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EFFICIENCY OF NOM REMOVAL AFTER COAGULATION-FILTRATION PROCESS USING FLUORESCENCE REGIONAL INTEGRATION METHOD

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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 determine the efficiency of coagulation-filtration process for removing NOM by using fluorescence spectra analysis. NOM surrogates, including total organic carbon (TOC), ultra violet absorbance at 254 nm (UV_{254}), specific UV absorbance (SUVA), and fluorescence spectra analysis with Fluorescence integration method were chosen to assess the organic matter removal. Experiment was conducted by using activated carbon or silica sand as filter media under various flow rate after $FeCl_3$ coagulation. Results revealed that activated carbon filter under lower flow rate rate showed better removal efficiency of NOM surrogates, around 40-60% and all fluorescence component, less than 40%, especially humic acid-like than silica filter media.

Introduction

Jagir River, which flows through big city Surabaya, is heavily polluted by industrial waste that is located on the river downstream. A treatment plant, which supplies tap and drinking water to Surabaya, was build in the downstream. This water treatment plant consists of mainly screening, coagulation, flocculation, sedimentation, filtration, and disinfection with chlorine. 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). The monitoring of NOM has proven to be of great importance in the water treatment field. NOM has been shown to be related to disinfection by-product formation, negatively affects water treatment processes such as membrane filtration, and promotes biological growth in distribution systems (Baghoth, et al., 2011; Matilainen et al., 2011). 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.

Fluorescence spectroscopy has been gaining traction as a promising method for NOM characterization (Sanchez et al., 2014; Baghoth et al., 2011). This type of analysis is completed through the collection of fluorescence excitation-emission matrices (FEEMs), which represent fluorescence intensity at various excitation-emission pairs. In comparison to other NOM characterization technique, including high performance size exclusion chromatograpy (HPSEC), FEEMs analysis is fast and provides consistent results with high sensitivity. FEEMs analysis involves identifying the location and magnitude of peaks of fluorescence intensity. A quantitative technique, fluorescence regional integration (FRI), was developed to analyse EEM data (Chen et al., 2003). The FRI technique was capable of quantifying differences in EEMs characteristics among samples and has potential use for water assessment.

The aim of this study is to determine the efficiency of coagulation-filtration process for removing NOM under various flow rate and media filter and to characterize organic fluorescence that could be removed through coagulation-filtration by using fluorescence spectra analysis. This study showed the performance of fluorescence excitation-emission matrices (FEEMs), 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 were taken from Jagir River in Surabaya city, Indonesia. Laboratory scale of water treatment apparatus was performed under flow rate (L/h) 30 and 60. $FeCl_3.6H_2O$ coagulant 200 mg/L dosage

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was added under rapid mixing 150 rpm, followed by slow mixing 35 rpm, settling flocs in sedimentation, then filtered under various media activated carbon or silica sand. Filtered water was 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. Fluorescence EEMs measurement were conducted using a Perkin-Elmer LS-50B luminescence spectrometer. The spectrometer used xenon excitation source, and excitation and emission slits were set to 10 nm. To obtain fluorescence EEMs, excitation wavelength were incremented from 200 to 400 nm at 5-nm steps, the emission was detected from 290 to 550 nm at 1-nm steps. Quinine sulphate solution (1 ug/L in 0.1 M H2SO4) was used to monitor stability of energy emitted by the xenon lamp in the fluorometer, and no change in quinine sulphate fluorescence was observed during the study. A technique, termed fluorescence regional integration (FRI), was developed to integrate the area beneath EEMs. Integration beneath EEMs within selected regions would represent the cumulative fluorescence response of organic matter with similar properties.

Results and discussion
Effect flow rate and filter media in removing NOM surrogates parameters
The effect of flow rate and filter media in filtration preceded by $FeCl_3$ coagulation on the NOM removal in Jagir River were measured by TOC, UV_{254} and SUVA under percentage removal, as shown in Fig.1, Fig. 2, and Fig. 3, respectively. As flow rate decreased, the removal of TOC increased, in-line with increasing UV_{254} removal. Activated carbon (CA) showed better removal of TOC and UV_{254} than silica sand. Combining flow rate 30 L/h and filter media activated carbon provided 60% removal of dissolved organic carbon, it is higher than 35% removal under flow rate 30 L/h and silica sand media (SI), as shown in Fig.1. In the filtration process, sampled passed through the filter, higher molecular size will be retained and the lower size will be filtered in the following media.
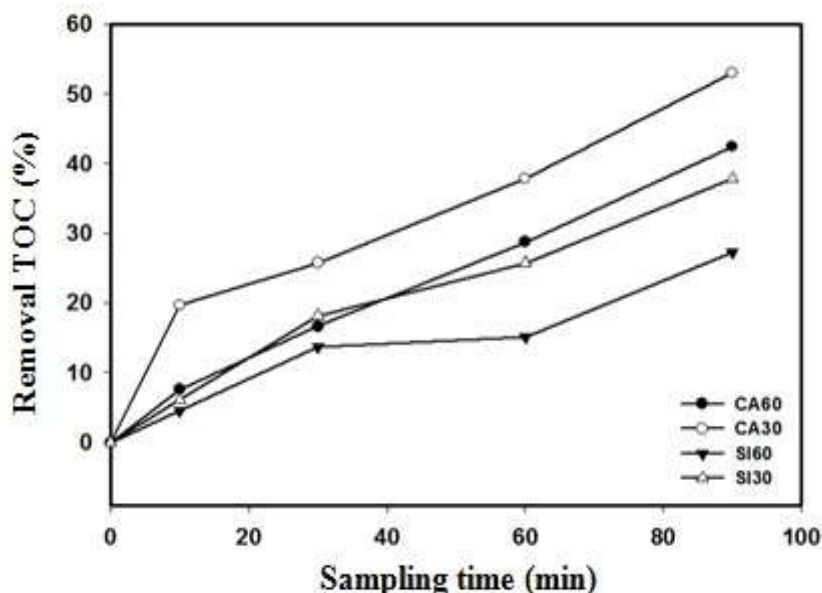

Figure 1. Removal of TOC as function of flow rate and filter media after coagulation-filtration

Similar results also was shown for UV254 removal, which is about 35-45%, as shown in Fig. 2. It indicated that coagulation followed by filtration is better to remove non-aromatic compound, since TOC removal is higher than UV_{254} removal
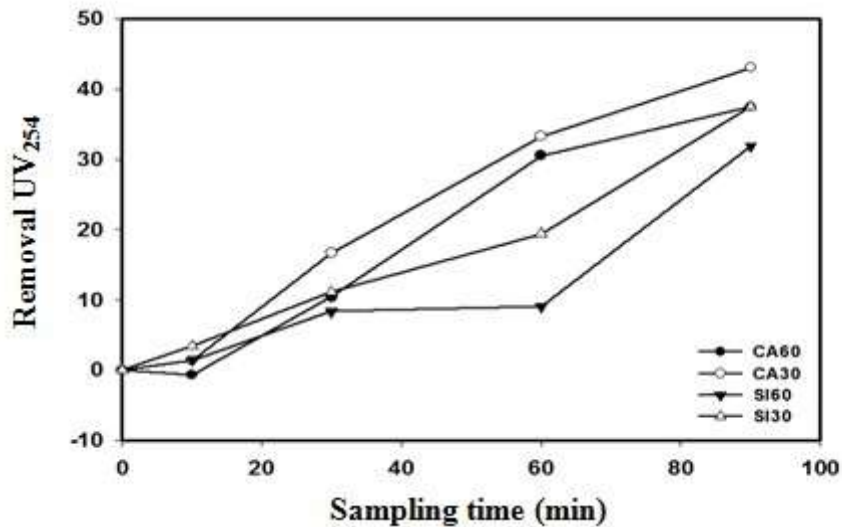
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Figure 2. Removal of UV$_{254}$ as function of flow rate and filter media after coagulation-filtration
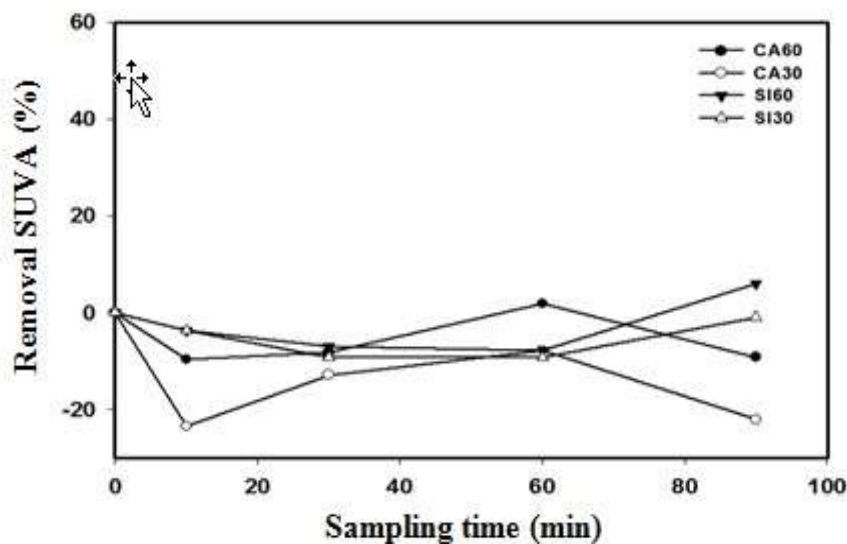

Figure 3. Removal of SUVA value as function of flow rate and filter media after coagulation-filtration.

The results showed consistent with insignificantly removal of 10% SUVA value, as shown in Fig. 3, probably due to water was mainly composed of hydrophilic properties. 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). Therefore, more higher floc will be settled in sedimentation process, and the lighter floc will be slipped out to filtration process. Flow rate influenced significantly to provide contact time for forming floc, settling floc, and for filtration. The longer contact time will cause longer interaction among components (Edzwald, 2011). Filter media properties influenced the adsorptive capacity to remove NOM. Discussion will be addressed to compare their properties, including porosity, micropore volume and pore size, surface area, and surface charge. Activated carbon has higher pore volume, higher inner pore size, and extremely higher surface area than silica sand, as shown in Table 1. However, silica sand have isoelectric pH less than 7. These properties will affect the inorganic removal than organic removal (Wang et al., 2009)

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Table 1. Comparison of filter media properties

Filter media	Pore volume (mL/g)	Pore size (nm)	Specific surface area (m^2/g)
Activated carbon	>0.39	1-100	>300
Silica sand	0	-	0.04

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Using F-EEMs with FRI method to identify NOM removal

Figure 4 shows distribution of NOM compositions with the same FEEMs method into five fractions. EEM peaks have been associated with humic-like, tyrosine-like, tryptophan-like, or phenol-like organic compounds Chen, et al. (2003). In general, peaks at shorter excitation wavelengths (<250 nm) and shorter emission wavelengths (<350 nm) are related to simple aromatic proteins such as tyrosine (Regions I and II). Peaks at intermediate excitation wavelengths (250-280 nm) and shorter emission wavelength (<380 nm) are related to soluble microbial byproduct-like material (Region IV). Peaks at longer excitation wavelengths (>280 nm) and longer emission wavelengths (>380 nm) are related to humic acid-like organics (Region V). For fulvic acids which have EEM with minimum excitation wavelengths of 250 nm indicated shoulders of EEM peaks located at shorter excitation wavelengths. Therefore, peaks at shorter excitation wavelengths (<250 nm) and longer emission wavelengths (>350 nm) are related to fulvic acid-like materials (Region III).
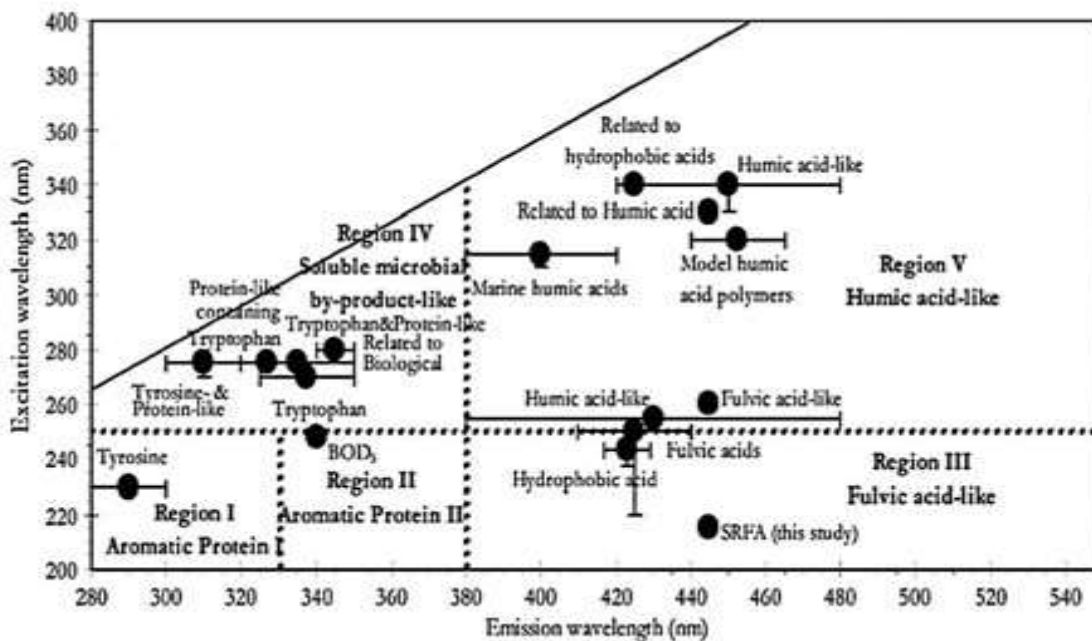

Figure 4. Location of EEM peaks based on defined excitation and emission wavelength boundaries for five EEM regions (Chen, et al. 2003)

Figure 5 shows percentage removal of organic component in each region and in total region. Region 1, Region 2, and Region 4, which is shown in Fig. 5a, Fig. 5b, and Fig. 5d, respectively, indicated aromatic protein and soluble microbial products hardly to be removed even under low flow rate and activated carbon as filter media. It shows only less than 25% removal. Meanwhile, region 3 or fulvic acid-like shows only 35% removal, which is slightly lower than 40% removal of region 5 or humic acid-like, as shown in Fig.5c and Fig. 5e, respectively.

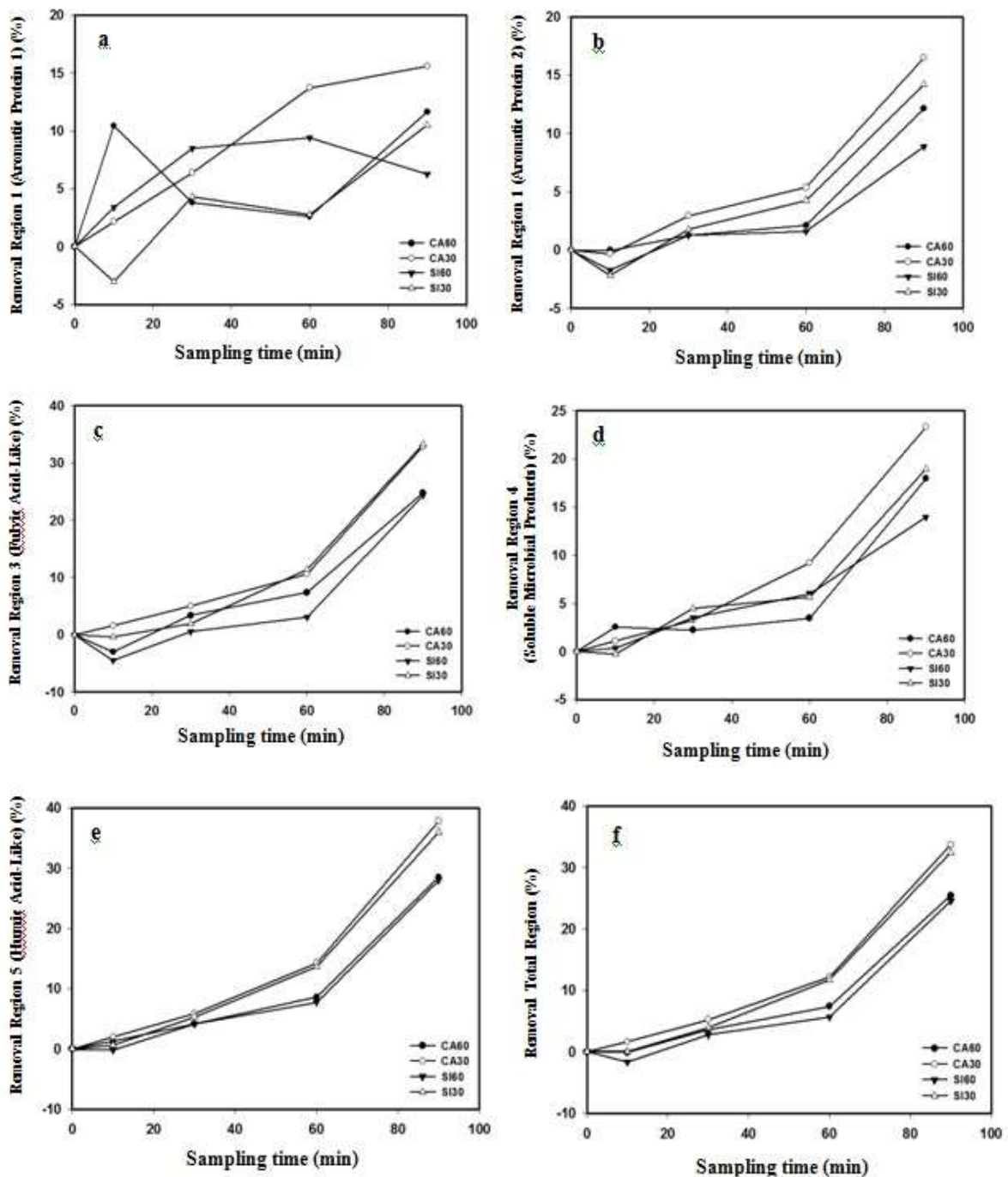INTERNATIONALJOURNALOFRESEARCH SCIENCE& MANAGEMENT

Figure 5. Removal of organic component: (a) aromatic protein 1; (b) aromatic protein 2; (c) fulvic acid-like; (d) soluble microbial product; (e) humic acid-like at different sampling time in coagulation-filtration process.

It seems that Jagir River was composed by aliphatic and hydrophilic component, and this is consistent with the results obtained from NOM surrogates parameters. Humic acid-like and fulvic acid-like were classified as humic substances, which are mostly aromatic and hydrophobic compound. Since less than 40% total removal of all those substances, it indicated that the remain component will be hydrophilic and aliphatic compound. Enhanced treatment* should be considered to improve efficiency NOM removal through coagulation-filtration process, for example: use double filter media, pre-treatment process or post treatment, in order to removal aliphatic and hydrophilic fraction.

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Conclusions

Based on this study, fluorescence EEM have been applied with FRI technique is usefull method to reveal characteristic of organic fractions by using coagulation followed by filtration in laboratory continues scale. Jagir River contains mainly aliphatic and hydrophilic humic subtances. It indicated by removal of NOM surrogates, such as TOC and UV_{254} is less than 60% and 40 %, respectively. Additionally, the total region removal of specific compound is also less than 40%, as identified by FRI method. Overall, assessment of NOM removal by coagulation-filtration under low flow rate 30 L/h and activated carbon filter media demonstrated significantly process than under flow rate 60 L/h and silica sand media. Further research should be considerd to enhanced coagulation-filtration treatment.

Acknowledgement

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