and intracellular substances due to their potential influence on bioreactor performance [156,159]. The extracellular substances are identified as being primarily composed of three fluorescence fractions including the protein-like substances, fulvic-like and humic-like materials among which the protein-like substances [157,156] reflect the changes in wastewater chemical oxygen demand [156]. In addition, it also showed that the intracellular fluorophores, proteins and nicotinamide adenine dinucleotide, had a better correlation with the bioreactor performance [156].

4. Summary

With the intensification of industry and agriculture, especially in developing countries, where urbanization is accelerating, the stress put on the environment is also increasing. The demand for water resources is also continually increasing in parallel to increase in pollution from industry and agriculture. Therefore, any enhancement of water quality monitoring and control, resulting in the improvement of water treatment

efficiency for WTPs is one of currently important topics. This article briefly reviews the specific application of 3-D fluorescence in monitoring NOM in WTPs. In this review, current research on the characterization of NOM by 3-D fluorescence, were reviewed. The 3-D fluorescence provides useful information to support better understanding of the performance of WTPs. The analysis of the source of pollution by NOM and online monitoring using the 3-D fluorescence in WTPs has been identified; the characterization of the transformation of NOM, especially in the DBPs formation, is a new challenge. Compared with the study of organic carbon compounds, research on the organic nitrogen compounds is relatively scarce. DON compounds are less abundant, harder in detection and responsible for creation of harmful nitrogen N-DBPs. In the WTPs, large molecular hydrophobic organic compounds are often easily removed, thus the reduction of C-DBPs is relatively effective. However, some small molecule organic hydrophilic compounds such as the protein, amino acid, amine compounds which are possibly correlated with the N-DBPs, are hard to deal with. The 3-D fluorescence offers the opportunity to provide more useful information revealing the mechanisms of their formation potential. These information provide support of man-made decision to prevent water from further pollution. The 3-D fluorescence monitoring of biological treatment systems has a potential to improve the online control of water quality. The 3-D fluorescence is relevant to membrane fouling analysis, but still needs to be further studied, especially in membrane fouling resulting from small molecular fractions of NOM. In order to ensure the safety of aquatic environment, the interactions between toxic and harmful substances and NOM is of considerable importance. The 3-D fluorescence monitoring of the optical properties of NOM in micro-scale is able to reveal their interation behaviors with toxic and harmful substances, which is essential for better understanding of pollution process control.

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