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Characterization of Natural Organic Matter by $FeCl_3$ Coagulation

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Abstract. Natural organic matter (NOM) is heterogenous mixture of organic compounds that enter the water from various decomposition and metabolic reactions, including animal, plant, domestic and industrial wastes. NOM refers to group of carbon-based compounds that are found in surface water and ground water. The aim of the study is to assess organic matter characteristics in Jagir River as drinking water source and to characterize the organic components that could be removed during coagulation. Coagulation is the common water treatment process can be used to remove NOM with $FeCl_3$ coagulant in various dosage. NOM surrogates, including total organic carbon (TOC), ultraviolet absorbance at 254 nm (UV_{254}) and specific UV absorbance (SUVA) were chosen to assess the organic removal. Results of jar test experiments showed that NOM can be removed about 40% of NOM surrogates with 200 mg/L $FeCl_3$. About 60% removal of total organic fraction, which is mainly humic substances, as detected by size exclusion chromatography (SEC).

1. Introduction

Jagir River was used as the sources water for drinking water supplies in water treatment plant in Surabaya city. However, Jagir river is very polluted due to discharging of wastewater from industrial and domestic from upstream, as shown by high concentration of DO minimum 0.8 mg/L. Discharge of untreated and treated wastewater into drinking water sources might contained organic matter, instead of natural organic matter [1]. Natural organic matter (NOM) in natural waters is heterogenous mixture of organic compounds that enter the sources water from various decomposition and metabolic reactions, including animal and plant (allochthonous) and from algal sources (autochthonous) [2]. NOM is composed of relatively high molecular weight to low molecular weight and also classified as humic matter and non-humic matter. The presence of NOM, aside from the obvious taste and aesthethic issues, can impact water treatment. In the final disinfection stage, NOM which is not removed by previous treatment processes can reacts with chlorine to form potentially carcinogenic disinfectant by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) [3].

Removal of NOM from water sources is highly dependent on the characteristics of the NOM present (e.g., molecular weight distribution, carboxylic acidity and humic substances content), its concentration and the removal methods applied. Different water treatment methods have been used for the removal of NOM from water sources with varying degree of success. Coagulation and flocculation is the most common and feasible processes to remove NOM due to aggregation mechanism [4]. The aggregation mechanisms through combination of charge neutralization, entrapment, adsorption and

complexation with coagulant metal ions into insoluble particulate aggregates [5]. Aluminium and ferric based coagulants is widely used in drinking water treatment [3, 6]. The most commonly used aluminium-based coagulant has been ferric chloride ($FeCl_3$), with other coagulants including aluminium chloride ($AlCl_3$). Trivalent ferric ions are released into a solution from the respective salt. $FeCl_3$ based coagulant are hydrolysed and form soluble complexes possessing high positive charges [5, 7].

The aim of this study is to assess organic matter characteristics in Jagir River as source water from drinking water and to characterize the organic components that could be removed during coagulation. This study showed the performance of high performance liquid chromatography-size exclusion chromatography (HPLC-SEC) with organic carbon detector, in addition to NOM surrogates parameters, such as total organic carbon (TOC), ultraviolet at 254 nm wavelength (UV_{254}) and specific UV absorbance (SUVA).

2. Material and method

Raw water samples was taken from Jagir River in Surabaya city, Indonesia. Jar test was performed using jar test apparatus Phipps & Bird, Richmond, Virginia. About 1000 ml of water sample and added various dosage of $FeCl_3.6H_2O$ coagulant to rapid mixing 150 rpm for 5 min, followed by slow mixing 35 rpm for 15 min, then settling for 30 min. Supernatant liquid was collected for organic carbon analysis. Various dosage of $FeCl_3$ is 5, 10, 25, 50, 100, 200 (mg/L).

2.1. Organic carbon analysis

Raw water sample and the samples after coagulation were filtered through 0.45 um membrane filter paper and were measured as total organic carbon (TOC) by using a Shimadzu TOC-5000A. 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} ratio to TOC concentration. HPLC-SEC analysis was conducted by using Dionex Ultimate 3000 HPLC system with a flow rate 0.5 mL/min. Chromatogram of HPLC-SEC were analyzed using peak fitting technique to provide quantitatively removal. Peakfit version 4, Systat Software is a commercially available software used for peak fitting technique.

3. Results and discussion

The characteristic of raw water quality parameters as represented by NOM surrogates TOC 3.6 mg/L and UV 254 0.078 cm^{-1}. SUVA value showed 2.2 L/mg-m which corresponded to the composition of NOM in Jagir River is mixture aquatic humics and non-humic, mixture of hydrophobicity and mixture molecular weight [2]. NOM component in Jagir River could be generated from domestic and industrial activities, in addition to organic matter that have been released due to microbial activities in the water bodies. Wastewater treatment could not remove all organic contaminants and when it was discharged into aquatic environment, the contaminant can ultimately lead to the growth of undesirable aquatic life [1]. Total organic carbon is always measured by TOC instrument operated with high-temperature combustion and infrared ray to detect the amount of formation of carbon dioxide. Hence, TOC instrument just could provide total carbon content and not distinguish the individual distribution of organic fraction. This lack of information could be solved using HPLC-SEC equipped with organic carbon detector system having an ability to provide the qualitative information of chromatogram as a function of elution time in minutes. According to the current reports [8,9], the diagram of HPLC-SEC shows some peaks respectively, biopolymer with elution time before 75 minutes, including polysaccharide, or amino sugars; humic substances with elution time after 75 min to 100 min and low molecular weight with elution time more than 100 min, as shown in Figure 1. According to Figure 1, raw water before and after treatment is dominated by humic substances.

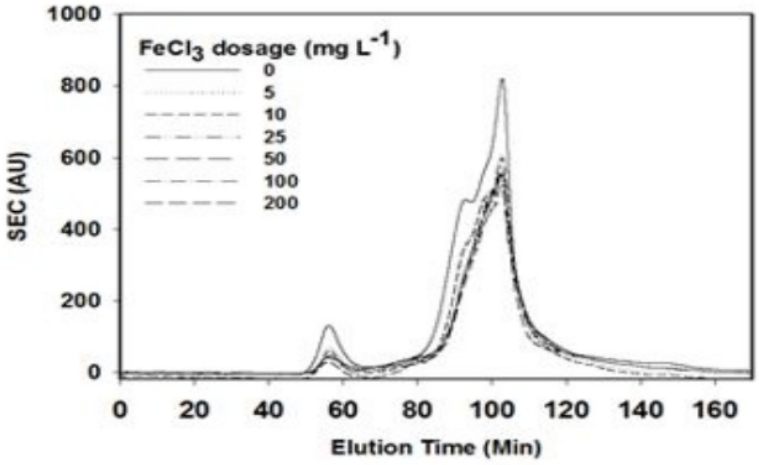

Figure 1. HPLC-SEC chromatograms of raw water before and after treated by $FeCl_3$ coagulation

3.1. Removal of NOM surrogates parameters

The effect of the various $FeCl_3$ dosage on the NOM removal in Jagir River were measured by TOC, UV_{254} and SUVA with the percentage removal of organic matter after coagulation (Figure 2). As $FeCl_3$ coagulant dosage increased, the removal of TOC increased, in-line with increasing UV_{254} removal. The aggregation mechanisms through organic matter removal could be a combination of charge neutralization, entrapment, adsorption, complexation, which would be different for types of organic matter due to the various composition of NOM [4]. After $FeCl_3$ coagulant was hydrolyzed and form several soluble complexes possessing high positive charges, thus adsorbing onto the surface of the negative colloids [5, 6]. It seems that Jagir River is mixture of aromatic and aliphatic compound, since overall organic removal is less than 40% indicated presence of remaining organic matters. Coagulation showed slightly higher UV_{254} removal than TOC removal; in addition to less than 10% insignificantly SUVA removal.

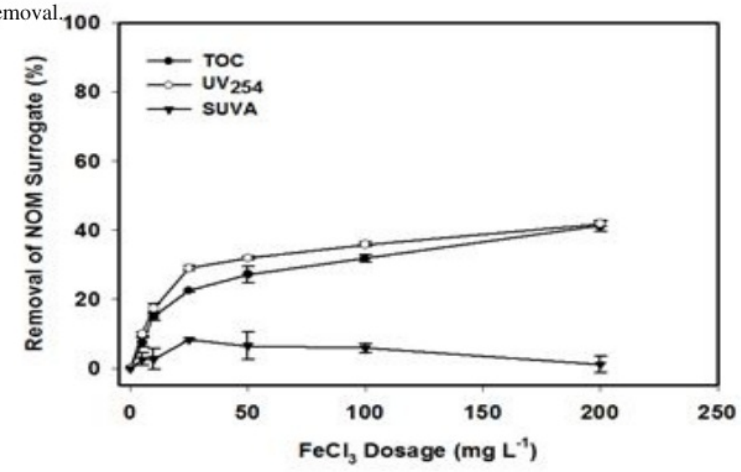

Figure 2. Removal of TOC, UV_{254} and SUVA value as function of $FeCl_3$ dosage.

3.2. Removal of organic fractions by using HPLC-SEC

Figure 3 shows percentage removal of organic fractions in Jagir River before and after coagulation. Distribution of organic fractions have been shown in Figure 1, then peak fitting technique was used to explain Figure 1 quantitatively. Coagulation with $FeCl_3$ decreased the NOM content effectively and led to the more disappearance of second peak or humic substances. Humic substances were more identified significantly removal than biopolymer and low molecular weight, as shown by increasing $FeCl_3$ dosage obtained increasing removal of humic substances. Insignificantly removal of biopolymer and low molecular weight indicated low efficiency of $FeCl_3$ in the coagulation process in removing organic fraction [4, 10]. It seems that high molecular weight in biopolymers probably contained more hydrophilic compound, since coagulation is hard to remove hydrophilic compound [7, 11, 12]. Low molecular weight content have been identified as higher carboxylic acid or highest content of acidic functional groups are the most difficult to destabilize by coagulation [7,13]. By comparing Figure 2 and Figure 3, total organic fraction removal is consistent with TOC and UV_{254} removal, while SUVA removal showed similar trend removal with biopolymers and low molecular weight removal. It indicated that $FeCl_3$ coagulation is easy to remove aromatic and hydrophobic compound and difficult to remove aliphatic and hydrophilic compound.

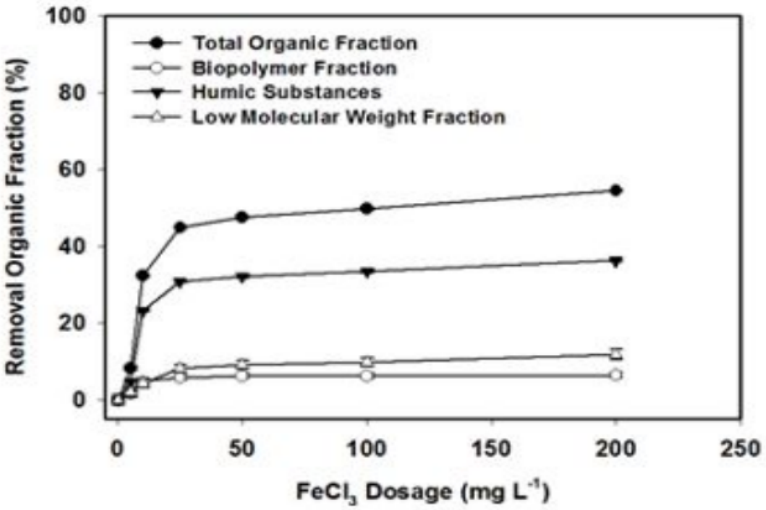

Figure 3. Organic fractions removal at various dosage of $FeCl_3$ coagulant.

4. Conclusions

Based on this study, size exclusion chromatography have been applied with peak fitting technique is usefull method to assess characteristic of organic fractions by using coagulation. $FeCl_3$ coagulant with jar test method was succesful in predict which organic fraction in Jagir River as removable and non-removable fractions, less than 60% of total fractions removal. Overall, assessment of NOM removal by coagulation was good, with variation removal less than 40% for UV_{254} since UV absorbance could detected aromatic compound significantly. Efficiency coagulation to remove organic fraction in different source water should be tested due to different characteristic of organic fractions.

Acknowledgments
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