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CHARACTERISATION OF NATURAL ORGANIC MATTER IN COAGULATION PROCESS BY USING SIZE EXCLUSION CHROMATOGRAPHY

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Abstract

Natural organic matter (NOM) refers to group of carbon-based compounds that are found in surface water and ground water. The aim of the study is to reveal organic matter characteristics in Jagir River as drinking water source and to characterize the organic components that could be removed by FeCl3 coagulation. Coagulation is the common water treatment process that can be used to remove NOM with FeCl3 coagulant in various dosage. NOM surrogates, including total organic carbon (TOC), ultra violet absorbance at 254 nm (UV254) and specific UV absorbance (SUVA) were chosen to assess the organic removal. Results of jartest experiments showed that NOM can be removed about 40% of NOM surrogates with 200 mg/L FeCl3. About 32% removal of dominated organic fractions humic substances from total fractions removal as detected by size exclusion chromatography (SEC)

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 (Shon et al. 2006). 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 (allochtonous) and from algal sources (autochthonous) (Edzwald 2011). NOM is composed of relatively high molecular weight to low molecular weight and also classified as humic matter and non-humic matter (Croue et al. 2003). 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) (Liang and Singer 2003; Wang et al. 2013).

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 (Wang et al. 2013). The aggregation mechanisms through combination of charge neutralization, entrapment, adsorption and complexation with coagulant metal ions into insoluble particulate aggregates (Chow et al. 2009). Aluminium and ferric based coagulants is widely used in drinking water treatment (Wang et al. 2013; Chow et al. 2009). The most commonly used aluminium-based coagulant has been alum ($Al_2(SO_4)_3$), with other coagulants including aluminium chloride ($AlCl_3$). Trivalent aluminium ions are released into a solution from the respective salt. Alum based coagulant are hydrolysed and form soluble complexes possessing high positive charges (Amirtharajah and Mills 1982; Her et al. 2002).

Characterization of NOM by high-performance size exclusion chromatograph (HPSEC) has proved a significant advancement in the development of separation system and detectors for qualitative information of varying apparent molecular weight (AMW) of NOM fractions (Chow et al. 2009; Korshin et al. 2009; Wang et al. 2013). Analysis of spectroscopy is often coupled with the advanced statistical and computational techniques for exploration of the distribution patterns qualitatively and quantitatively, currently peak-fitting is a technique to resolve the overlapped chromatographic peaks (Chow et al., 2008).

The aim of this study is to reveal organic matter characteristics in Jagir River as source water fro drinking water and to characterize the organic components that could be removed by using $FeCl_3$ 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).

Materials and methods

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).

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-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. Sample fractionated with a Hewlett-Packard HPLC 1100-series system, equipped with a diode arrat UV detector 254 nm and a TSKgel G3000SW 7.5mm(ID) x 30 cm column. Sodium acetate 0.01 M was used as an eluent at a flow rate 1 ml/min. Injection volume was 30 µL.

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.

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 (Edzwald 2011). 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 can 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 (Shon et al. 2006). 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 absenct 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 (Matilainen et al. 2010; Huber et al. 2011), 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.

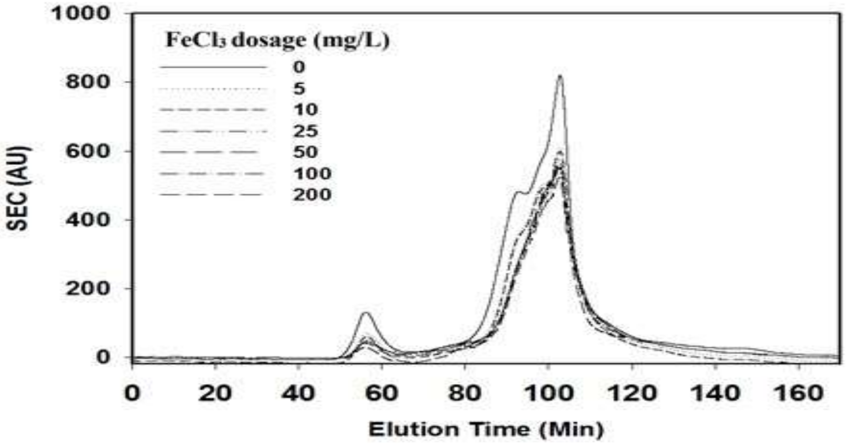

Figure. 1 HPLC-SEC chromatograms of raw water before and after treated by FeCl3 coagulation

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 (Chow et al. 2009). After $FeCl_3$ coagulant was hydrolyzed and form several soluble complexes possessing high positive charges, thus adsorbing onto the surface of the negative colloids (Amirtharajah et al. 1982; Jarvis et al. 2004). 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 slighlty higher UV_{254} removal than TOC removal; in addition less than 10% insignificantly SUVA removal.

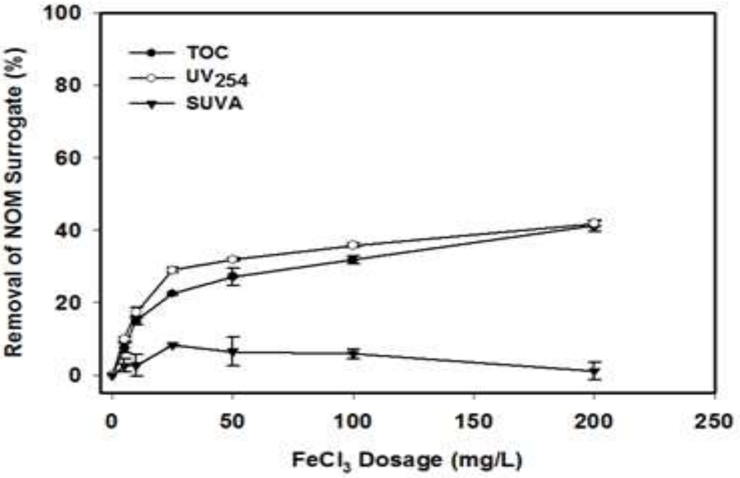

Figure 2. Removal of TOC, UV_{254} and SUVA value as function of $FeCl_3$ dosage.

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 identified significantly 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. (Chow et al. 2009; Matilainen et al. 2010). It seems that high molecular weight in biopolymers probably contained more hydrophilic compound, since coagulation is hard to remove hydrophilic compound (Her et al

. 2002; Huber et al. 2011). 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 (Amirtharajah et al. 1982). 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 coagulation is easy to remove aromatic and hyrophobic compound and difficult to remove aliphatic and hydrophilic compound.

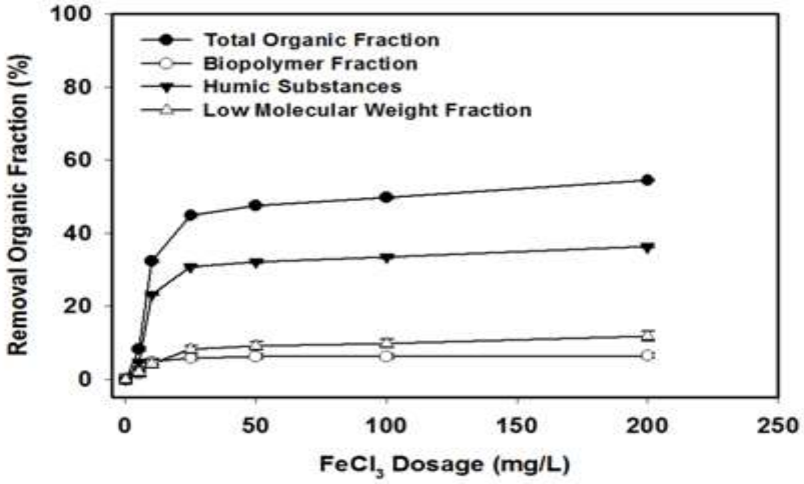

Figure 3 Organic fractions removal at various dosage of $FeCl_3$ coagulant.

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Conclusions

Based on this study, size exclusion chromatography have been applied with peak fitting technique is usefull method to reveal characteristic of organic fractions by using coagulation. Jagir River contains aromatic and hydrophobic humic subtances as dominant compound and $FeCl_3$ 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, even though coagulant is difficult to remove hydrophilic compund. Efficiency coagulation to remove organic fraction in different source water should be tested due to different characteristic of organic fractions.

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