Effect of Flow Rates and Filter Media in Removing Natural Organic Matter as Detected by Using Fluorescence Excitation Emission Matrices

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EFFECT OF FLOW RATES AND FILTER MEDIA IN REMOVING NATURAL ORGANIC MATTER AS DETECTED BY USING FLUORESCENCE EXCITATION EMISSION MATRICES

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ABSTRACT

Natural organic matter (NOM) in water is mixture compound of organic, which is derived from animal and dead plant, microorganism and degradation by-products. NOM has various quantity and composition, however has low concentration in water and hardly detected and classified. Water treatment processes have different ability to remove NOM, it depends on the characteristic of NOM. This research aims to characterize NOM in laboratory scale of water treatment under various flow rate and filter media by using spectroscopy and fluorescence analysis. Source water contains aromatic and hydrophobic compound with TOC 3.3 mg/L and SUVA 2.17 L/mg.m. Fluorescence method identified that source water contain of humic acid-like 52% and fulvic acid-like 26%. Coagulation-filtration with flow rate 30 L/hour and activated carbon could removed TOC 55%, UV_{254} 45%, and humic acid-like and fulvic acid-like around 35-38%.

Keywords: natural organic matter, coagulation-filtration, filter media, flow rate.

INTRODUCTION

Natural organic matter (NOM) is one of the parameter that affect water quality during treatment process (Matilainen et al., 2010). Natural organic matter, especially in waters composed of a group of organic carbon derived from plant or aquatic biota as well as from organic materials derived from industrial and domestic waste. NOM is responsible for the formation of disinfection by-products, causing the re-growth of biology in the water distribution system, the main contribution of NOM is causing the problem of color, taste and smell, and also transport of inorganic and organic pollutants (Kim, et al., 2005). Coagulation and filtration are two common processes carried out on water treatment, coagulation is mixing water and coagulant and thus forming floc that can precipitate, and formed floc will be filtered on the filtration process for reducing turbidity. NOM could be removed in the process of coagulation and flocculation is through the mechanism of formation of aggregates floc. Filtration is the cleaning of solid particles from a fluid by passing the filtration medium, on which solids will precipitate out. Coagulation process is determined by the dose and the type of coagulant, while filtering is strongly influenced by the type of filter media (Edzwald, 2011; Matilainen et al., 2005).

Spectrophotometric can be used to analyze the concentration of a substance in a solution based on the absorbance of the color of the solution at a particular wavelength. Some spectrophotometric method, for example: dissolved organic carbon, or TOC, measure all the dissolved organic material without knowing what kind of organic material contained in water (APHA, 2005), spectroscopic methods UV/Vis UV254 provides information on the organic matter content of aromatic carbon. SUVA value provides an indication of the type of organic material that is dominant in water. SUVA value > 4 indicates the composition of the aqueous and organic humic with high molecular weight. SUVA value 2-4 indicates a mixture of organic material and non-humus humus, while SUVA value < 2 indicates a non-humic dominant components (Edzwald, 2011). The other spectrophotometric method is using fluorescence. Fluorescence is the emission of light radiation by a material after excited by the high-energy light beam. Fluorescence is a process of moving the energy levels of the excited atoms to the state to a stable state, and this process takes approximately 1 nano seconds (Leenheer et al., 2000).

Therefore, this study aimed to characterize the type of natural organic matter which successfully removed in the process of coagulation and filtration under various filter media and flow rates through fluorescence analysis.

METHODOLOGY

The study focused on characterization of NOM in source water through water treatment unit, including coagulation with coagulant FeCl3, sedimentation, and filtration with activated carbon or silica sand media, and detected by using spectroscopic methods. Experiment was conducsted under continues process with flow rates 30 L/hr or 60 L/hr. Characterization of NOM using the spectrophotometric method, including NPDOC analysis, analysis of UV at a wavelength of 254 nm or UV254, calculation SUVA (Edzwald 2011 and Her, et al., 2002). Characterization of NOM by using Fluorescence Excitation Emission

Matrices (FEEMs) Perkin Elmers types LS55. The quantification of fluorescence analysis will be solved by Fluorescence Regional Integration (FRI) method, in order to determine the area of fluorescence (Chen et al., 2003).

RESULT AND DISCUSSION

Water Quality Analysis

Sample was taken from Jagir River on June 2016. Firstly, sample was analyzed to observe the initial water quality of the Jagir River. The optimum dosage of $FeCl_3$ coagulant 200 mg/L, were determined based on the dosage which is obtained from 1st year of previous study. Table 1 shows Jagir River water quality data prior to coagulation-filtration. Jagir River has a neutral pH, low turbidity, it is probably due to sample was taken during the dry season. Low alkalinity will affect the dose of coagulant. Low value of organic pollutants, which is indicated by dissolved oxygen (DO) and biological oxygen demand (BOD), is probably due to effect of dry season and sun exposure resulting in the degradation of organic matter (Delpla *et al.*, 2009).

Table 1. Water quality of jagir river before treatment process

Water quality parameter	Concentration
pH	6.8
Turbidity (NTU)	45
Alkalinity (mg/L)	60
[illegible] (mg/L)	3.0
TOC (mg/L)	3.3
UV_{254} (cm^{-1})	0.072
SUVA (L/mg.m)	2.17

According to Edzwald (2011), the value of SUVA in Jagir River categorized as non-mixture of humic and humic, also a mixture of aliphatic and aromatic components as well as a mixture of hydrophobic and hydrophilic components. The mixture of organic material components shows the influence of natural organic matter derived from domestic sewage or industrial wastewater (effluent organic matter) and terrestrial (allochtonous) as well as organic materials resulting from the micoorganism in water (autochtonous).

Effect of Filter Media and Contact Time to Removal of Natural Organic Matter

Coagulation with $FeCl_3$ 200 mg/L remove NOM in terms of total organic carbon (TOC), UV_{254} to indicate aromaticity of organic matter, and in terms of SUVA value to represent the polarity of NOM. Based on Figure 1., Figure 2. and Figure 3. which shows the removal of NOM under various flow rates and filter media, which is shown as TOC, UV_{254} and SUVA. Each parameter has the ability to detect natural organic matter. TOC provides information on the quantity of organic matter without knowing the type or quality of the organic material.

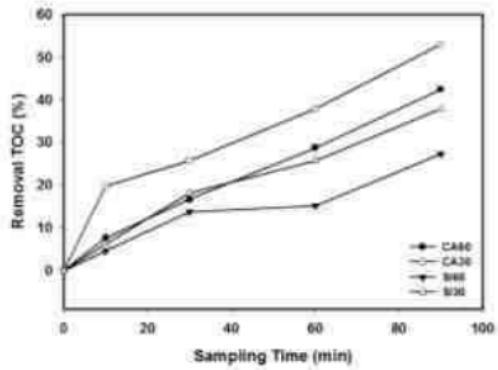

Figure 1. TOC removal under different flow rates and filter media.

Based on Figure 1, coagulation could removed less than 60% of TOC under activated carbon media with flow rates 30 L/h. It shows higher removal than using silica sand, about 35%. This means that more than 40% NOM still remained in the sample, which is probably a type of non-aromatic, aliphatic and smaller molecular weight, because coagulant $FeCl_3$ with activated carbon media has not been able to remove those kind of components. This is also supported by Figure 2, which indicates removal of aromatic components around 45% with active carbon media and flow rates 30 L/hr, and 35% removal of TOC with silica sand and flow rate 30 L/hr.

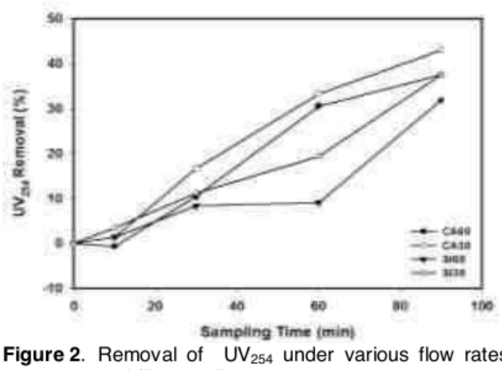

Figure 2. Removal of UV_{254} under various flow rates and filter media.

UV_{254} has lower removal than TOC, it seems that the filtration process is more effective for non-aromatic components. UV_{254} shows aromatic components are easily removed by coagulation because the aromatic components generally have large molecular weight, which is easily tied or formed aggregates with coagulant. TOC detected all organic components that could not be identified its properties. But through filtration process, non-aromatic components shows better removal, it means that filtration with activated carbon has a good capability to remove non-aromatic components.

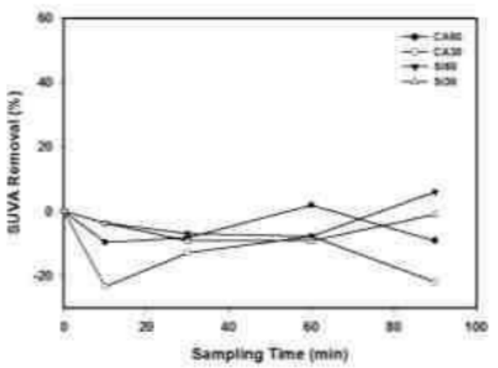

Figure 3. Removal of organic carbon in terms of SUVA value under various flow rates and filter media.

Based on Figure 3, removal of SUVA value, which shows less than 10%, indicates that the organic component is dominated by hydrophilic and those components are quite difficult to be removed or bounded by coagulant or by both filter media. Overall, the composition of organic matter varies greatly, therefore its removal also vary. It corresponds to the mechanisms in removing of organic matter through coagulation and filtration processes will be different for certain types of NOM contained in water.

Aromatic properties and components that have high molecular weight generally excluded through the coagulation process by sweep flocculation mechanism, whereas if the formed aggregates are monomers or intermediate polymers, the mechanisms is complexation, adsorption, or charge neutralization co-precipitation. The formed floc during coagulation have different properties or characteristics, including size, structure and strength (Edzwald, 2011). While in the process of filtration, activated carbon media will filter out fine particles, which couldn't settle simultaneously, then activated carbon will adsorb NOM that has been bonded in the formed floc.

Effect of Filter Media and Contact Time to Removal the Fluoresence of Natural Organic Matter Based on its Region

This part focused on the type of organic matter based on the classification of their region, as shown in Figure 4. Fluorescence Regional Integration techniques (FRI) is used to determine the extent of each region, in order to obtain the effectiveness of the removal of NOM fluorescence based on its flow rates and types of filter media, as described in Figure 5 and Table 2. Coagulation under 200 mg/L $FeCl_3$ and activated carbon or silica sand have removed fluorescence of NOM succesfully such as those obtained by FEEMs with the FRI method. The organic fractions, which is represented by all regions, could not be removed under short contact time, t=10 minutes. It is probably due to the formed floc could not bind NOM and filter media less capability to adsorb NOM under a very short time. Some research found that NOM with hydrophilic properties will be difficult to be bound by the coagulant.

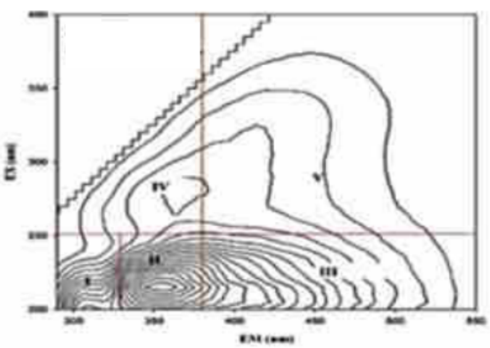

Figure 4. Classification of the NOM region based on its fluorescence properties.

Table 2. Excitation and emission of each NOM region

Region	Excitation (nm)	Emission (nm)	Component
I	< 250	< 330	Aromatic Protein 1
II	< 250	330 - 380	Aromatic Protein 2
III	< 250	380 - 550	Fulvic Acid-Like
IV	250 -400	<380	Soluble Microbial Products
V	250 -400	380 - 550	Humic Acid-Like

It seems that aliphatic hydrophilic component is mostly dominant in Jagir River. Removal of Region 1 aromatic protein 1 (Figure 5a), Region 2 aromatic protein 2 (Figure 5b) and Region 4 soluble microbial products (Figure 5d) seems difficult to be removed under flow rates 60 L/h and silica sand or activated carbon, though under flow rates to 30 L/hr with actrivated carbon. Coagulation and filtration processes under various flow rates and filter media filters has capability around less than 25% for removing Region 1, Region 2 and Region 4. Region 3 fulvic acid-like could removed about 35% under both media and the same flow rates (Figure 5c). While Region 5 humic acid-like obtained 40% removal with activated carbon media and reached 35% by silica sand media (Figure 5e). Activated carbon demonstrates presents more better performance than than silica sand, probably due to activated carbon has larger surface area than the silica sand (Velten *et al.*, 2011). It is consistent with the previous studies (Chow *et al.*, 2009; Edzwald, 2011).

It also has been observed that the effectiveness of $FeCl_3$ as coagulant has an important role before filtration process. $FeCl_3$ coagulant performed in wider pH range although the optimum pH is at pH of 4.5-6. In the pH range 5-7, iron (III) has a lower minimum solubility level than alum, it resulted in the formation of more hydroxide under low coagulant doses. Therefore, hydrolysis of $FeCl_3$ coagulant will produce more hydrolyzed products (Chow *et al.*, 2009; Edzwald, 2011). However, at low doses, humic as anion will bind to cationic coagulant, then formed floc become increasingly congested. Further, increasing dose $FeCl_3$will result in an aggregate acid hydrolysis products Fe humus to cause competition between the components of humic during the destabilization process of colloids. Additionally, since $FeCl_3$ has higher molecular weight, therefore, under the same dose, $FeCl_3$ with other coagulant dose (e.g., alum) will produce 2.8 times more hydroxide products than alum hydroxide. Overall, the combination of coagulation and filtration process has removed NOM about 25% to 35% (Figure 5f). Lower flow rates, 30 L/hr, and activated carbon media produces optimum removal as compared with higher flow rates.

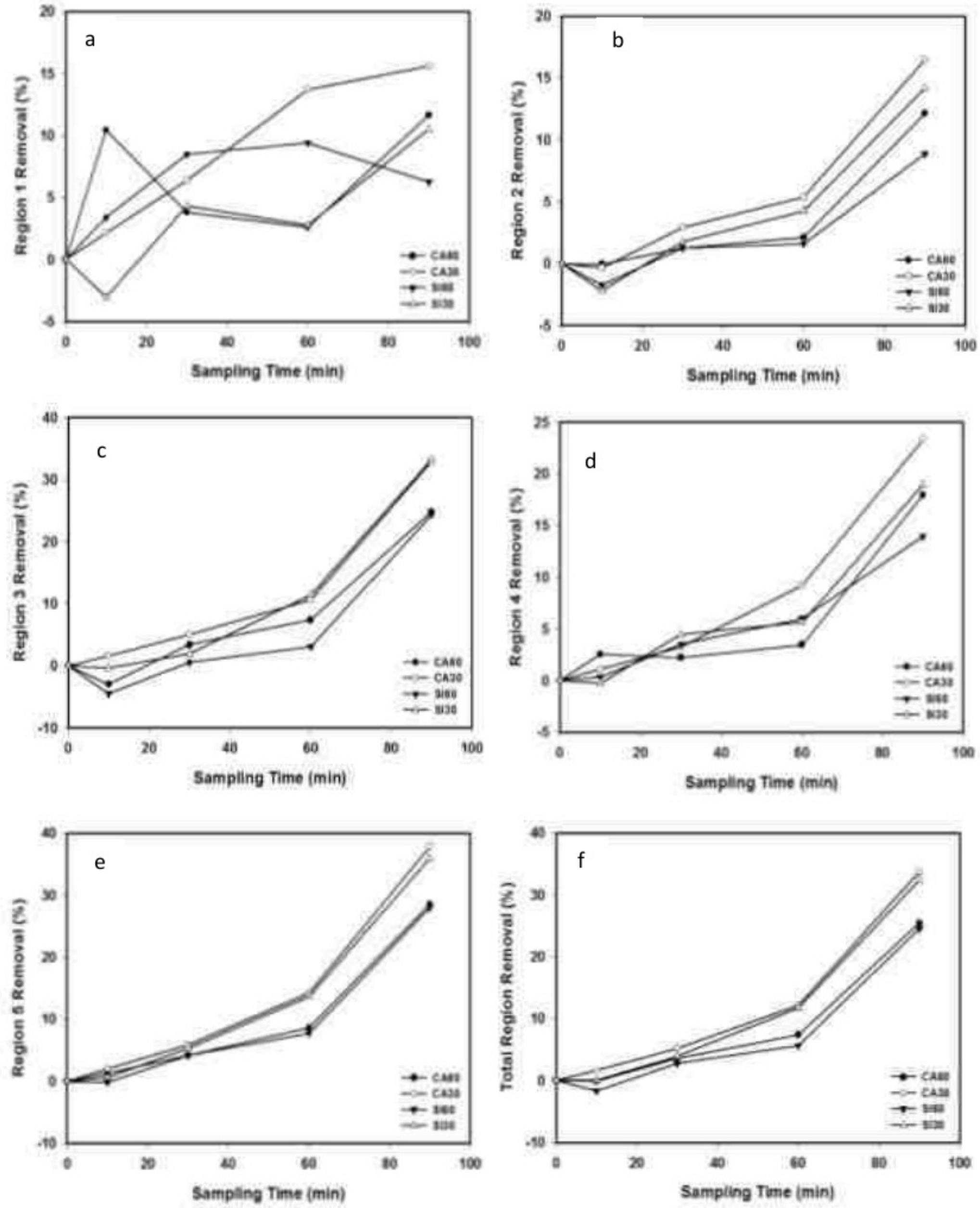

Figure 5. Removal of NOM in each region under various flow rates and filter media based on fluorescence analysis

CONCLUSION

Water quality analysis indicates that River Jagir, Surabaya is mainly composed of aromatic components and slightly hydrophobic, with TOC 3.3 mg/L, SUVA value 2.17 L/mg.m FEEMs measurement and FRI analysis classified Jagir River into five types of organic components, namely the aromatic proteins 1 and 2 (5%), soluble microbial products (15%), fulvic acid-like (35%), and humic acid-like (45%). The process of coagulation and filtration with flow rate 30 L/h removed 50% TOC with activated carbon media and 35% with silica sand media. it is also able to remove aromatic organic or UV_{254} up to 40% with activated carbon media and 35% with silica sand media.5. However, coagulation-filtration has less performance in removing hydrophilic organic components, as indicated by removal of SUVA about less than 10%. Coagulation and filtration with flow rates 30 L/h shows higher removal of fluorescence organic matter, about 35%, as compared with flow rates of 60 L/hr (25%). Substance humic fluorescence, including humic acid and fulvic acid-like-like, is more easily removed by coagulation. Based on HPSEC analysis, biopolymers showed high removal, which indicates that the fluorescence of humic substances is a type of biopolymer.

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