JOP 1569_Using Fluorescence Spectroscopy to Assess Organic Matters in Activated Persulfate

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Submission date: 04-Dec-2020 04:56PM (UTC+0700)
Submission ID: 1464496633
File name: JOP_1569_Using_Fluorescence_Spectroscopy_to_Assess.pdf (981.08K)
Word count: 1855
Character count: 10238

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Abstract. Surface water contains organic matters from human activities, discharged industrial wastewater, and generated from microbial activities in water body. Persulfate is one of the strongest oxidants and could be used to oxidize organic matters. Fluorescence excitation emission matrices is one of the qualitative methods to identify organic matters properties, instead of chromatography and ultraviolet visible detection. The objective of this study was to identify dissolved organic matter in source and treated water by using peroxidation activated persulfate followed by coagulation. Sampel was analyzed by using fluorescence excitation emission matrices (FEEMs) to assess its properties. The results showed that Activated persulfate has a good performance as pretreatment, in order to oxidize organic matters, further the coagulation is suitable treatment to combine with peroxidation activated persulfate. Those treatment resulted lower fluorescence intensity in all regions, including aromatic protein, fulvic acid-like, soluble microbial products, and humic acid-like.

1. Introduction

Dissolved organic matter contain in source water, such as in surface water. Many treatment processes has been proposed in order to reduce organic matters in aquatic water. The main issue of existence of organic matters is the reactivity of organic matters with disinfectant, such as chlorine, in water treatment process. Reactivity organic matters with disinfectant will generate by-products chemical from disinfections process or it has been know as DBPs, for example trihalomethanes (THMs) and haloacetic acids (HAAs), instead of removal of pathogen in treated water [1,2]. Many methods has been conducted to monitor DBPs generation through removing organic matters before disinfection process. It has been well known that coagulation has a good performance in removing organic matters, however its ability compete with its function to remove suspended solid and turbidity [3,4]. Therefore, pretreatment of coagulation should be considered in order to enhance coagulation processes. Preoxidation by using persulfate has been applied lately to remove pathogen due to its high oxidation potential (2.12 V) [5,6]. According to its ability to oxidize pathogen, therefore this study has an idea to apply persulfate for removing organic matters and reduce DBPs eventually. Previous studies has shown the performance of persulfate, activated persulfate, and it has shown a high removal of organic matters [6,7]. Most of previous studies applied organic matters surrogates to measure its concentration quantitatively, such as total organic carbon (TOC) concentration, aromatic compound value in term of ultraviolet (UV) at 254 nm wavelength, specific ultraviolet (SUVA) value [2,3,8]. Qualitatively, fractionation according to molecular weight of organic by using chromatography technique with number of detector, differentiation of functional group of organic by using spectrophotometric, differentiation of fluorophores properties of organic by using fluorophotometer, has been considered

to characterize organic matters based on their properties, and according to electromagnetic properties. [2-4,7,9]. Fluorophotometer or fluorescence could detected organic properties based on fluorophores compounds. It has been known that aromatic compounds has double bond carbon and could detect by fluorescence spectroscopy. FEEMs method classified organic matters based on aromatic compounds, humic-like, by-products from microbial, fulvic-like, as shown as a peak or high intensity in the region distribution of fluororescence figure [3,9]. According to information explained previously, the objective of this research is to estimate fluorophores organics properties by using FEEMs analysis, in order to know organic fractions distribution based on their intensity and wavelength measurement.

2. Materials and methods

Source water was collected from Surabaya River, on April 2019. Sample, including raw water and treated water was filtered using 1.2/0.5 μm and filter paper 0.45 μm because this research concerned on the identification of dissolved organic matters during peroxidation and coagulation. Stock solution effluent of 100 mM $Na_2S_2O_8$ and $FeSO_4.7H_2O$ was prepared. A specific aliquot from stock solution was diluted to get 0.5; 1; 5; 10 mM persulfate concentration and 0;1;2;4 mM $FeSO_4$. Experimental was carried out with jartest equipment with contact time 5; 10; 20; 30; 40; 50; 60 minutes, adjusted speed slow mixing 35 rpm. Source and treated water was measured the fluorophores compounds by using spectrometer Perkin Elmer LS-45. Samples were detected under quartz cells 1-cm, and fluorescence signal was adjusted with excitation wavelength (Ex) 200 nm to 400 nm with increment 10-nm and 300 nm to 57.5 nm of emission wavelength (Em) with increment 0.5 nm [3,7].

3. Results and discussion

Fluorophores compounds indicated organic matters, which has the same components with absorb the same light at the same excitation and emission wavelength. According to excitation and emission wavelength, fluorophores of organic matters region was separated into 5 areas, including Area I (Em less than 330 nm) and Area II (Em 330 nm to 380 nm) is Aromatic Protein with similar Ex less than 250 nm, Area III is Fulvic-Like with Ex less than 250 nm and Em 380 nm to 550 nm, Area IV is Soluble Microbial Products with Ex 250 nm to 400 nm and Em less than 380 nm, Area V is Humic-Like with Ex 250 nm to 400 nm and Em 380nm to 550 nm [10]. Figure 1 described the fluorophores of organic matters in raw samples and treated samples under different treatment. The results showed that raw water contain of fulvic-like (Area III) at high intensity, followed by humic-like (Area V), and low intensity of aromatic protein I and II, and the lowest intensity is soluble microbial products I Area IV.

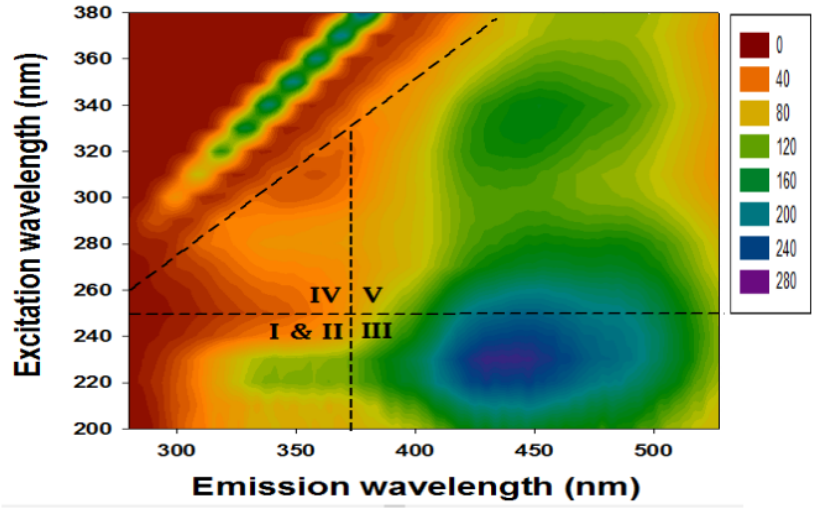

Figure 1. Fluorophores of organic matters in raw water

It seems that raw water contain more humic substances-like compounds in term of humic and fulvic acid-like. It indicated that allochtonous matters could acted as the main contribution of organic sources in raw water [8,10]. After treatments, firstly without activated persulfate and without coagulation or the raw water was treated by persulfate only, it showed that fulvic acid-like intensity decreased and shifted into lower excitation, while humic acid-like peak has lower intensity than ever, though still at the same peak (Figure 2).

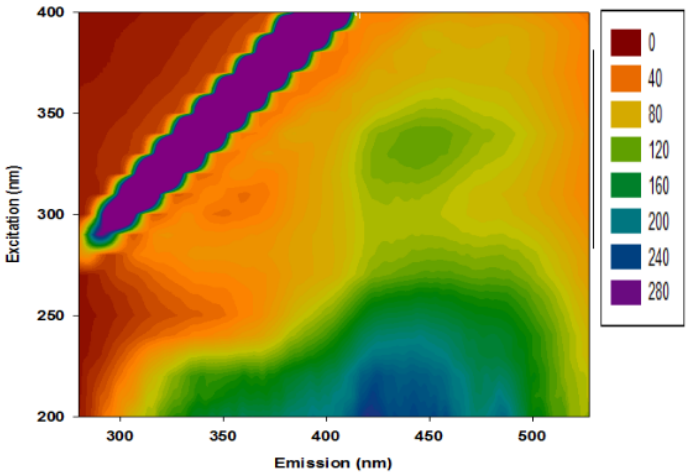

Figure 2. Fluorophores of organic matters after treatment with 1mM Persulfate

Secondly treatment, without activated persulfate and alum coagulation, the results showed that all region (fulvic-like, humic-like, aromatic protein, soluble microbial products) presented lower intensity than raw water, even lower fluorescence intensity than first treatment (Figure 3). Third treatment, activated persulfate with 4 mM FeSO4 and without coagulation, the results showed that all region has a very low intensity, as indicated through the initial colour of peak in each region has changed into different colour. It indicated that activated persulfate has a higher efficiency to reduce organic matters than coagulation, and has a good performance than persulfate only (Figure 4) [6,7,11].

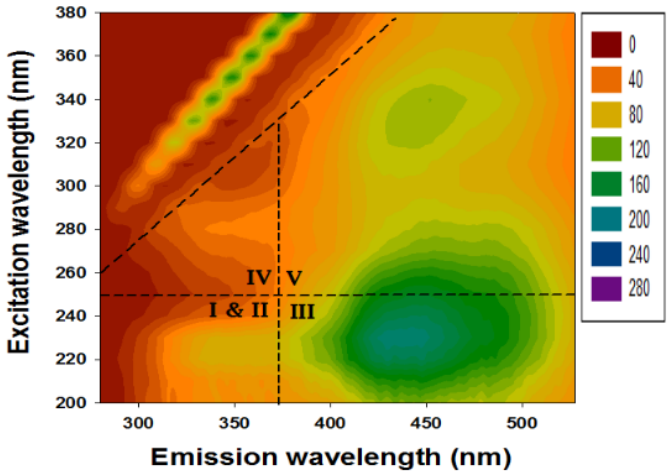

Figure 3. Fluorophores of organic matters after treatment with 1mM Persulfate combined with Alum coagulation

Fourth treatment, activated persulfate continued by alum in coagulation, the results showed increasing removal of organic matters. As seen on Figure 5, all regions presented lower intensity as shown in brownish colour. It indicated that activated persulfate and coagulation has a very good option for removing organic matters and to control the formation DBPs in aquatic water and in source water. Activated persulfate by adding ferrous iron will provide a higher availbale Fe^{2+} concentration, which could increase formation ferric ions. Ferric ions has a high reactivity with persulfate to produce more sulfate radical. Sulfate radical has a strong potential oxidation to oxidize organic matters into lower molecular weight [5-7]. In addition, alum coagulant will entrap, adsorb, and catch the oxidized organic matters in term of lower molecular weight [2-4,8]. Therefore, combination of activated persulfate with alum coagulation will generate high removal of organic fractions.

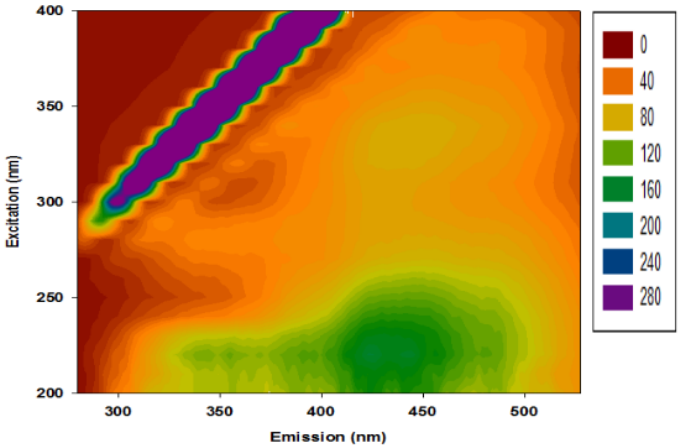

Figure 4. Fluorophores of organic matters after treatment with 4 mM FeSO4 and 1mM Persulfate (activated persulfate)

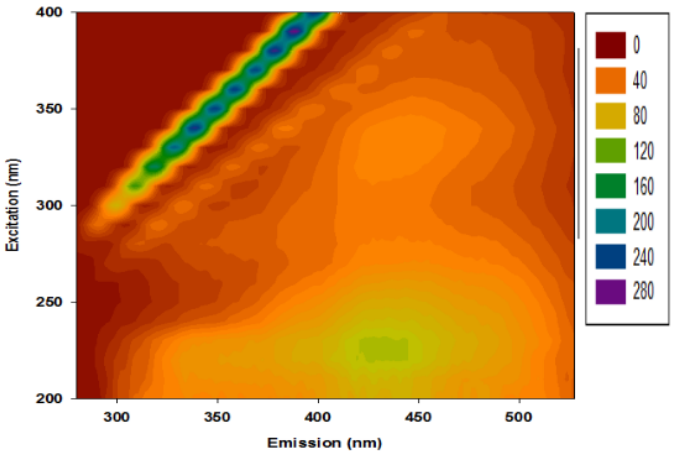

Figure 5. Fluorophores of organic matters after treatment with 4 mM FeSO4 and 1mM Persulfate (activated persulfate) combined with Alum Coagulation

4. Conclusions

Activated persulfate has a good performance as pretreatment, in order to oxidize organic matters, further the coagulation is suitable treatment to combine with peroxidation activated persulfate. Those

treatment resulted lower fluorescence intensity in all regions, including aromatic protein, fulvic-like, microbial by-products of microbial, and humic-like. FEEMs method could assessed the organic matters characteristics and could be used to detect the changing of organic properties during peroxidation with activated persulfate followed by alum coagulation.

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Acknowledgments

Great appreciation for research funding is delivered to Kementerian Riset, Teknologi dan Pendidikan Tinggi, Indonesia with contract no. 086/SP2H/LT/DRPM/2019).

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