

Characterization of Dissolved Organic Matter in Landfill Leachate during Two-Stage Membrane Bioreactor Treatment

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ABSTRACT

Landfill leachate is a complex wastewater containing high concentration of dissolved organic matter (DOM). In this study, DOM in raw leachate and treated water from pilot-scale two-stage membrane bioreactor (MBR) installed at solid waste disposal site were investigated by using fractionation method, fluorescence excitation-emission matrix spectroscopy (FEEM) and fourier transform infrared (FTIR). The fractionation results showed hydrophilic (Hyl) compound was the most abundant fraction in DOM of raw leachate, whereas the dominant fraction of DOM in mixed liquor inside MBR and its effluent was fulvic acid (FA). The fluorescent peaks of protein-like, humic and fulvic-like substances were detected in influent DOM, while the fluorescence peaks of MBR and effluent DOM were humic and fulvic-like substances. From the FTIR results, absorption bands that could be related to humic acid (HA) and FA were found in both MBR and effluent DOM. The characterization of DOM indicated that the most of Hyl and protein-like substances could be significantly removed by microbial process in MBR. Furthermore, a part of humic substance (HA and FA) could be eliminated by microbial and filtration processes.

Keywords: Dissolved organic matter, membrane bioreactor, fractionation, landfill leachate

1.0 INTRODUCTION

Landfill leachate is a high strength wastewater consisting of dissolved organic matter (DOM) and total organic carbon [1]. DOM is often considered as a mixture of hydrophilic and humic substances with different molecular weight. Chemical composition in wastewater can play a significant role in its biodegradability, pollutant biotransformation, and performance of treatment process [1, 2], therefore the understanding of DOM characteristic is necessary to optimize the efficiency of leachate treatment system.

Membrane bioreactor (MBR) is an attractive treatment system for leachate treatment and reuse as it is a compact system and capable of complete solid removal, high pollutant removal efficiency, and lower

sludge production when compared with conventional activated sludge [3]. Recently, two-stage MBR was developed by additional inclined plate separator tank [4] to minimize the operating biomass for the following aerobic reactor. The application of this system was applied to treat partially stabilize leachate without excess sludge withdrawal [5]. High treatment efficiency could be achieved along the operation period. Nevertheless, removal of COD was considered at moderate level in comparison with BOD. This phenomenon was also found in the leachate treatment by MBR with an air-lift bioreactor due to an incapable treatment of hardly biodegradable DOM [6].

The correlations of DOM in leachate and their treatment have been investigated using several measurement methodologies [7, 8]. However, there is still

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inadequate information regarding DOM in leachate during MBR treatment, especially the relation between DOM characteristics and its removal in the process. In this study, the degradation, transformation, and removal of DOM due to biological and filtration treatment process were determined using various techniques (XAD-8 fractionation, FEEM and FTIR). The characterization results were provided a greater understanding of DOM removal efficiency during the treatment.

2.0 RESEARCH METHODOLOGY

2.1 Leachate Samples Collection

The two-stage MBR pilot-scale treatment unit [5] consists of an anoxic tank with incline tube followed by aerobic tank with submerged membrane module (Fig.1). Six modules of 0.4 μm polyethylene (PE) hollow-fiber membrane (Sterapore SURTM) were installed inside aerobic tank to achieve the maximum treatment capacity of 2 m^3/day . The aeration was continuously supplied to maintain dissolved oxygen (DO) concentration of 3-4 mg/l. Mixed liquor suspended solids (MLSS) concentration was controlled in the range of 10-12 g/l by re-circulating excess sludge from aerobic tank back to anoxic tank. Total hydraulic retention time (HRT) in the whole system (anoxic and aerobic stages) was maintained at 24 hours. The membrane permeate flux was kept constant under intermittent mode (10 min on and off) whereas trans-membrane pressures (TMP) were recorded along the operation period. Chemical cleaning of membrane module was performed when the TMP exceeded the recommended value specified by the manufacturer.

Samples were taken from the following locations, i) leachate preparation tank, feeding wastewater was prepared by mixing fresh and stabilized leachate at 1:10 volumetric mixing ratio. The collected samples from this tank were termed as influent, ii) Aerobic tank, mixed liquor samples of leachate taken from aerobic tank were termed as MBR, iii) Treated water tank, the membrane permeate samples representing treated leachate collected from this tank were termed as effluent.

2.2 Analytical Methods

Determinations of influent, MBR and effluent characteristics during treatment period in term of biochemical oxygen demand (BOD_5) and chemical oxygen demand (COD) were performed following Standard Methods [9]. Dissolved organic matters (DOM) of samples were prepared by 1:10 dilution and filtration through a GF/C filter. All of DOM samples were analyzed for the parameters described as follows.

Dissolved organic carbon (DOC) was measured using Shimadzu TOC-5000 total organic carbon analyzer. UV absorbance at 254 nm (UV_{254}) was determined by Hach DR/4000U spectrophotometer with a quartz cell. UV_{254} analytical results were employed to calculate specific UV absorbance (SUVA_{254}), i.e. UV_{254} divided by DOC.

Hydrophobicity of DOM was determined by fractionation with Amberlite XAD-8 resin. DOM was fractionated into humic acid (HA), fulvic acid (FA) and hydrophilic (HyI) fractions according to adopted fractionation method [1]. The concentration of each fraction was quantified by measuring its DOC.

Fluorescence excitation-emission matrix (FEEM) spectroscopy of DOM was determined on a Jasco

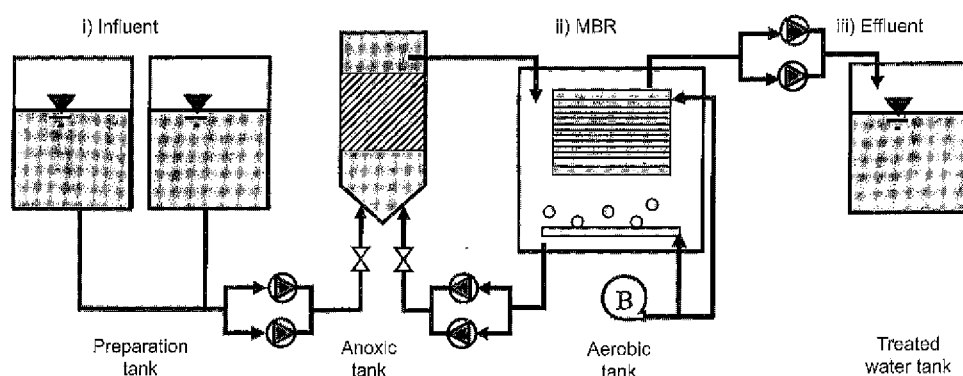


Figure 1 Schematic of two-stage MBR and sampling points

FP-8200 spectrofluorometer using a 1 cm quartz cell. Before EEM analysis, all samples were diluted to DOC of 10 mg/l and adjusted to pH 7. EEM spectra were collected at an excitation (Ex) wavelength from 200 nm to 500 nm and emission (Em) wavelength from 250 nm to 600 nm with 5 nm increments. The spectra were scanned with a 5 nm slit bandwidths at a scan rate of 2,000 nm/min.

Fourier transform infrared (FTIR) was employed to determine the functional groups on a Perkin-Elmer spectrum spotlight FTIR imaging system with micro-ATR technique. DOM samples were freeze-dried for 24 h under -50°C . The FTIR spectra of powder samples were examined in a middle wavelength infrared of $4000\text{--}600\text{ cm}^{-1}$ with 4 cm^{-1} resolution.

3.0 RESULTS AND DISCUSSION

3.1 Leachate and DOM Characteristics

Table 1 presents the characteristics of leachates influent, MBR and effluent during the operation. The influent leachate was classified as moderate biodegradable with average COD of 9,400 mg/l, BOD of 3,891 mg/l and DOC of 3,695 mg/l [10]. After leachate treatment the effluent concentration of COD, BOD and DOC were reduced to an average value of 1,313 mg/l, 133 mg/l and 502 mg/l respectively. Accordingly, about 86% of COD and DOC removals and 96% of BOD removal efficiency were achieved. Comparing between MBR and effluent characteristics, their qualities were not differ much in term of DOC (about 10%) but there was some greater difference in terms of BOD and COD (40-80%) which indicates the effect of membrane filtration in retaining particulate matter contributed in both BOD and COD measurements.

Specific UV absorbance at 254 nm (SUVA_{254}) of effluent DOM showed a significant increase in comparison with that of influent DOM from 0.51 to $2.84\text{ lmg}^{-1}\text{m}^{-1}$, whereas it was similar to MBR DOM ($2.76\text{ lmg}^{-1}\text{m}^{-1}$). SUVA_{254} is a parameter that represents the ratio of aromatic carbon content to total DOM. The low SUVA_{254} indicates the low content of aromatic organic carbon. In this study, the result of increased SUVA_{254} indicated that the MBR treatment process was probably incapable for removing aromatic carbon compounds from the influent DOM. The characterization results identified that the leachate DOM was significantly eliminated by the treatment process and remaining DOM in effluent was higher in a form of aromatic carbon compounds than that in the influent.

3.2 DOM Fractionation

The fractionation distribution and DOC concentration of HA, FA, and Hyl fraction of DOM samples are presented in Table 2 and Fig. 2. DOM fraction could be used to characterize the group of organic compounds containing in water sample. For instance, humic substance consisted mainly of bio-refractory and aromatic organic substances, while Hyl fraction had lower aromatic organic content and easily degradable component [1]. The DOC of the influent was mainly composed of the Hyl fraction (68%w/w), followed by 23% of FA and 9 % of HA fraction, whereas the MBR and effluent were dominated by FA fraction accounting for 44% and 50%. The Hyl fraction was found as secondary group at 33% and 36%, and the HA fraction was accounted for 22% and 13% respectively. This suggested the significant increase of

Table 1 Characteristic of leachate collected samples

Parameter	Influent	MBR	Effluent
pH	6.98	8.60	8.85
BOD ₅ (mg/l)	3,891 (63)	580 (21)	133 (32)
COD (mg/l)	9,400 (200)	3,400 (346)	1,313 (241)
DOC (mg/l)	3,695 (25)	567 (7)	502 (8)
UV ₂₅₄ (cm ⁻¹)	18.86	15.24	14.29
SUVA ₂₅₄ (lmg ⁻¹ m ⁻¹)	0.51	2.76	2.84

N=3, samples collected in January 2012

the hydrophobic fraction in terms of FA and HA after the MBR treatment

During the treatment, the Hyl concentration was reduced from 2,215 mg/l to 183 mg/l in MBR and 162 mg/l in the effluent, indicating that the Hyl fraction was obviously removed after MBR treatment. The Hyl removal could be explained by biodegradation reaction of activated sludge since this organic fraction has high biodegradable characteristic, whereas the lower removal efficiency was achieved for the FA and HA fractions. The FA concentration was reduced from 719 mg/l to 254 mg/l in MBR and 225 mg/l in the effluent, and the HA was reduced from 207 mg/l to 100 mg/l in MBR and 40 mg/l in the effluent. The biological treatment for high molecular weight (MW) compounds such as humic substance has been identified as originated from bio-sorption in the first step because the micro-organisms cannot directly uptake these high MW compounds [11]. In this study, the FA fraction was found more efficiently removed than that of the HA fraction in the biological MBR treatment which was probably due to less complex molecular structure of FA compared to that of HA. On the other hand, the HA fraction was efficiently removed during membrane filtration. The resulting of the reduced HA

fraction could be possibly relating to adsorption of compounds onto the membrane surface. The increased hydrophobicity property of membrane surface by foulant layer accumulation could result in a highly rejection of the strongly hydrophobic characteristic of the HA fraction [12].

Table 2 DOC concentrations of DOM fractions along the treatment process

Fraction	Influent DOM	Mixed liquor DOM	Effluent DOM
HA (mg/l)	207	100	40
FA (mg/l)	719	254	225
Hyl (mg/l)	2,215	183	162

3.3 Fluorescence EEMs of DOM

Fluorescence EEM was used to provide additional information of fluorescence properties of DOM in leachate during the MBR treatment. There were six

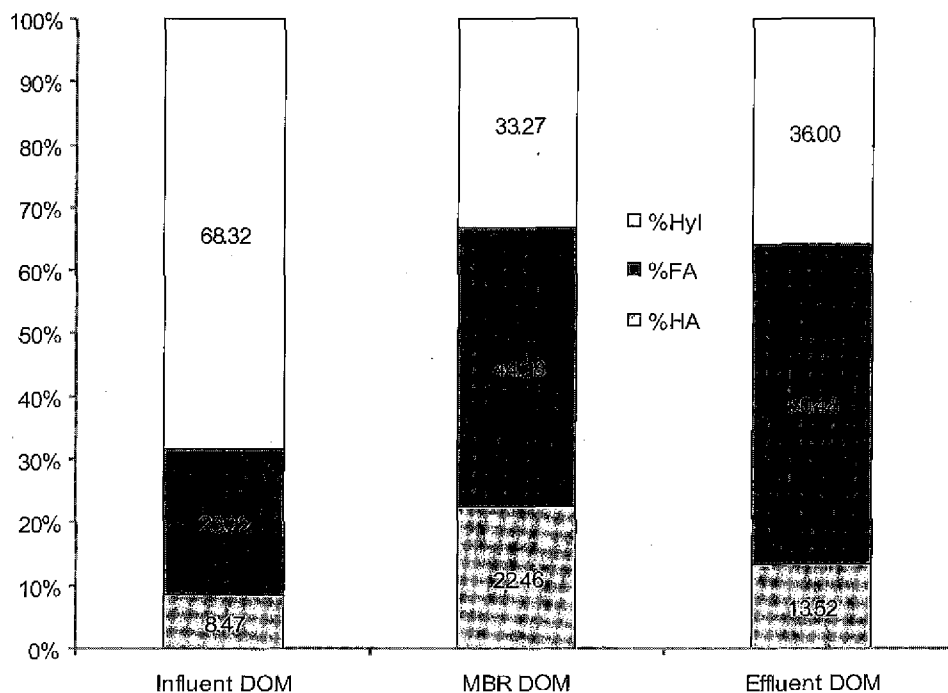


Figure 2 Percentages of DOM fractions distribution in influent, MBR and effluent

principal fluorescence peaks that are illustrated in Fig. 3. Based on the fluorescence EEMs of DOM in landfill leachate reported in previous research [13], the putative origin of each fluorescence peak obtained from this study are identified. For the influent DOM, the fluorescence peak at $Ex/Em = 270-280/300-310$ (peak A) was attributed to be a tyrosine-like substances. The fluorescence peak at $Ex/Em = 230-240/330-340$ (peak B) and at $Ex/Em = 280-290/310-340$ (peak C) were related to tryptophan-like substances. The peak at $Ex/Em = 290-310/400-420$ (peak D) was suggested to be humic-like substances and labeled as fulvic-acid like [7]. There were two new fluorescence peaks in the MBR DOM, the peak at $Ex/Em = 220-230/400-420$ (peak E) which was similar to humic-like substances, and another peak at $Ex/Em = 250-260/460-470$ (peak F) which is still unclear but possibly related to the pyrenyl functional group or humic-like substances. The fluorescence peaks of protein-like substance (peak A, B, and C) mostly disappeared from the system after the biological treatment process, whereas the humic-like substances (peak D) were shifted to the longer wavelengths as compared to that of the influent DOM. The extended of wavelengths implied an increasing of molecular size, aromatic polycondensation, and degree of humification [2]. As for the effluent DOM, the location of humic-like substances at fluorescence peak D were again shifted as compared to that of the MBR DOM, and part of humic-like substances at peak E was removed after the membrane filtration. The remaining

of fluorescence peak F demonstrated non-biodegradable character which could not be removed in the treatment system [13]. The FEEM results indicated that the MBR treatment system could remove most of protein-like substances and some part of humic-like substances.

3.4 FTIR OF DOM

The FTIR spectra of DOM samples are shown in Fig. 4 and the general assignments of the main FTIR spectra are detailed in Table 3. The FTIR spectrum pattern of the influent DOM was rather different from that in the MBR and effluent DOM, while the quite similar FTIR spectrum was found in both of the MBR and effluent DOM, that explained the transformation of functional groups and molecular structures importantly occurred due to the biological treatment process. For the influent DOM, it was found the absorbance bands at $2950-2880\text{ cm}^{-1}$ could be related to C-H stretching bond from carboxylic group in leachate which was also obtained in the MBR and effluent DOM. Furthermore, the absorbance bands that detected only in the influent DOM were the absorbance band at $1565, 1415, \text{ and } 1130-1000\text{ cm}^{-1}$. This absorbance bands were probably related to N-H in plane second band of amides, stretch of carboxylic acid groups, and C-O stretching of carbohydrate or polysaccharide-like substance respectively. For the MBR and effluent DOM, the FTIR spectrum showed the absorbance bands of the aromatic C=C stretch at $1620-1580\text{ cm}^{-1}$ indicating the existence of aromatic structures and the bands between $1700-1630\text{ cm}^{-1}$ illustrating the C=C stretching of carboxylic acid and amide group in that DOM. This finding on absorbance bands indicated the presence of fulvic acid and humic acid which have relatively strong absorbance band at $1710-1690\text{ cm}^{-1}$ and 1630 cm^{-1} [2]. Moreover, the absorbance bands at $2550-2540\text{ cm}^{-1}$ and 1400 cm^{-1} could be attributed to carboxylate ions and N-O stretch of nitrate, indicating the degradation of carboxylic acids and amide groups in this process. Nevertheless, the absorbance bands at 834 and 705 cm^{-1} indicated the remaining of amide group of the treated DOM. The FTIR spectra results showed the significant increasing of aromatic and carboxylic group that could be related to humic substances and partial degradation of carboxylic acid and amide group in the MBR process for leachate treatment.

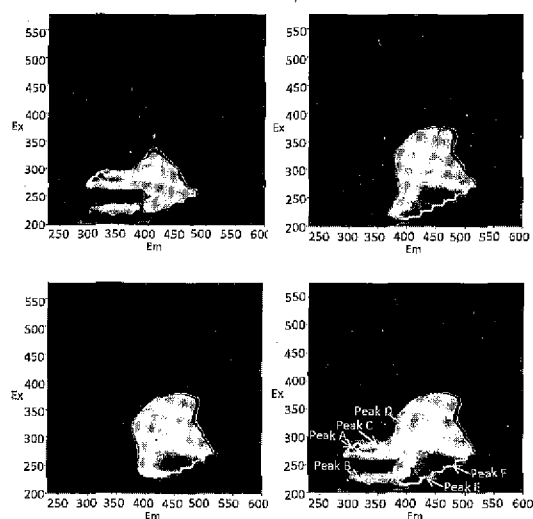
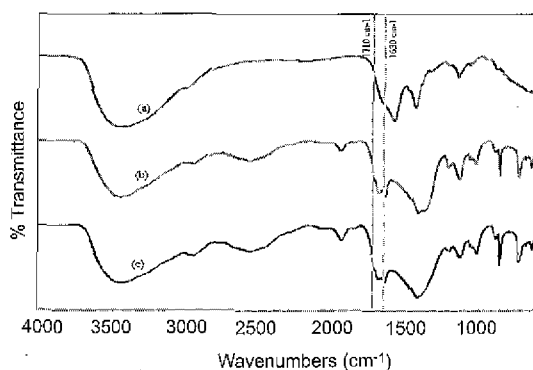


Figure 3 Fluorescence EEMs of DOM samples (a) Influent DOM, (b) MBR DOM, (c) Effluent DOM, and (d) summary of fluorescence peak position

Table 3 General assignments of FTIR spectra [7, 8]

Wave length (cm ⁻¹)	Assignment
2950-2850	Asymmetrical and symmetrical stretching of methyl and methylen C-H
2850-2500	Carboxylate ion
1725-1640	C=O stretching of carboxylic acids
1620-1580	Aromatic C=C double bonds that are conjugated with C=C of COO ⁻
1570-1540	N-H bending vibration of amide group (amid-2)
1420-1410	O-H vibration of carboxylic group C-H deformation abutted upon C=O
1400	Nitrate
1120-1000	C-O stretching of carbohydrates, esters and polysaccharide of polysaccharide-like substances
850-650	C-H vibration of N-H out of plane

**Figure 4** FTIR spectra of DOM samples of Influent DOM (a), MBR DOM (b), and Effluent DOM (c)

4.0 CONCLUSIONS

Dissolved organic matter of landfill leachate composed of various fractionated components. The DOM classified as Hyl fraction and protein-like substances could be efficient removed by biological activities in MBR process. The humic-like substances and its fractions (HA and FA) was observed as the most abundant fractions in MBR and effluent DOM, and filtration process in MBR also contributed to significant removal of their fractions.

ACKNOWLEDGEMENT

This research was financially supported by the Japan International Cooperation Agency (JICA) under the Research and Development for Water Reuse Technology in Tropical Region (Water InTro) Project.

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