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Tracking of Dissolved Effluent Organic Matter (dEfOM) in wastewater treatment plant by using fluorescence method

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Abstract. Discharge of wastewater into water body can change the quantity and quality of natural organic matter (NOM) in source water, because wastewater may contain dissolved effluent organic matter (dEfOM). dEfOM consists of a heterogenous mixture of organic compounds with various structures, such as dissolved organic matter, microbial by-products, endocrine disrupting compound, etc. The objectives of this study is to track the fate of dEfOM by using fluorescence excitation emission matrices (FEEMs) in order to apply of reclaimed water from industrial wastewater. Tracking of NOM was observed in industrial park of wastewater treatment, which is consist of equalization tank, coagulation, flocculation, sedimentation, activated sludge tank and clarifier tank. FEEMs with parallel factor analysis (PARAFAC) analysis decomposed the organic matter in wastewater into two components, namely component C1 at (Ex/Em): 330(235)/410 is humic acid like and fulvic, component C2 at (Ex/Em): 280(230)/350 is soluble microbial products and aromatic protein. Characteristic of dEfOM depends on the wastewater characteristic and its treatment processes.

1. Introduction

Discharging of effluent from treated wastewater is an one of the contributed source of organic matter to aquatic systems. The contribution of organic matter from wastewater effluent discharge severely affects water quality, particularly in water treatment processes. The sustained increase in quantity and quality of organic matter in raw water will decrease the performance of water treatment processes and add the advanced technology of water purification, such as dosage increasing for coagulant, oxidant, disinfectant, and also membrane fouling, decreasing adsorption capacity of activated carbon [1]. Effluent organic matter (EfOM) is the organics in the sewage that cannot be removed during wastewater treatment. Constituents of EfOM in wastewater can be classified as synthetic organic compounds and microbial by-products derived from biological wastewater treatment processes. EfOM are typically cell fragments and macromolecules, such as polysaccharides, proteins, lipids, carbohydrates, amino acids, vitamins and chlorophyll [2].

EfOM from different types of wastewater could have various compounds, which differ from terrestrial organic matter. Component hydrophobic and transphilic of EfOM are derived from microbial sources, EfOM contains between 60-80% hydrophilic material [3]. Coagulation, flocculation, sedimentation and rapid sand filtration is mostly used and feasible method to treat organic matter. The remaining organic matter can be further removed by advanced treatment processes, such as adsorption with activated carbon [4], biofiltration, ion exchange [5], pellet softening



[6], ozonation [7], membrane technology [8], advanced oxidation process (AOP), such as hydroxyl radical.

Combined treatment process and hybrids with different combination of those mentioned methods have been employed for removal of EfOM. The objective of these combined systems is to maximise the removal of different fractions of the NOM. Some of these methods include: coagulation followed by ultrafiltration, ozonation followed by granular activated carbon, activated carbon filter followed by reverse osmosis, biofiltration followed by nanofiltration, ion exchange followed by activated carbon filtration and ozonation followed by biofiltration and membrane processes [6,9]. However, some researchs showed that the biological treatment processes will produce soluble microbial products (SMPs) and extracellular polymeric substances (EPS) material [10,11]. Several research projects had investigated using biological processes or combined chemical processes with biological processes to remove organic matter [12,13].

Several methods for organic matter composition and structure have been developed in the last decades, such as NMR, FTIR, HPSEC, EEM spectroscopy, which detect organic matter based on their properties [14]. Nevertheless, characterization of EfOM in wastewater plant in Indonesia and concern to water reuse or wastewater reclamation is still a few. Therefore, an interest in characterizing EfOM has become more important.

2. Research Methods

Wastewater effluent was collected from wastewater treatment plant of industrial park. The wastewater treatment train include inlet chamber, equalization tank, coagulation, flocculation, sedimentation, activated sludge tank, clarifier and indicator pond. Sample was taken in each effluent unit process twice per-week for one month. As this study focused on characterization of EfOM, the collected effluent wastewater was filtered through 1.2/0.5 μm and 0.45 μm disposable capsule filters (both from Millipore Corporation, USA) to remove any suspended solids before further usage.

Wastewater effluent samples were analysed for bulk parameter characteristics, including dissolved organic carbon (DOC) by using a total organic carbon analyzer (Model TOC-5000A, Shimadzu, Japan), ultraviolet absorbance at wavelength 254 nm (UV_{254}) by using a UV-VIS spectrophotometer (Model UV-2600, Shimadzu, Japan), and pH measurement [15].

Fluorescence measurements have been undertaken using a Perkin Elmer LS-55 luminescence spectrometer was used to measure fluorescence signal with excitation wavelengths 200-400 nm at 10-nm and emission wavelength 0.5-nm increment from 300 to 547.5 nm. EEMs were measured using 1-cm path length quartz cells. EEM of Milli-Q water samples was collected throughout the experiment period. Water Raman scatter peak were eliminated by subtracting the EEMs of Milli-Q water blank and normalized to the area under the water Raman peak of the blank at excitation wavelength 350 nm, producing data in Raman Units (R.U.).

PARAFAC analysis applied all EEM datasets fluorescence, which uses an alternating least-square algorithm to decompose the data signal into a set of trilinear terms and a residual array, as described with:

$$x_{ijk} = \sum_{f=1}^F a_{if} b_{jf} c_{kf} + e_{ijk} \quad i = 1, 2, \dots, I; \quad j = 1, 2, \dots, J; \quad k = 1, 2, \dots, K; \quad f = 1, 2, \dots, F$$

where x_{ijk} is fluorescence intensity of the i th samples at the j th variable (emission mode) and at k th variable (excitation mode); a_{if} is the concentration of the f th analyte in the i th sample; b_{jf} is the fluorescence quantum efficiency of the n th analyte at emission wavelength j ; c_{kf} is the specific absorption coefficient at excitation wavelength k ; F is the number of fluorophores (components) and e_{ijk} is the residual noise, representing the variability not accounted for by the model [16]. drEEM toolbox in Matlab® (<http://www.models.life.ku.dk/drEEM>) [17], was used to generate parallel factor analysis (PARAFAC) models.

3. Result and Discussion

3.1. Bulk wastewater quality for industrial wastewater treatment train

Figure 1 shows the variation of organic matter surrogates in term of DOC concentration, UV_{254} and SUVA value of treated wastewater in each unit process. The variation was more pronounced for the treatment by coagulation, flocculation, sedimentation, and activated sludge processes. Unit process of inlet chamber and equalization tank has the highest value, while the effluent of sedimentation has the lowest value for organic carbon and UV_{254} . It indicated that aromatic protein, which composed organic carbon in wastewater, are more amenable to be removed in the physical treatment, such as coagulation, flocculation and sedimentation. It is consistent with that reviewed in the previous study [18,19].

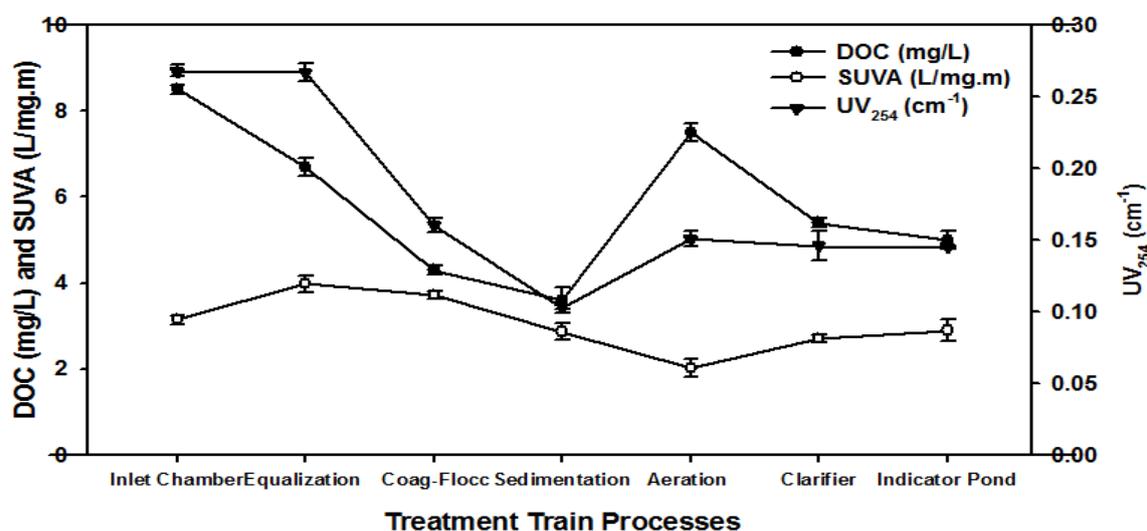


Figure 1. The variation of DOC, UV_{254} , and SUVA value of effluent wastewater treatment of industrial park.

Figure 2 shows the percentage reduction of organic matter TOC, UV_{254} and SUVA value across the wastewater treatment processes. The general trend is a reduction in DOC through equalization, coagulation, flocculation, sedimentation, and insignificantly removal in clarifier after activated process and in the indicator pond. Activated sludge process could increase the organic compound, which represented through increasing DOC and UV_{254} concentration. In addition, biological process could degrade hydrophobic and hydrophilic compound as detected by SUVA value. Biological processes, which involved microbiology for biodegradation, could release organic matter, such as soluble microbial products (SMPs) as by-product during their metabolism processes. SMPs will be derived during substrate utilization and may released from cell lysis during biomass decay [20].

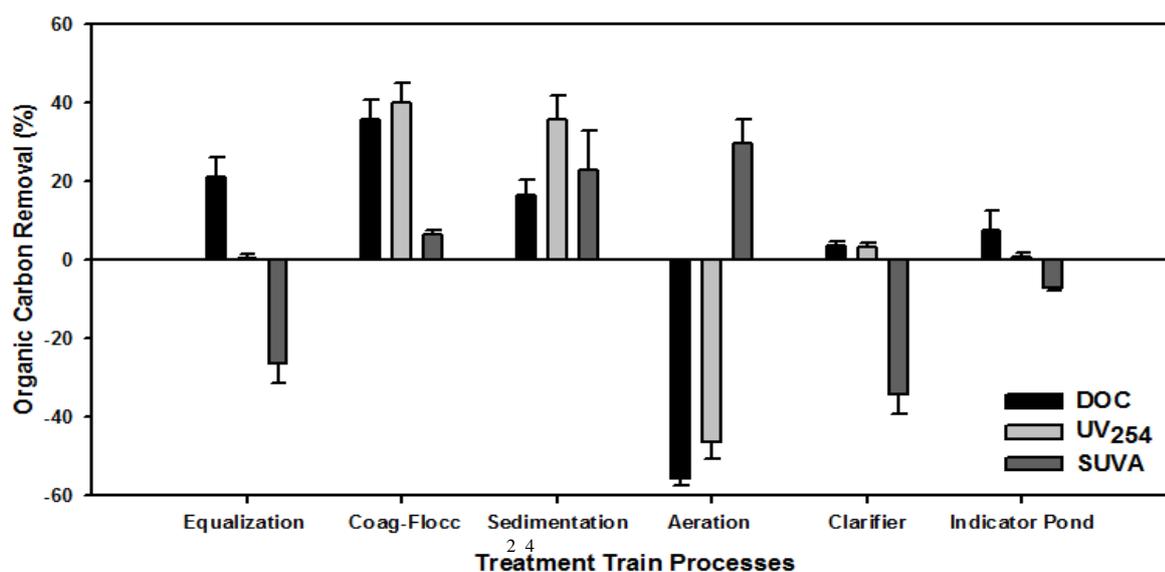


Figure 2. The changing of DOC, UV₂₅₄, and SUVA value of effluent wastewater treatment of industrial park in every sampling unit.

3.2. Using Fluorescence Excitation-Emission Matrices (F-EEMs) to Characterize dE_{OM} Contained in the Wastewater

Parallel Factor Analysis (PARAFAC) was needed to model the dataset of fluorescence excitation emission matrices (F-EEMs). The specific data set with non-negativity constraints were used on all modes during preprocessing dataset. The F-EEMs were also Raman calibrated by normalizing to the area under the Raman scatter peak of Milli-Q water samples, in order to remove scatter. Measurement at excitation wavelengths below 220 nm were excluded, because 5 samples were identified by leverage plots (about 9% of 56 samples) as outlier. Each dataset was normalized to its total signal before PARAFAC modelling in order to reduce correlation between components. After preprocessing, PARAFAC modelling was applied for each data. A series of PARAFAC models consisting of 2 components were generated and those number of fluorescence components was validated using split half analysis and split half validation. Finally, PARAFAC analysis decomposed the organic matter in treated wastewater into two components, as shown in Figure 3.

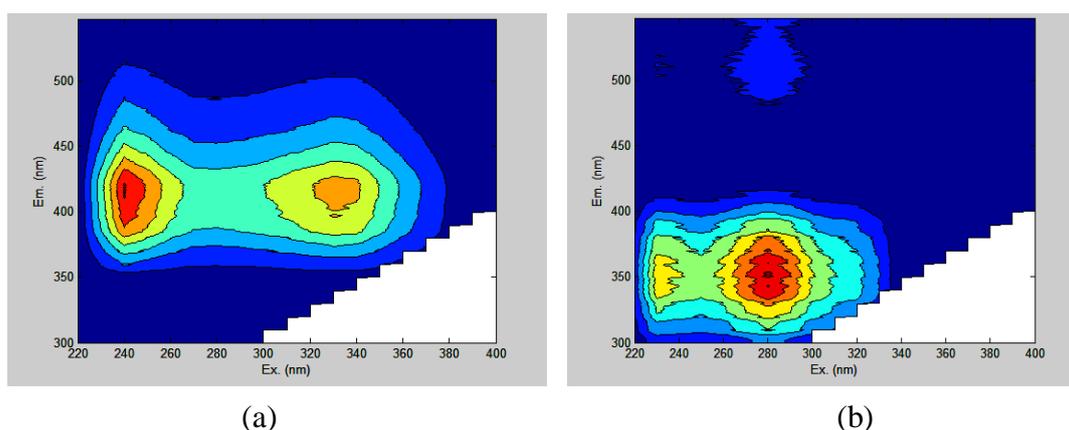


Figure 3. Fluorescence (a) Component 1 and (b) Component 2 have been found from effluent of wastewater treatment in industrial park.

The fluorescence components in this study are comparable with previously classified components [21,22]. The component C1 comprises two peaks centered at excitation/emission (Ex/Em): 230/410 nm, which is identified as fulvic acid-like and also as the main peak, the second peak of component C2 at (Ex/Em): 330/410 nm, as humic acid-like. The component C2 had first and secondary excitation peak, about 280 nm and 230 nm, respectively, and with single emission peak about 350 nm, and it is

identified as soluble microbial products (SMPs) and aromatic protein, respectively. Further, the component distribution in the source and treated water was described in terms of F_{max} in order to attempt the relative contribution of the PARAFAC fluorophore to the tracking of dissolved organic matter. However, the higher F_{max} does not indicate a major existence of the component in the all sample [23].

Effluent of wastewater treatment was composed of fluorescence soluble microbial products as dominant component and followed by humic acid-like and aromatic protein. The presence of those component probably contributed by the biological activities which released their metabolite products. Previous studies have mentioned that biological process might released organic compound during metabolism and decay [20], whether as extracellular polymeric substances (EPS), SMPs, and inert biomass [10].

4. Conclusion

This study concludes that FEEMs analysis revealed that two component, (Ex/Em): 230/410 nm; (Ex/Em): 330/410 nm, derived from PARAFAC modelling were the major organic component in effluent wastewater from industrial park. F-EEMs and dE_fOM bulk parameter demonstrated that wastewater treatment train had applied, significantly reduced the aromaticity of organic carbon matter in water. Coagulation-flocculation and sedimentation removed organic carbon significantly. Biological process gives higher contribution to the existence of dE_fOM than other processes.

5. Acknowledgment

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