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Characteristics of Natural Organic Matter (NOM) Surrogates Under Different Disinfection Processes

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Abstract: In this study, Natural Organic Matter (NOM) surrogates which is represented by Total Organic Carbon (TOC), absorption of UV-light (UV_{254}) and Specific Ultraviolet Absorption (SUVA) value was used to characterize organic matter in water treatment process under different disinfection processes. The reduction of NOM surrogates was also examined at the same time. The results show that TOC has been reduced to 26% under coagulation with ferric chloride, insignificantly removal in sedimentation and 39% removal in filtration with activated carbon. During disinfection, TOC reduction is higher than other NOM surrogates. Effect of disinfection processes, dosage and reaction time to NOM surrogates reduction indicated that NOM decrease with increasing reaction time, increasing dosage caused increasing reduction of NOM and UV disinfection contributed to the higher degree processes of organic matter than chlorination disinfection.

Key words: NOM, water treatment, disinfection, dosage, reaction time, sedimentation

INTRODUCTION

Investigations have been conducted to explore the components and characteristics of organic matter to determine its behavior in water and how to effectively remove it during treatment. The diversity of molecules that constitute Natural Organic Matter (NOM) and the relative low concentrations of NOM in water often makes characterization difficult. Thus, methods that can either accurately characterize NOM in these dilute solutions or isolate and concentrate NOM are essential. Despite the thousands of compounds that make up NOM, it is important to provide information about the quantity of NOM that are dominant precursor for DBPs. Total Organic Carbon (TOC) is the sum of particulate and Dissolved Organic Carbon (DOC), existing inorganic carbon is removed by acidification. A widely accepted operational definition of DOC is the organic carbon in the water sample filtered through a 0.45 μm filter. It is the most commonly used approach to quantify NOM for measuring the organic carbon mass in a sample. Ultraviolet (UV) light at 254 nm is absorbed by a variety of organic compounds with an aromatic structure or compounds that have conjugated C = C double bonds (Tran *et al*., 2015). Aquatic humic matter which is likely to be the predominant organic compounds has conjugated C = C double bonds structural features, so, they absorb more light per unit concentration of DOC than other types of NOM in water supplies. Specific Ultraviolet Absorption (SUVA) provides a simple way to characterize the nature of NOM and is calculated from measurements of UV_{254} and TOC samples. Although, water contain a mixture of types of NOM, the SUVA can provide an indication of what types of organic compounds dominate (Sillanpaa *et al*., 2015).

Disinfection, one of the water treatment process unit is necessary for the deliberate reduction of the number of the pathogenic microorganisms in order to prevent acute outbreaks of potentially deadly diseases and other deleterious health effects. However, an unintended consequence of disinfection process is production of Disinfectant By-Products (DBPs) when the existed NOM in water reacted with disinfectant, such as chlorine, ozone, chlorine dioxide and chloramines (Han *et al*., 2015). Trihalomethanes (THMs) and Haloacetic Acids (HAAs) are probably the most prevalent DBPs and have been found to have carcinogenicity and other adverse health effects. One of the factors influencing the levels of DBPs formation is the characteristic of NOM, such as chemical or physical properties, to react with disinfectants (Reckhow and Singer, 2011; Hidayah *et al*., 2017). Ultraviolet (UV) disinfection has been well known as effective method to inactivate microorganism without creating any toxic byproducts. UV light allows for higher quality of water standards without adding in any chemicals. However, UV light has lack of residual in public water supply applications (Hijnen *et al*., 2006).

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Regarding to organic precursors material or NOM, the formation of DBPs does not only depend on the quantity of NOM but also its physical and chemical structure. The relationship relating to the formation of DBPs may be better understood and controlled by first gaining a better understanding of the NOM, naturally occuring precursors that are the cause of their formation. The bulk NOM parameters, DOC, UV_{254} and SUVA value, also have been frequently correlated with DBPFP (Bieroza *et al*., 2010; Hidayah *et al*., 2017). In this study, NOM surrogates was used to characterize the NOM in the source water and treated water from coagulation, sedimentation, filtration and disinfection with chlorine and UV light. At the same time, the removal of NOM surrogates by two different disinfection method was also examined.

MATERIALS AND METHODS

Raw water samples was taken from Jagir River in Surabaya, Indonesia. Laboratory scale of water treatment apparatus included coagulation, sedimentation, filtration and disinfection, it was performed under flow rate 30 L/h. $FeCl_3.6H_2O$ coagulant 200 mg/L dosage was added under rapid mixing 150 rpm, followed by slow mixing 35 rpm, settling flocs in sedimentation, then filtered through activated carbon. Disinfection is applied by various disinfectant under different dosage and different contact time. Various dosage of sodium hypochlorite (N) is 20, 40, 60 (mg/L) with reaction time 1, 2, 4, 8, 16 (h) have been applied for disinfection process, instead of various UV light intensity (U) 20, 40, 60 (mJ/cm^2) with exposure time 0.12, 0.25, 0.5, 1, 2 (h). Raw water and filtered water were collected for organic carbon analysis. Raw water sample and treated water were filtered through 0.45 um membrane filter paper and were measured as Total Organic Carbon (TOC) by using a Shimadzu TOC-V_{CPN} organic carbon analyzer. UV_{254} absorption was measured with UV-VIS spectrophotometer Shimadzu UV-1601 to detect aromaticity properties of organic compound. In order to provide an indication of what type of organic compounds dominate, SUVA value also was calculated based on the UV_{254} over to TOC concentration.

RESULTS AND DISCUSSION

Characteristics of source water: The general water quality of Jagir river as source water is shown in Table 1. It is noted that pH 6.8 indicated normal pH in raw water. According to organic matter surrogates, TOC value indicates that the source water has quite high dissolved organic content. UV_{254} value is 3.3, it has been known and attributed to aromatic compound because UV light at 254 nm is adsorbed by organic with aromatic structure that have conjugated C = C double bond (Tran *et al*., 2015). Further, the SUVA value indicates that the dissolved organics is rich in hydrophilic compounds. As certain types of NOM adsorb UV_{254} light per unit concentration of DOC to a great degree than other types, SUVA is an indicator of NOM composition in water. It have been reported that water samples with SUVA values higher than 4, indicate that NOM is composed mainly of aquatic humic matter, while water samples with SUVA values lower than 2 contain mainly non-humic matter which generally is more hydrophilic, compare to humic matter (Sillanpaa *et al*., 2015).

Table 1: Characteristics of source water

	Water quality			
Sample	pH	TOC (mg/L)	UV_{254} (cm^{-1})	SUVA (L/mg-m)
Source water	6.8	5.4	0.180	3.33

Characteristic of NOM surrogates for water treatment processes: Figure 1 shows the NOM surrogates reduction of water samples collected from laboratory scale of water treatment processes. TOC concentration of raw water have been reduced to 26% in the coagulation with Ferric Chloride ($FeCl_3$). Ferric salts commonly used in coagulation processes include Ferric Chloride ($FeCl_3$). Trivalent ferric ions are released into a solution from the respective salt. They are hydrolysed and form soluble complexes possessing high positive charges (Johnson and Amirtarajah, 1983). Also, it has been well-established in the literature that coagulation is more amenable to remove organic matter than any processes (Hidayah *et al*., 2016; Wang *et al*., 2013; Sillanpaa and Matilainen, 2015). Further, sedimentation slightly reduced TOC to 29.6%. TOC removal reached high removal to 38.9% after filtration with sand and activated carbon media.

Research by Cahyonugroho *et al*. (2016) showed that activated carbon which has higher pore volume, higher inner pore size and extremely higher surface area than silica sand, influenced the adsorptive capacity to remove NOM. Regarding to molecular weight, Low Molecular Weight (LMW) NOM constituents have access to a large percentage of the activated carbon pore volume and thus could be well removed based on size considerations (Velten *et al*., 2011). However, LMW compounds may also be relatively hydrophilic, hence, less adsorbable (Sillanpaa and Matilainen, 2015). The percentage removal of TOC by NaOCl in disinfection is almost similar with UV process, about 40-50% under different dosage. Oxidation of organic matter in disinfection could breakdown high molecular weight into lower molecular weight, even at

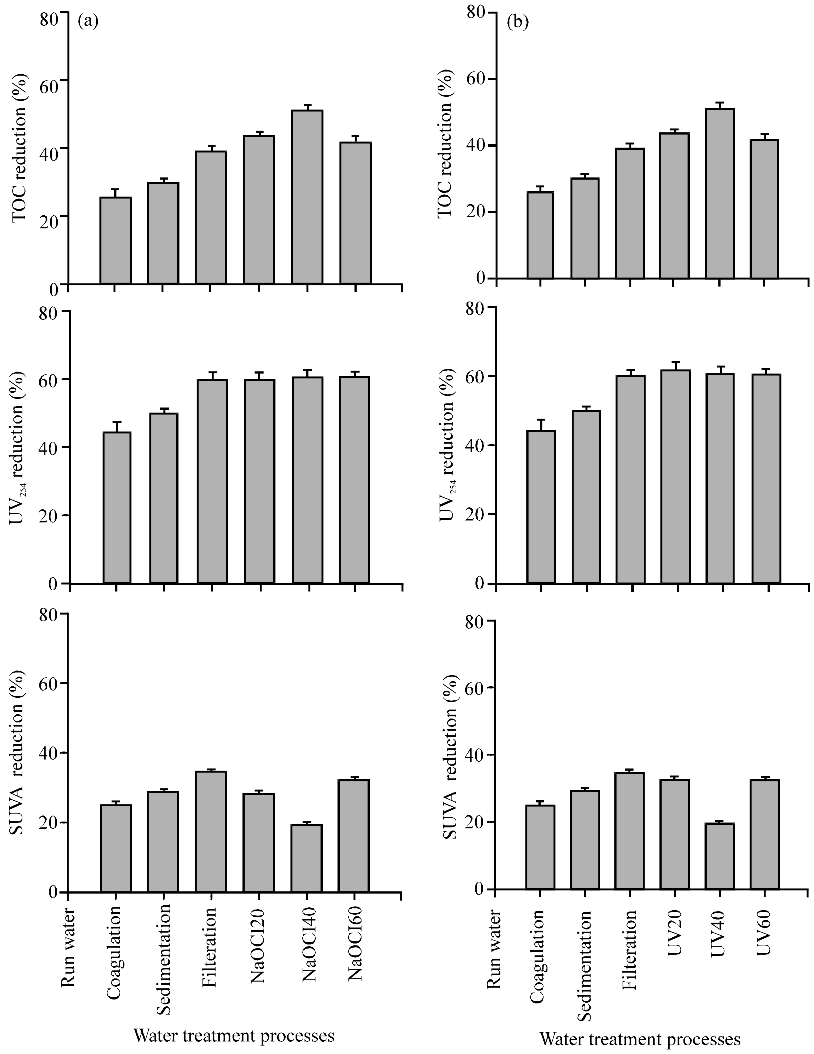

Fig. 1: Reduction of NOM surrogates across water treatment processes with: a) Chlorination and b) UV disinfection

higher dosage NOM has been oxidized further into more hydrophilic (Kim and Yu, 2005; Liu *et al*., 2009). The percentage reduction in both disinfection indicated that about half of organic matter which is high molecular weight, could be oxidized into lower molecular and the remain organic matter could be characterized as low molecular weight compound. Meanwhile, comparison among TOC, UV and SUVA value removal showed that UV removal resulted the highest reduction, on average 60%. This can be explained by the fact that compounds containing aromatic structure and conjugated C = C double bond of NOM absorb more UV light per unit concentration of DOC than the general NOM molecules (Hidayah *et al*., 2016).

Effect of disinfection processes, dosage and reaction time to nom surrogates reduction: Figure 2 shows NOM surrogates reduction, as compared to that of the initial concentration from filtration effluent, under different disinfection processes, dosage and reaction time. First, it can be seen that the TOC, UV_{254} and SUVA value decrease with increasing reaction time. Reaction time attributed to the exposure or contact time of organic matter with disinfectant. The longer exposure time will give longer oxidation process of organic matter and causes degradation of high molecular weight into lower molecular (Edzwald and Tobiason, 2011).

Second, Fig. 2 reveals that increasing dosage caused increasing reduction of TOC, UV_{254} and SUVA value. It shows that TOC has a much higher reduction than all other NOM surrogates (UV_{254} and SUVA value), about 63% in UV disinfection. The results showed a contradiction over the characteristic of NOM surrogates during water treatment processes (Fig. 1) which shows

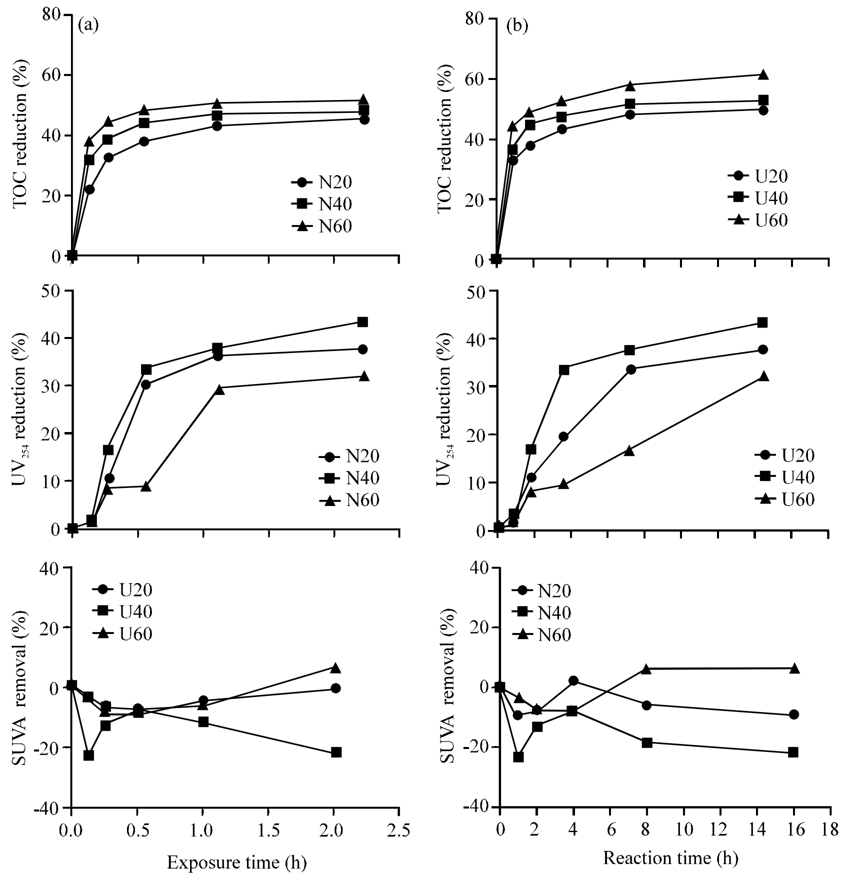

Fig 2: NOM surrogates reduction under different disinfection processes, dosage and reaction time: a) Chlorination and b) UV light

UV_{254} has the highest removal. It seems that high molecular weight, including aromatic compound had been breakdown into lower molecular prior to disinfection process, therefore, lower molecular weight and aliphatic were more identified during disinfection than high molecular weight and aromatic compound.

Third, comparison between disinfection with chlorination and UV light in all NOM surrogates revealed that UV disinfection has higher reduction than disinfection with NaOCl. It indicated that UV process is more amenable to reduce organic matter than disinfection with NaOCl. It could be explained that UV light transmitted into a water is absorbed by nucleic acids of a microorganism, it causes damage to the genome, rendering the microbes unable to replicate (Linden and Rosenfeldt, 2011). It means that organic matter compound which is derived from microbes will decrease. In addition, molecular size distribution of NOM shifts toward smaller molecules during UV irradiation at levels typical of drinking water disinfection (Reckhow and Singer, 2011). Changes in NOM size and functional group content would be expected to have an impact on organic matter characteristic in treated water. Over all, UV light contributed to the higher degree processes of organic matter than chlorination disinfection.

CONCLUSION

Based on the results from the NOM ssurrogates of the source water and treated water from FeCl3 coagulation, sedimentation, activated carbon filtration and two different disinfection processes, namely: chlorination and UV, it reveals that, among all NOM surrogates, UV removal resulted the highest reduction, on average 60%. Effect of disinfection processes, dosage and reaction time to NOM surrogates reduction indicated that NOM decrease with increasing reaction time, increasing dosage caused increasing reduction of NOM and UV disinfection contributed to the higher degree processes of organic matter than chlorination disinfection. Even, TOC has a much higher reduction, about 63%, than all other NOM surrogates (UV_{254} and SUVA value).

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