Characteristics of dissolved organic matter (DOM) in leachate with different landfill ages

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Abstract

The main objective of the study was to investigate the characteristics of dissolved organic matter (DOM) in leachate with different landfill ages through the chemical, spectroscopic, and elemental analysis. Humic acid (HA), fulvic acid (FA), and hydrophilic (HyI) fractions were isolated and purified by the XAD-8 resin combined with the cation exchange resin method. The analytical results of fluorescence excitation-emission matrix spectroscopy (EEMs) revealed that the fluorescence peaks were protein-like fluorescence for young landfill leachate, while the fluorescence peaks for medium and old landfill leachate were humic-like and fulvic-like fluorescence, respectively. Elemental analysis showed that carbon, hydrogen, and nitrogen content decreased with landfill age, while the oxygen content increased. Moreover, the nitrogen content in these isolated fractions followed: HA > HyI > FA. The results of elemental analysis, FT-IR, and fluorescence EEMs also confirmed that aromatic carbons and portions of aliphatic functional groups were more abundant in leachate samples with increasing landfill age.

Key words: dissolved organic matter (DOM); fluorescence EEMs; DOM fractionation; landfill; leachate

Introduction

In 2002, approximately 94% of the municipal solid waste (MSW) generated in China was disposed in landfill (Wang *et al*., 2006). However, anaerobic degradation of solid waste results in the production of leachate and landfill gas for a very long time in a conventional landfill. Leachate and landfill gas are the potential pollution sources for the surrounding environment, and the long-term environmental impacts will last for several decades (Cossu *et al*., 2003; Bilgili *et al*., 2007). Therefore, there has been increased emphasis on landfill leachate management in the recent years especially for municipal areas (Amakrane *et al*., 1997; Bohdziewicz *et al*., 2001; Kargi and Pamukoglu, 2003; Ahmet and Fikret, 2004). However, treatment of leachate is very complicated, expensive, and generally requires various process applications owing to variations of composition of the landfill leachate over the age of landfill. For instance, in China, few landfill leachate treatment plants using biological process can meet the discharge standard (Li *et al*., 2002; Xu *et al*., 2006). Thus, the leachate should be characterized and complex compositions have to be considered before a suitable treatment strategy is developed (Kargi and Pamukoglu, 2003).

A number of authors have presented that a major part

of complex organics consists of dissolved organic matter (DOM) in landfill leachate and the characteristics of DOM can guide the selection of the treatment process (Fujita *et al*., 1996; Wang *et al*., 2004; Rivas *et al*., 2004; Leenheer and Croue, 2003; He *et al*., 2006). DOM also plays a significant biochemical and geochemical role in landfill system, and interacts with several inorganic and organic pollutants. For instance, DOM has a wide range of molecular weights and sizes, ranging from a few hundred to hundreds of thousands of Daltons. Moreover, a number of functional groups in DOM, such as carboxylic, phenolic, and carbonyl etc. allow them to interact with various substances in the environment (Jones and Bryan, 1998). Several studies have investigated the biogeochemical properties of landfill leachate. A recent study by He *et al*. (2006) investigated the characteristics of the DOM in the leachate from simulated bioreactor landfill columns. Ozkaya *et al*. (2006) studied the change of soluble substrate concentrations in leachate from field scale MSW test cells, and the results indicated that the biodegradable fraction of substrate can be effectively removed in biological treatment system, but its non-biodegradable fraction passes through the system unchanged. Furthermore, non-biodegradable compounds of leachate gradually increase as a landfill waste stabilizes.

Some studies also suggested that the aromatic com-

ponents and molecular size of the DOM increased with increasing landfill age, and young leachate had a narrower molecular weight range at low molecular weight, whereas older leachate had a wider range of molecular weight with a high molecular weight fraction being present (Kang *et al.*, 2002; Calace *et al.*, 2001). The close correlation between the characteristics of DOM in leachate and treatment performance has been revealed in the recent years (He *et al.*, 2006; Xu *et al.*, 2006). He *et al.* (2006) presented that biological treatments degrade organic matters of low molecular weights, and physical-chemical methods are preferred for handling the refractory organics of high molecular weights, and the coagulation-sedimentation was found effective to remove hydrophobic organic matter of high molecular weights and of high aromatic extent.

Fluorescence excitation-emission matrix (EEM) spectroscopy provides considerable detailed information about fluorescence properties of DOM that may reveal important information about its composition and biogeochemical cycling (Burdige *et al.*, 2004; Marhuenda-Egea *et al.*, 2007). With this technique, a three-dimensional picture is generated of fluorescence intensity as a function of excitation and emission wavelength. Fluorescence spectroscopy has high sensitivity and specificity, and was already used in natural water quality monitoring. Rapid analyses are now possible using fluorescence spectrophotometers such that an EEM can be generated in approximately 1 min (Baker and Curry, 2004). This technique has been applied to the study of DOM from different sources (Coble, 1996; Mobed *et al.*, 1996; Mayer *et al.*, 1999; Parlanti *et al.*, 2000; Provenzano *et al.*, 2001; Baker, 2001, 2002, 2005; Baker and Inverarity, 2004; Chen *et al.*, 2003; Jaffe *et al.*, 2004; Sierra *et al.*, 2005b). Thus, fluorescence analyses may provide a rapid method to characterize organic matter and to fingerprint organic pollutants in the leachate (Baker, 2005). Moreover, Fourier transform infrared spectra (FT-IR) was also used to describe the process of waste degradation (Smidt and Katharina, 2007; Smidt *et al.*, 2002, 2005; Sierra *et al.*, 2005a; Lguirati *et al.*, 2005; Kang *et al.*, 2002). However, few efforts have been made to characterize DOM in the leachate using three-dimensional EEM fluorescence spectroscopy and FT-IR spectra.

In this study, the main objective was to investigate the characteristics of DOM in leachate with different landfill ages through chemical, spectroscopic, and elemental analysis. The results of this study may provide basic information for leachate treatment process optimization with respect to landfill age and quick judgment of humification degree of leachate by analyzing the excitation-emission matrix spectroscopy (EEMs) and FT-IR characteristic of DOM along with chemical analysis in the leachate.

1 Materials and methods

1.1 Samples

Leachate was collected from Asuwei sanitary landfill site, located in Beijing, China, with different landfilling ages for different landfill cells. The landfill site has been accepting municipal wastes since 1994, with an initial design capacity of 12,000,000 m^3. The average waste input in the landfill is about 2,000 t/d and the leachate quantity is about 1,000 m^3/d. We collected leachate samples from three different points in Asuwei sanitary landfill site; new landfill cell where the wastes between 2003 and 2006 were deposited (sample A), medium-aged landfill cell where the wastes between 1994 and 2003 were input (sample B), and old landfill of more than 10 years from a landfill bioreactor (sample C). The vertical sampling wells were drilled at different landfill cells and fitted with multi-hole PVC pipes. Approximately 2 L samples were obtained from the vertical sampling wells by pump. All samples in plastic bottles were stored under 4°C in the refrigerator as soon as they were carried to the laboratory. The water quality of the leachate was analyzed.

1.2 Experimental methods

The leachate samples were centrifuged with a rotating speed of 12,000 r/min for 20 min under 4°C, and filtrated through glass-fiber membrane (0.45 μm) to remove suspended materials that may react with DOM. The organic matter in the filtrate was DOM. The total organic carbon (TOC) of the DOM was determined by TOC analyzer (Shimadzu TOC-5000, Japan).

1.2.1 Fluorescence EEMs

The EEMs of DOM were measured by fluorescence spectrometer (Perkin Elmer Luminescence Spectrometer LS50B, USA). EEMs are a collection of a series of emission spectra over a range of excitation wavelengths, and can be used to identify fluorescent compounds present in complex mixtures. The spectrometer displayed a maximum emission intensity of 1,000 arbitrary units (a.u.). A xenon excitation source was used in the spectrometer, and the excitation and emission slits were set to a 10-nm band-pass. Each EEM spectrum was generated by scanning excitation wavelengths from 200 to 480 nm at 10 nm steps, and detecting the emission fluorescence between 200 and 600 nm at 10 nm steps. The scan speed was 1,200 nm/min, permitting collection of a complete EEM spectrum in about 60 s. A 290-nm cutoff filter was used in scanning to limit second-order Raleigh scattering. The spectrum of double distilled water was recorded as blank.

EEMs are illustrated as the elliptical shape of contours (Fig.1). The X-axis represents the emission spectra from 200 to 600 nm, whereas the Y-axis represents the excitation wavelength from 200 to 450 nm. Contour lines, as the third dimension, are shown for each EEM spectrum to represent the fluorescence intensity.

1.2.2 Fourier transform infrared (FT-IR)

Fourier transform infrared spectra are commonly used to identify functional groups by measuring the vibrational frequencies of molecules when they are scanned with an infrared light. There are four basic steps towards the collection of an FT-IR spectrum: preparation of the sample, collecting the background, collecting the spectra, and peak picking. The filtrate was freeze-dried for 72 h
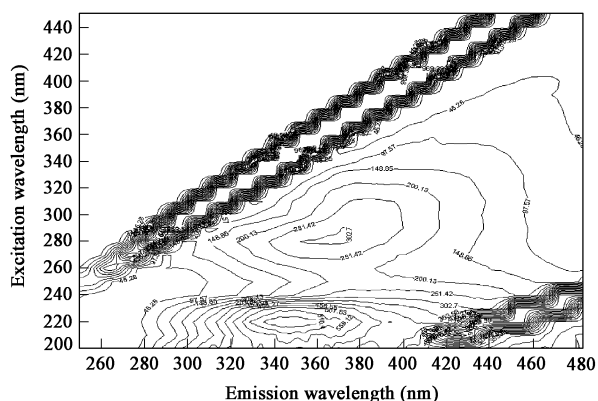
Fig. 1 EEM spectra example illustrated as the elliptical shape of contours.

under –50°C by FD-1D-50 freeze-dryness meter, which was obtained from Beijing Boyikang Instrument Co. Ltd., China. Two milligram portions of each sub-sample was ground with 300 mg KBr and compressed under vacuum for 10 min (Christensen *et al.*, 1998). A background spectrum was scanned first, to eliminate peaks that would "contaminate" spectra, such as atmospheric CO_2 and H_2O. Then, a sample was placed within a Nexus 670 series FT-IR spectrophotometer and scanned from 4000 to 400 cm^{-1}.

1.2.3 Fractionation of DOM

The methods described by Christensen *et al.* (1998) and Ma *et al.* (2001) were adopted herein for DOM fractionation in leachate. The DOM in leachate was fractionated into humic acid (HA), fulvic acid (FA), and hydrophilic (HyI) fractions. Amberlite XAD-8 resin was obtained from Rohm and Haas Co., USA and 732 cation exchange resins were obtained from Beijing Huideyi Co. Ltd., China. XAD-8 and 732 resins were cleaned by the method described in the literature (He *et al.*, 2006). The concentrations of HA, FA, and HyI fractions were represented by measuring the dissolved organic carbon (DOC) concentration of samples. After the DOC measuring, all fractions were freeze-dried under –50°C by the FD-1D-50 freeze-dryness meter.

1.2.4 Elemental analysis

Elemental analysis was performed on freeze-dried samples of HA, FA, and HyI using Vario El elemental analyzer (Elementar Co., Germany).

2 Results and discussion

2.1 Water quality of the leachate

The analytical results of the water quality of the leachate samples are presented in Table 1. It was found that the leachate possessed typical characteristics with different sampling point, and landfill age played an important role in determining the leachate characteristics, that is, some parameters (such as COD, BOD, DOC, and VFA) decreased as the landfill age increased. The BOD/COD ratio was significantly reduced from 0.75 of sample A to 0.08 of sample C, which indicated that the biodegradability of the organic matter in the leachate decreased with landfill age. High concentration of volatile fatty acids and low pH value of sample A indicated that it was in acid phase, while no volatile fatty acids of sample C were detected (Table 1).

### 2.2 Fluorescence EEMs of DOM

Each EEM provides spectral information about the organic matter compositions of leachate sample. Fluorescence spectra, such as those we have obtained, contained a number of distinct peaks that are generally ascribed to either humic-like or protein-like fluorescence, and at least four peaks were readily identified from the EEM fluorescence spectra (Fig.2). The first main peak was a distinctive and intense fluorescence peak at excitation and emission wavelengths (Ex/Em) of 210–230 nm/340–360 nm (peak A), which was identical in location to the diagnostic fluorescence centre observed previously (Baker and Curry, 2004). The second main peak was identified at Ex/Em of 270–280 nm/340–380 nm (peak B). The two peaks have been ascribed as protein-like peaks, in which the fluorescence was associated with the tryptophan and tyrosine (Baker, 2001; Chen *et al.*, 2003; Yamashita and Tanoue, 2003; Baker and Inverarity, 2004). A third peak was located around Ex/Em of 310–340 nm/420–440 nm (peak C), which was attributed to aromatic and aliphatic groups in the DOM fraction and commonly labeled as fulvic-like (Coble, 1996). In these leachates, we also observed a fourth peak at Ex/Em of 220–240 nm/420–440 nm (peak D), a poorly understood fluorescent centre widely attributed to a component of the humic fraction (Coble, 1996; Burdige *et al.*, 2004; Yan *et al.*, 2000).

For young landfill leachate (sample A), the fluorescence peaks were peaks A and B (Fig.2a), which were identified as being most likely to relate to the biodegradable fraction of leachate. The studies of Cammack *et al.* (2004) and Elliott *et al.* (2006) showed peaks A and B to be directly

Table 1 Water quality analysis of three leachate samples[a]

Parameter[b]	COD (mg/L)	BOD (mg/L)	BOD/COD	DOC (mg/L)	VFA (mg/L)	NH_4^+-N (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)	Cl^- (mg/L)	pH	Conductivity (μS/cm)
Sample A	53,200	39,900	0.75	19,500	10,300	2,760	1.63	163	6,150	6.7	31,500
Sample B	13,100	3,668	0.28	4,632	3,126	3,210	3.02	79	7,960	8.1	37,200
Sample C	1,863	149	0.08	796	ND^c	796	1.86	18	8,250	8.8	29,100

COD: chemical oxygen demand; BOD: biological oxygen demand; DOC: dissolved organic carbon; VFA: volatile fatty acid. [a] Each value is the average of three measurements; [b] sample A: new landfill cell (< 4 years); sample B: medium-aged landfill cell (4–13 years); sample C: old landfill cell. [c] Not detected.
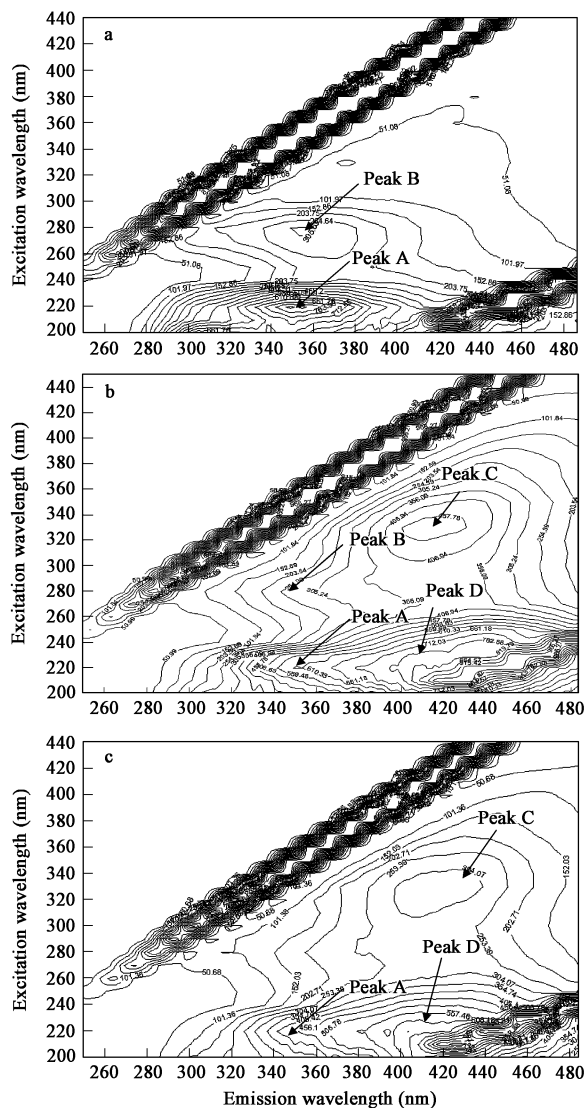
Fig. 2 EEM fluorescence spectra of the DOM. (a) sample A; (b) sample B; (c) sample C. Samples A, B, and C are the same as in Table 1.

associated with the growth stage of bacterial communities. Their results suggested that peaks A and B are more

labile fractions of DOM, which are preferentially degraded through the treatment process. However, as the landfill age increased, the fluorescence intensity of peak A and B decreased for samples B and C as compared to that of sample A (Figs.2b and 2c), and peak B was almost disappearing in sample C. The fluorescence peaks for medium and old landfill leachate (samples B and C) were mainly peaks C and D (Figs.2b and 2c). The peak locations of medium and old landfill leachate fluorescence spectra were slightly different. The locations of these peaks for the old landfill leachate were red shifted to longer wavelengths than those of the medium landfill leachate. Such differences implied an increase of molecular size, aromatic polycondensation, level of conjugated chromophores, and humification degree of dissolved organic matter as the landfill time increased, which were in accordance with the previous studies (Senesi *et al.*, 1991; Kang *et al.*, 2002). The results indicated that most organic matters are biodegradable in the leachate at the beginning of landfill, and become nonbiodegradable such as humic acid and fulvic acid at the late stage of landfill (Zouboulis *et al.*, 2003).

Our findings suggested that fluorescence can be used as a rapid and sensitive measurement of organic matter composition of leachate samples. Additionally, the EEM measurement of the DOM along with COD and BOD parameters can reflect the humification degree of leachate and offer a quick judgment method for estimating the characteristics of dissolved organic matter in landfill leachate.

2.3 Fourier transform infrared of DOM

Infrared spectra representing progressing stages of an individual process can serve as a qualitative tool for monitoring chemical groups and bands of DOM in leachate and provide more information about the structural changes of DOM evolution. The assignments of the major infrared spectral bands of landfill leachate are listed in Table 2. The spectra in Fig.3 are the FT-IR spectra of the DOM in the leachate that provided information about specific molecular structures and various functional groups.

Table 2   Assignments of the FT-IR spectral peaks of leachates[a]

Wavelength (cm^{-1})	Vibration	Functional group or component	Wavelength (cm^{-1})	Vibration	Functional group or component
3,400	O–H stretch	Bonded and non-bonded hydroxyl groups and water	1,425	COO– stretch	Carboxylic acids
3,180–3,090	NH$_2$ stretch (2 bands)	Primary amides		C–O stretch	Carbonate
3,920	C–H stretch	Aliphatic methylene	1,384	N–O stretch	Nitrate
2,850	C–H stretch	Aliphatic methylene	1,320	C–N stretch	Aromatic primary and second amines
2,590–2,560	S–H stretch	Thiol group	1,265–1,240	C–O	Carboxylic acids
2,520		Carbonate		C–N	Amide II
1,740–1,720	C=O	Aldehyde, ketone, carboxylic acids, esters	1,250–900	C–O–C, C–O	Polysaccharides
				C–O–P	Phosphodiesters
1,640	C=O	Amide I, carboxylates			
	C=C	Aromatic ring modes, alkenes	1,140–1,080	S–O stretch	Inorganic sulfates
1,635	O–H bend	Adsorbed water	875	C–O out of plane	Carbonate
1,600	N–H in plane	Amines	850–750	NH$_2$ out of plane	Primary amine group
1,600–1,590	C=C	Aromatic skeleton	750–700	N–H wag	Secondary amine group
1,570–1,540	N–H in plane	Amides II	680–610	S–O bends	Inorganic sulfates
1,515–1,505	Aromatic skeletal	Lignin			

[a] The assignments are based on the literature (Lguirati *et al.*, 2005; Kang *et al.*, 2002; Sierra *et al.*, 2005a; Smidt and Katharina, 2007).
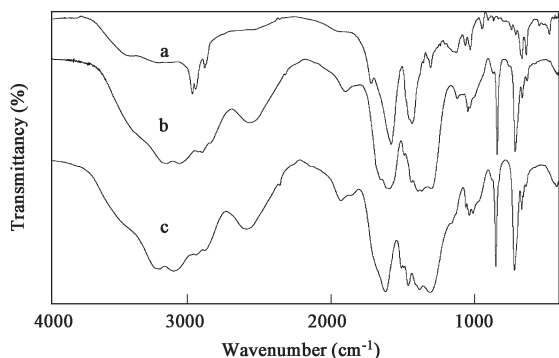
Fig. 3 FT-IR spectra of the DOM of different landfill age leachates. (a) sample A; (b) sample B; (c) sample C.

The FT-IR spectrum of the DOM (line a in Fig.3) for sample A (young landfill leachate) showed signals at 2,959, 2,934, and 2,873 cm^{-1}, which were attributed to asymmetric and symmetric stretching of methyl and methylene groups, as well as a band at 1,111 cm^{-1} owing to the stretching C–O bonds in alcohols and ethers. Moreover, signals at 1,707, 1,560, and 1,419 cm^{-1} due to the first, second, and third band of amides (stretching of C=O, N–H in plane and C–N bonds, respectively) and the bands at 680–610 cm^{-1} and 1,140–1,050 cm^{-1} can be attributed to inorganic sulfates (S–O bends and S–O stretch, respectively).

The FT-IR spectrum of the DOM (line b in Fig.3) for sample B (medium-landfill age leachate) indicated nitrogen containing compounds by the N–H stretch at 3,180 and 3,097 cm^{-1} (double band of primary amides), N–H in plane-bend at 1,560 cm^{-1}, the C–N stretch at 1,371 cm^{-1}, and the N–H wag vibration at 834 and 705 cm^{-1}. The S–H stretch vibration at 2,599 cm^{-1} of thiols was also presented in the FT-IR spectrum of sample B (Sierra *et al.*, 2005a; Smidt and Katharina, 2007; Lguirati *et al.*, 2005;

Table 3 Concentrations of organic carbon of HA, FA, and HyI in leachate samples (unit: mg/L)

Parameter	Sample A	Sample B	Sample C
HA	80	632	351
FA	4,420	1,760	389
HyI	14,900	2,130	56

HA: humic acid; FA: fulvic acid; HyI: hydrophilic.

Kang *et al.*, 2002). For old landfill leachate of sample C, the FT-IR spectrum (line c in Fig.3) was similar to that of medium-landfill age leachate, but had some changes with increasing and decreasing peaks heights. Moreover, slight peak shifts were observed, which indicated changes in the molecule structure.

2.4 Fractionation of DOM

The concentrations of organic carbon of HA, FA, and HyI fractions in leachate samples are listed in Table 3. The HyI fractions accounted for 76.4%, 47.1%, and 7.0%, respectively, of the total organic carbon (TOC) of young (sample A), medium (sample B), and old landfill (sample C) leachate samples, respectively. The FA fractions consisted of 23.2%, 40.4%, and 48.9%, and the HA fractions accounted for 0.4%, 13.6%, and 44.1% of TOC in the three leachates, respectively. These results were quite consistent with the findings of He *et al.* (2006).

2.5 Elemental analysis

Elemental analysis along with some ratios such as H/C, O/C, and N/C can provide valuable information of the composition and possible structure of HA, FA, and HyI fractions. The elemental analysis results for isolated HA, FA, and HyI fractions of each sample are listed in Table 4. The HA extracted from the leachate contained higher content of carbon, hydrogen, and nitrogen and lower content of oxygen than the FA and HyI samples. Moreover, carbon, hydrogen, and nitrogen content decreased with landfill age, while the oxygen content increased. The nitrogen content in these isolated fractions followed: HA > HyI > FA, and the HA and HyI fractions had twice more nitrogen than FA, which was consistent with that found in literature (Ma *et al.*, 2001; Watt *et al.*, 1996; Christensen *et al.*, 1998). The high concentration of nitrogen in each sample may be caused by the high ammonia nitrogen concentrations of leachate (Kang *et al.*, 2002). The H/C ratio indicated a chemical structure consisting predominantly of aromatic framework and having significant portions of aliphatic functional groups. Moreover, the H/C ratio increased in the order of HA < FA < HyI, indicating a more aliphatic character of the hydrophilic fraction. The high O/C ratio of FA implied that the FA contained a high proportion of O-alkyl and carboxylic acid functional groups, which

Table 4 Elemental composition and atomic ratio for isolated fraction of DOM samples

Sample	Elemental composition (%)				Atomic ratio		
	C	H	N	O	H/C	N/C	O/C
HA-A	54.24	6.46	5.70	31.82	1.43	0.09	0.44
HA-B	50.21	5.77	7.03	34.14	1.38	0.12	0.51
HA-C	49.06	5.60	8.01	35.98	1.37	0.14	0.55
Leachate[a,b]	50.3–56.2	5.8–8.8	5.7–8.3	26.7–37.7	1.35–1.88	0.09–0.13	0.36–0.56
FA-A	42.35	5.01	2.08	44.04	1.42	0.042	0.78
FA-B	41.97	4.86	2.55	45.89	1.39	0.052	0.82
FA-C	41.61	4.79	2.96	47.71	1.38	0.061	0.86
Leachate[a,b]	33.1–53.6	3.8–6.4	2.3–12.0	32.8–60.8	1.29–2.53	0.04–0.23	0.47–1.38
HyI-A	35.37	5.36	5.36	49.52	1.82	0.13	1.05
HyI-B	31.25	4.66	5.47	50.42	1.79	0.15	1.21
HyI-C	35.83	5.23	3.76	48.73	1.75	0.09	1.02

A, B, C indicate samples A, B, and C. [a] Kang *et al.*, 2002; [b] Chai *et al.*, 2007.

was similar to the findings of Chai *et al.* (2007). The results of elemental analysis suggested that the number of O-containing functional groups in FA decreased with landfill age.

3 Conclusions

The DOM in leachate with different landfill ages was characterized by three-dimensional fluorescence EEMs, containing at least four distinct peaks that were generally ascribed to either humic-like or protein-like fluorescence. For young landfill leachate, the fluorescence peaks were protein-like fluorescence, while the fluorescence peaks for medium and old landfill leachates were humic-like and fulvic-like fluorescence, respectively. Our findings indicated that fluorescence may be used as a rapid judge of the organic matter characteristics of leachate samples.

We also found that Infrared spectra representing the progressing stages of an individual process may serve as a qualitative tool for monitoring chemical groups and bands of DOM in leachate and provide more information about the structural changes of DOM evolution. The DOM fractionation and elemental analysis of isolated fractions showed that the aromatic components and the degree of humification increase with the increasing landfill age. The information on the characteristics of DOM in different landfill age leachate can be referred in various related research fields, such as the optimization of leachate treatment processes.

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