



Pretreatment Comparison Between Preoxidation and Prechlorination on the Changing of Natural Organic Matter

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ABSTRACT

Surface water is mainly used as source water after treatment process to produce drinking water or clean water. The existence of natural organic matter (NOM) in surface water caused some problems in water treatment, instead of taste and aesthetic issues. Preoxidation and prechlorination are oxidation processes that have been used widely for different purposes in water treatment process. The objective of the study was to compare performance of permanganate preoxidation and prechlorination in removing NOM and to know the changing of NOM in term of its functional group properties by using Fourier-Transform Infrared (FTIR). TOC concentration and UV_{210} value were used to represent NOM parameter. The results showed that prechlorination has a higher performance to treat NOM in water than permanganate preoxidation. Further, prechlorination could be considered as pretreatment of coagulation in order to improve its performance in removing TOC concentration and aromatic compounds. FTIR could be applied to track the changing of NOM functional groups, and organic properties in prechlorination followed by alum coagulation have the lowest percentage transmittance.

INTRODUCTION

Aquatic natural organic matter (NOM) is a complex mixture of organic compounds in aquatic environment. NOM could be generated in water due to microbial activities and degradation of dead organisms, such as algae. NOM could be formed from land and soil that is transported to the water body through watershed runoff or washing out of upstream water bodies. Recently, industrial activities and its biological treatment contributed to the increasing of organic matter compounds in water bodies, or it is known as the effect of effluent organic matter (EfOM) (Shon et al. 2012). Surface water is mainly used as source water for water treatment process to produce drinking water or clean water. The existence of NOM in surface water causes some problems in water treatment, besides taste and aesthetic issues. For example, higher NOM concentration needs higher coagulant demand, incomplete NOM removal in coagulation can cause membrane fouling, and NOM will compete with the target compounds in advance process, such as ion exchange and activated carbon (Han et al. 2015). In disinfection process, NOM which is not removed by previous treatment, can react with chlorine and form disinfectant by-products (DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs) (Reckhow & Singer 2011).

Number of treatment processes have been applied to remove NOM in source water. However, NOM removal is highly dependent on the characteristics of NOM and its

concentration. Coagulation is most widely used in water treatment processes. It has been known that coagulation could be applied to remove NOM through aggregation mechanism (Silanpaa et al. 2018, Hidayah et al. 2016). The removal mechanism of NOM will be different for specific types of NOM, because NOM has different characteristics. Aromatic and humic substances organic matter is mainly removed by coagulation through entrapment, charge neutralization and adsorption (Silanpaa et al. 2018), while aliphatic and non-humic substances can be removed by advanced treatment processes, such as membrane filtration, adsorption and ion exchange (Lamsal et al. 2012). Preoxidation has been known as pretreatment to improve coagulation process. Preoxidation could be conducted by ozone, chlorine, chlorine dioxide, permanganate, while each of preoxidant has its advantages and disadvantages. Preoxidation has various mechanisms to destroy the organic coating on the surface of particles, even preoxidant permanganate generated manganese dioxides in-situ to support organic settling. However, the higher dosage of permanganate could cause colour problems in the treated water (Ma et al. 2001, Hidayah & Yeh 2018). Prechlorination, which has high oxidation potential, is a strongest oxidant and has been applied in water treatment process, especially in post chlorination to remove pathogens. However, disinfectant by-products (DBPs) will be formed in the treated water due to chlorine is very reactive and easy to react with NOM (Kristiana et al. 2014).

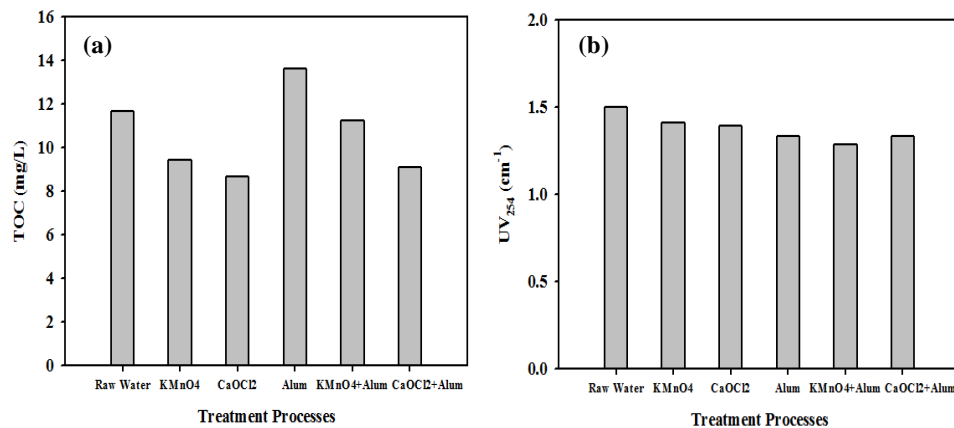


Fig. 1: NOM concentration in terms of (a) TOC concentration and (b) UV₂₁₀ value under different treatment processes.

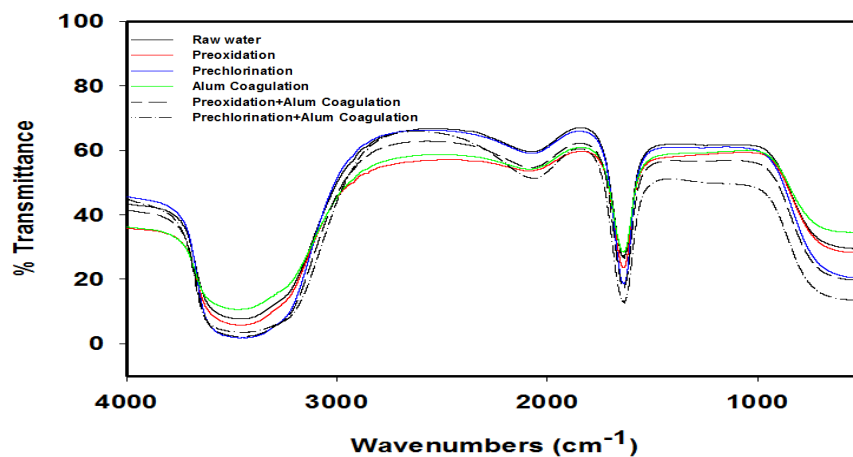


Fig. 2: Spectrum FTIR of the source water and treated water from different treatment process.

According to organic matter properties, it has been found that permanganate causes a reduction of high molecular weight biopolymers (Xie et al. 2016, Hidayah et al. 2017), while chlorine reduces high molecular and humic substance-like compounds (Hua & Reckhow 2007). However, few studies have investigated the changing of organic matter properties, in terms of its functional groups, in both preoxidation and prechlorination followed by coagulation. This study compared the performance of preoxidation and prechlorination in removing NOM and looked into the changing of NOM in terms of its functional group properties by using Fourier-Transform Infrared (FTIR). Surface water was treated by permanganate preoxidation and prechlorination followed by alum coagulation.

MATERIALS AND METHODS

The sample was collected from Jagir River, a main surface water source for water treatment plant in Surabaya, during

dry season. The experiment was conducted by using jar test apparatus (Phipps & Bird, Richmond, VA, USA). A litre of source water sample was placed in the six stirrers at a time under different treatments, including: raw water only, 0.8 mg/L KMnO₄ (Merck, Germany) preoxidation, 25 mg/L CaOCl₂ (Merck, Germany) prechlorination, 35 mg/L (Al₂(SO₄)₃·18H₂O (Merck, Germany), 0.8 mg/L KMnO₄ followed by 35 mg/L alum, 25 mg/L CaOCl₂ followed by 35 mg/L alum. Dosage was obtained from preliminary experiment. The contact time for preoxidation and prechlorination was 60 minute under slow mixing at 35 rpm. Alum coagulation was setup under 100 rpm flash mixing for 3 min, followed by 35 rpm slow mixing for 15 min, and settling for 30 min. Sample was filtered through 0.45 μm (cellulose acetate, Toyo Roshi, Japan) before further measurement.

The sample was analysed for TOC by using total organic carbon analyser (Model TOC-500, Shimadzu, Kyoto, Japan). UV₂₁₀ was measured using UV/vis spectrophotom-

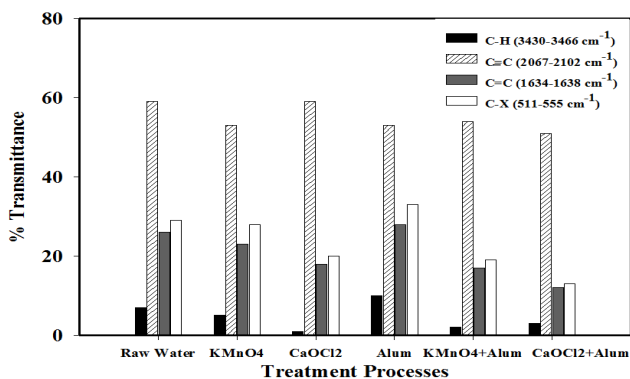


Fig. 3: Percentage transmittance of spectrum from FTIR analysis of the source water and treated water.

eter (Model U-2001, Hitachi, Japan) with a 1 cm quartz cell (APHA 2012). The powder of raw water and treated sample obtained via freeze-drying method was analysed for the structural and organic characteristics by FTIR. Briefly, KBr pellets were prepared by grinding the samples with spectrographic grade KBr in an agate mortar utilizing a fixed amount of sample (1%, wt%). FTIR spectroscopy (Thermo Nicolet NEXUS 670) was used to identify the functional groups, scanning from 4000 cm^{-1} to 400 cm^{-1} .

RESULTS AND DISCUSSION

Effect of preoxidation and prechlorination as coagulation pretreatment on NOM concentration: Figs. 1a & 1b showed NOM concentration in terms of TOC concentration and UV_{210} value under different treatment processes, respectively. First, source water has a high TOC concentration of 11.67 mg/L and contain aromatic compounds with conjugated C=C double bond, as indicated by UV_{210} value. The high NOM concentration is probably due to human activities like discharge of domestic wastewater into Jagir River. According to the sampling site, area around Jagir River is indicated with high density population, and domestic wastewater discharged directly to the river. In addition, an industrial park has been settled down at the upstream of Jagir River and its effluents are discharged to the river. It has been well known that wastewater treatment from industrial activities might contribute to the quantity and quality of organic matter in the river bodies, or it is known as effluent organic matter (Shon et al. 2012). Second, all treatments could remove the organic matter concentration, except alum coagulation. Decrease of TOC concentration seems less than 50%, which indicates that source water contain mainly non-aromatic compounds. Meanwhile, increased TOC concentration during alum coagulation is probably due to the formed floc which may contain organic matter. Preoxidation, prechlorination, and pretreatment followed by alum coagulation has a high reduction of NOM. Third, prechlorination

showed a higher performance in removing TOC concentration than the other methods. It is probably due to hypochlorite, a hydrolysis product of chlorine in water, oxidized the coating organic matter into lower molecular weight or transformed aromatic or high molecular weight of organic into different compounds (Xie et al. 2016, Hidayah et al. 2017, Cahyonugroho & Hidayah, 2018). This suggestion is supported by UV_{210} value, which showed decreasing concentration in all treatment processes. UV_{210} detected aromatic compounds, therefore decreasing UV_{210} value indicated that aromatic compounds have been reduced. It has been well established that aromatic and humic substances are easy to be degraded by coagulation only, preoxidation, and combination of water treatment processes (Edzwald & Tobiason 2011).

Effect of preoxidation and prechlorination as coagulation pretreatment on the changing of NOM: Fig. 2 showed the spectrum from FTIR analysis of the source water and treated water from different treatment processes, and the percentage transmittance of FTIR spectrum is described in the histogram graph as shown in Fig. 3. First, the results indicate that source water contains four peaks, which identify the four major functional groups including: C-H compounds at wavelength 3430-3466 cm^{-1} , triple bond C \equiv C compounds at wavelength 2067-2102 cm^{-1} , double bond C=C compounds at wavelength 1634-1638 cm^{-1} , and C-X compounds at wavelength 511-555 cm^{-1} . Second, source water mainly contains of group triple bond C \equiv C compounds. It is consistent with the TOC concentration and UV_{210} value, as compared with Fig. 1a & Fig. 1b, which showed less than 50% decreasing value of NOM concentration.

Third, all treatment processes identify the decreasing of functional group compounds, except in alum coagulation process. This result is consistent with the TOC concentration and UV_{210} value. Alum coagulation performed increasing percentage transmittance of all functional groups, except triple bond C \equiv C compounds. It seems that three functional groups C-H, C=C, and C-X compounds represented a group of compounds that is related to increasing TOC concentration in alum coagulation. Fourth, prechlorination followed by alum coagulation showed a higher reduction of percentage transmittance of organic matter, it means that prechlorination-alum coagulation could be considered as an alternative process to remove NOM in water.

CONCLUSION

Source water of Jagir River contains high TOC concentration, aromatic compounds and mainly composed of single and triple bond organic matter. This study concluded that alum coagulation only removes aromatic organic com-

pounds in source water. Therefore, alum coagulation needed a pretreatment to improve coagulation efficiencies in removing NOM. Preoxidation and prechlorination could be considered as pretreatment of coagulation process. Prechlorination followed by alum coagulation performed a higher reduction than preoxidation-alum coagulation. However, prechlorination-alum coagulation need a further process to remove nonaromatic compounds, such as triple bond $C\equiv C$ compounds.

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