Continuous In-situ Identification of Fouling on Hollow Fiber Membrane by Solid-State 3D-EEM

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Summary : We innovatively applied solid-state 3D-EEM to continuous in-situ observation of membrane fouling. Based on observation and PARAFAC analysis, protein-like and humic-like substances were considered to be responsible for physical irreversible membrane fouling (PIMF). Further, the transition of membrane fouling was also successfully observed by continuous observation with the combination of PARAFAC.

Introduction : Membrane treatment technology has been widely used for water purification process. However, the inevitable acceleration of transmembrane pressure caused by membrane fouling is still an avoidable problem[1]. To control and prevent the occurrence of fouling, we have to identify the characteristics of the causes of fouling and take measures it by either pretreatment installation, membrane modification or parameter optimization[2]. Ideally, the major causes of foulant should be observed continuously during the operation, but in fact characterization of their composition or quantification is still difficult without autopsy with the combination of some advanced chemical analytical tools such as ^{13}C-NMR or FTIR[3]. 3D-EEM is a promising tool for characterization of membrane foulants and it has been applied to the solution that contained the foulants chemically extracted from membranes which experienced a long-term operation[4]. Nowadays, solid-state 3D-EEM has been developed and used in the field of soil characterization or pharmaceutical manufacturing processes. We believed that solid-state 3D EEM would be also applicable to the monitoring of foulants which accumulating on the surface of membrane. In the present study, the solid-state 3D-EEM was first applied to the continuous in-situ monitoring of membrane fouling and the future perspectives and limitations were discussed on the basis of the results obtained in this study.

Material and Methods : Water samples used in this study was collected from Yodo River, Osaka, Japan. Hollow fibre PVDF membrane with nominal pore size of 0.1 μm was used for the filtration. Two minutes of backwashing was conducted every 30 minutes of filtration to eliminate the accumulation of reversible foulants. After each backwashing process, solid-state 3D-EEM was applied to the surface of membrane fibre. Schematic diagram of in-situ 3D-EEM observation was shown in Figure 1. An optical fiber was used to deliver emission light to membrane and collect fluorescence light. Photomultiplier tube (PMT) voltage selected was 700V. In addition, spectrum calculation was carried out by subtracting spectrum of new membrane from spectra of fouled membrane. Parallel factor (PARAFAC) analysis was selected to identify the main components in calculated spectrum.

Results and Discussion : Figure 1 showed the lifting of trans-membrane pressure (TMP), indicating the occurrence of irreversible membrane fouling. Just after the starting of operation, the significant peaks in solid-state 3D-EEM has emerged and grew their spectra intensity as the fouling developed. In addition, after 2 hours of operation, some new peaks have occurred on longer wavelength position. This clearly demonstrated that the solid-sate 3D-EEM would be possible to catch the foulant characteristics without any suspension of the operation. For more precise discussion about the changes in foulant characteristics, PARAFAC analysis was applied for all the spectra obtained in this study and we found that three components were isolated. Component 1 positioning

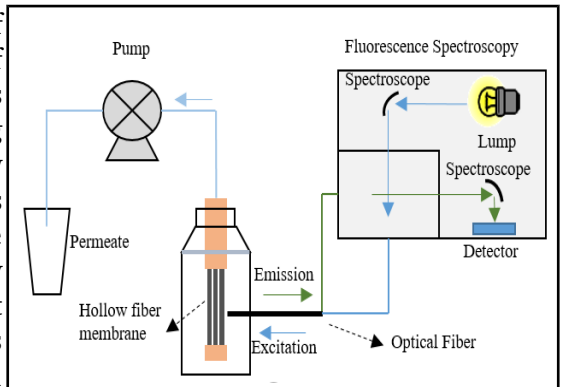


Figure 1: Schematic of in-situ 3D-EEM observation.

at 330/270 nm, Component 2 positioning at 440/350 nm and Component 3 positioning at 350/220 nm would be designated as humic substances, protein-like and protein-like substances, respectively [5]. However, the peaks observed here is slightly different from previous studies. The comparison of solid-state 3D-EEM and liquid-state 3D-EEM revealed the fluorescence feature is different between solid and liquid (data was now shown in this study). Therefore, the database of the solid NOM should be established in further study to estimate the characteristics based on each peak.

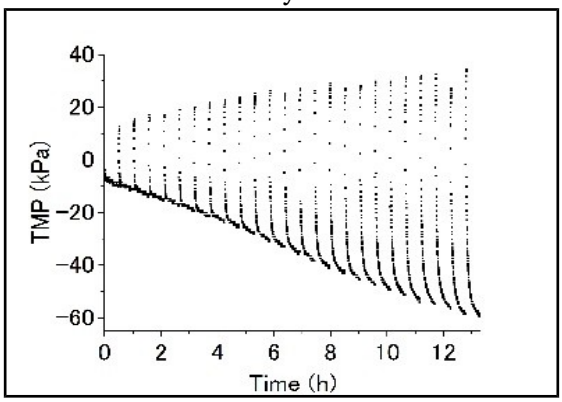


Figure 2 TMP trend of filtration.

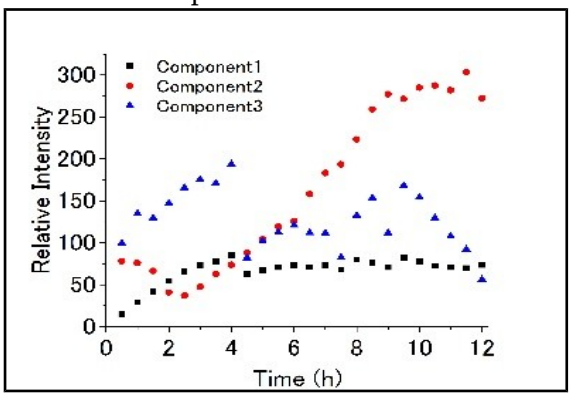
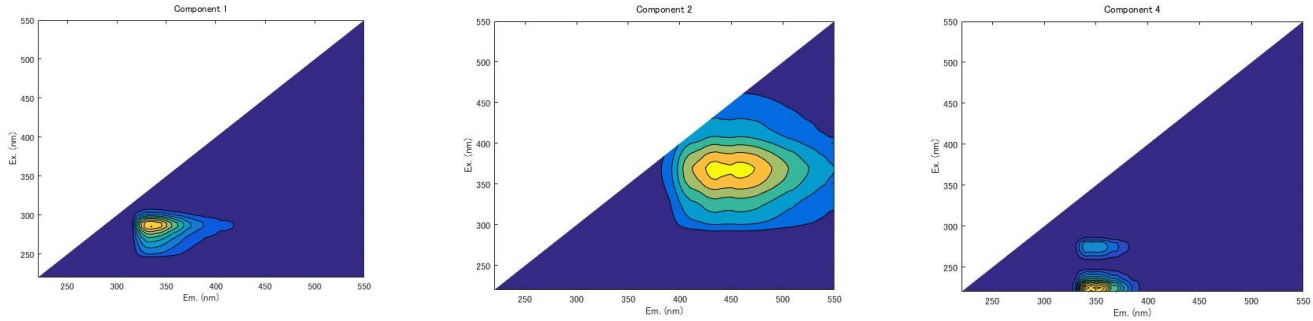


Figure 3 Time-scale Relative Identity of components.

Figure 3 shows the changes in F_{max} of each component as a function of operation time. Reflecting the trend of 3D-EEM spectra, the trend in F_{max} changes is different depending on components. The value of component 1, or protein-like substances, rapidly increased just after the operation start and their value was saturated after 4 hours of filtration. On the other hand, the value of component 2 and 3 increased after 2 or 4 hours of operation. This is explained by changes in fouling mechanisms, namely conditioning changed to pore blocking or cake accumulation. On the basis of Figure 3, it is assumed that conditioning of protein-like substance continued until 2 hours of operation and cake accumulation or pore blocking has started after 4 hours of operation. The information obtained by solid-state 3D-EEM would be possible to give us the alarming of the timing for chemical cleaning or membrane replacement. Such information is quite difficult to be obtained by the observation of TMP trend. With an installing the solid-state 3D-EEM to the membrane module, we really hope that the autonomous membrane treatment system will be achieved.



Component 1 **Component 2** **Component 3**

Figure 4 3D-EEMs of three components isolated by PARAFAC analysis.

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