



Occurrence and removal of organic micropollutants in the treatment of landfill leachate by combined anaerobic-membrane bioreactor technology

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Abstract

Organic micropollutants, with high toxicity and environmental concern, are present in the landfill leachate at much lower levels than total organic constituents (chemical oxygen demand (COD), biochemical oxygen demand (BOD), or total organic carbon (TOC)), and few has been known for their behaviors in different treatment processes. In this study, occurrence and removal of 17 organochlorine pesticides (OCPs), 16 polycyclic aromatic hydrocarbons (PAHs), and technical 4-nonylphenol (4-NP) in landfill leachate in a combined anaerobic-membrane bioreactor (MBR) were investigated. Chemical analyses were performed in leachates sampled from different treatment processes, using solid-phase extraction and gas chromatography with electron capture detector and mass spectrometry. Concentrations of OCPs, PAHs, and 4-NP in the raw leachate were detected within the range from ND (not detected) to 595.2 ng/L, which were as low as only 10^{-7} – 10^{-5} percentage of TOC (at the concentration of 2,962 mg/L). The removal of 4-NP was mainly established in the MBR process, in agreement with removals of COD, BOD, and TOC. However, the removals of OCPs and PAHs were different, mainly achieved in the anaerobic process. High removal efficiencies of both total organic constituents and organic micropollutants could be achieved by the combined anaerobic-MBR technology. The removal efficiencies of total organic constituents were in the order of BOD (99%) > COD (89%) > TOC (87%), whereas the removal efficiencies of investigated organic micropollutants were as follows: OCPs (94%) > 4-NP (77%) > PAHs (59%).

Key words: anaerobic; landfill leachate; membrane bioreactor; organic micropollutant

Introduction

Landfill leachate constitutes a very complex mixture, which may contain a large number of xenobiotic organic compounds encountered in the solid waste disposal site or formed as a result of chemical and biological processes within the landfill (Banar *et al.*, 2006; Urase and Miyashita, 2003). Among them, some organic micropollutants identified are highly toxic, carcinogenic, or even mutagenic, such as polycyclic aromatic hydrocarbons (PAHs), halogenated pesticides, phenols, and so on, although they are often found in trace levels ($\mu\text{g/L}$, ng/L or even lower) (Banar *et al.*, 2006; Ozkaya, 2005). These organic micropollutants may create a potential risk to the quality of receiving water bodies and become a new pollution source of groundwater or surface waters (Alkalay *et al.*, 1998; Baun *et al.*, 2004). Hence, several studies have reported growing concern on identification, occurrence, and toxicity of these organic micropollutants in landfill leachates (Banar *et al.*, 2006; Baun *et al.*, 2003, 2004; Bras

et al., 2000; Castillo and Barcelo, 2001; Grøn *et al.*, 2000; Herbert *et al.*, 2006; Nascimento Filho *et al.*, 2003; Noma *et al.*, 2001; Ozkaya, 2005; Urase and Miyashita, 2003), which are summarized in Table 1. Organic micropollutants contribute little to the level of total organic constituents, such as chemical oxygen demand (COD) and total organic carbon (TOC). Therefore, the main removal of COD and TOC may not indicate the significant decrease of trace organic contaminants, which has been seldom reported.

The treatment of leachate is very complicated, expensive, and generally requires various and combined process applications (Ozturk *et al.*, 2003). Biological techniques, anaerobic and aerobic treatment systems, have been studied in landfill leachate during the last few decades, which have shown high performance. However, there are still some problems and challenges depending on characteristics of leachate (such as age) for application of biological techniques, which are hardly efficient for removal of biorefractory organics (Wiszniewski *et al.*, 2006). Hence, physicochemical processes, such as membrane processes, advanced oxidation processes, and so on, have been widely used as posttreatment of biologically pretreated landfill

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Table 1 Identified organic micropollutants in landfill leachates

Chemical	Sample	Occurrence level ($\mu\text{g/L}$)	Analysis method	Reference
Alkanes, alkenes	Raw	–	SPME, GC/MS	Banar <i>et al.</i> , 2006
Alkylphenols	Raw	ND–22.1	SPE, GC/MS	Baun <i>et al.</i> , 2003
	Raw	ND–27.3	SPE, GC/MS	Baun <i>et al.</i> , 2004
Bicyclo compounds	Raw	ND–151	SPE, GC/MS	Baun <i>et al.</i> , 2003
	Raw	ND–255	SPE, GC/MS	Baun <i>et al.</i> , 2004
Bisphenol A	Raw	ND–8,400	SPE, GC/MS	Urase and Miyashita, 2003
	After	–		
BTEX	Raw	ND–278	LLE, GC/MS	Baun <i>et al.</i> , 2003
	Raw	ND–2,220	LLE, GC/MS	Baun <i>et al.</i> , 2004
C3-benzenes	Raw	ND–50.2	LLE, GC/MS	Baun <i>et al.</i> , 2003
	Raw	ND–152	LLE, GC/MS	Baun <i>et al.</i> , 2004
Chlorinated aliphatics	Raw	ND–8.61	LLE, GC/MS	Baun <i>et al.</i> , 2004
Chlorophenols	Raw	ND–0.35	SPE, GC/MS	Baun <i>et al.</i> , 2003
	Raw	ND–10.2	SPE, GC/MS	Baun <i>et al.</i> , 2004
	Raw	5	XAD-8, GC/MS	Grøn <i>et al.</i> , 2000
	Raw	ND–130	SPME, GC/FID	Ozkaya, 2005
Lactones	Raw	–	SPME, GC/MS	Banar <i>et al.</i> , 2006
Nonylphenol, nonylphenol ethoxycarboxylates	Raw	ND–7.0	SPE, GC/MS	Baun <i>et al.</i> , 2004
Organic acids	Raw	–	SPME, GC/MS	Banar <i>et al.</i> , 2006
	Raw	ND–2.10	SPE, GC/MS	Baun <i>et al.</i> , 2003
	Raw	0.6–19.3	SPE, GC/MS	Baun <i>et al.</i> , 2004
Organochlorine pesticides	Raw	ND	SPME, GC/ECD	Bras <i>et al.</i> , 2000
Organophosphorus	Raw	0.66	SPE, LC-APCI-MS	Castillo and Barcelo, 2001
Pesticides	Raw	17.5–260	SPE, GC/MS	Baun <i>et al.</i> , 2003
	Raw	ND–150	SPE, GC/MS	Baun <i>et al.</i> , 2004
Phthalic acid esters	Raw	–	SPME, GC/MS	Banar <i>et al.</i> , 2006
	Raw	1–340	LLE, GC/MS	Baun <i>et al.</i> , 2004
	Raw	0.78–3.0	SPE, LC-APCI-MS	Castillo and Barcelo, 2001
	Raw	–	SPE, GC/MS	Nascimento Filho <i>et al.</i> , 2003
Polychlorinated biphenyls	Raw	ND–1.213	SPME, GC/MS	Herbert <i>et al.</i> , 2006
Polycyclic aromatic hydrocarbons	Raw	–	SPME, GC/MS	Banar <i>et al.</i> , 2006
	Raw	ND–305	SPE, GC/MS	Baun <i>et al.</i> , 2003
	Raw	ND–114.7	SPE, GC/MS	Baun <i>et al.</i> , 2004
	Raw	ND–60.529	SPME, GC/MS	Herbert <i>et al.</i> , 2006

Occurrence level: range, or mean value for occurrence level of individual chemical; Raw: raw leachate; After: sample that is after treatment; –: quantitative results not available; ND: not detected.

leachates (Ahn *et al.*, 2002; Chen and Liu, 2006; Ozturk *et al.*, 2003).

In this study, a combined system comprised of a membrane bioreactor (MBR) and an anaerobic filter pre-treatment was applied to treat a municipal landfill leachate. The aim of this study was to investigate the occurrence and removal of some representative organic micropollutants in the leachate, PAHs, organochlorine pesticides (OCPs), and 4-nonylphenol (4-NP), by this combined treatment system. The study was also focused on comparison between the removal of these organic micropollutants and total organic constituents (COD, BOD, and TOC).

1 Materials and methods

1.1 Materials

The calibration mixture of 17 OCPs, including α -HCH, β -HCH, γ -HCH, δ -HCH, *p*, *p'*-DDT, *p*, *p'*-DDD, *p*, *p'*-DDE, methoxychlor, heptachlor, heptachlor epoxide, aldrin, dieldrin, endrin, endrin aldehyde, endosulfan I, endosulfan II, and endosulfan sulfate, was purchased from Supelco, USA. Each component at the concentration of 250 $\mu\text{g/ml}$ except methoxychlor at 1,000 $\mu\text{g/ml}$ in hexane:toluene (50:50, V/V). The calibration mixture of 16 PAHs, including acenaphthene (1,000

$\mu\text{g/ml}$), acenaphthylene (2,000 $\mu\text{g/ml}$), anthracene (100 $\mu\text{g/ml}$), benzo[a]anthracene (100 $\mu\text{g/ml}$), benzo[a]pyrene (100 $\mu\text{g/ml}$), benzo[b]fluoranthene (200 $\mu\text{g/ml}$), benzo[ghi]perylene (200 $\mu\text{g/ml}$), benzo[k]fluoranthene (200 $\mu\text{g/ml}$), chrysene (100 $\mu\text{g/ml}$), dibenzo[a,h]anthracene (200 $\mu\text{g/ml}$), fluoranthene (200 $\mu\text{g/ml}$), fluorene (200 $\mu\text{g/ml}$), indeno[1,2,3-cd]pyrene (100 $\mu\text{g/ml}$), naphthalene (1,000 $\mu\text{g/ml}$), phenanthrene (100 $\mu\text{g/ml}$), and pyrene (100 $\mu\text{g/ml}$), was purchased from Supelco, USA, with each component in methanol:methylene chloride (50:50, V/V). Technical 4-NP (mixture with branched alkyl chain, 99% purity) was obtained from Acros Organics, USA. Surrogates including tetrachloro-*m*-xylene and decachlorobiphenyl mixture (for OCPs, 200 $\mu\text{g/ml}$ each component in acetone), phenanthrene- d_{10} (for PAHs, 2,000 $\mu\text{g/ml}$ in methanol), and bisphenol A- d_{16} (for 4-NP, 50 mg) were all obtained from Supelco, USA. Internal standards including pentachloronitrobenzene (for OCPs, 200 $\mu\text{g/ml}$ in methylene chloride) and 4-*n*-nonylphenol (for 4-NP, 99.7% purity) were purchased from Supelco, USA, whereas internal standard hexamethylbenzene (for PAHs, 99.5% purity) was purchased from EQ Laboratories Inc., Germany. The derivatization reagent for 4-NP analysis, N, O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMCS), was obtained from

Fluka and Riedel-Haën (Switzerland).

All solvents were of HPLC grade, purchased from J.T. Baker, USA. Silica gel (60/200 mesh, ultra pure) and neutral aluminum oxide (50/200 mesh, ultra pure) were obtained from Acros Organics, USA, heated at 180 and 250°C for 12 h, respectively, and then both were cooled in a desiccator and deactivated using 3% of deionized water.

1.2 Leachate collection

Landfill leachate samples were collected from A'suwei Municipal Landfill in the north of Beijing, China, which is in operation since 1996. The collected leachate was stored at room temperature before pumped into the treatment system. The whole treatment system consisted of two main parts, an anaerobic filter followed by a membrane bioreactor (MBR). The anaerobic filter was applied as pretreatment, with 60 L of efficient volume. The MBR was composed of a bioreactor with 80 L of efficient volume and two membrane modules. Detailed conditions for MBR have been reported by Chen and Liu (2006), the important specifications are given in Table 2.

Table 2 Specifications of the MBR

Parameter	Description
Membrane	0.22 μm hollow fiber of polyvinylidene fluoride (PVDF)
Effective membrane area	0.1 m^2 for each membrane module
Transmembrane pressure (kPa)	9.0
Steady-state MLSS (g/L)	10.1
Total HRT (d)	9.5
DO (mg/L)	0.85

MLSS: activated sludge concentration; HRT: hydrodynamic retention time; DO: dissolved oxygen.

The activated sludge taken from a sewage treatment plant in Beijing was fed in the MBR, and the start-up procedure of MBR has been described in detail in the other article (Chen and Liu, 2006). Water samples were collected from 4 stages after continuous operation for 114 d in the treatment system, including raw leachate from landfill (L1), the effluent from anaerobic filter (L2), the supernatant of mixed liquor in MBR (L3), as well as the effluent from MBR (final effluent, L4). Water samples were collected in brown glass bottles with glass seals and were kept at 4°C until extraction. Storage period did not exceed 7 d.

1.3 Sample preparation

Water samples were spiked with surrogates for different analytes before extraction. For OCP and PAH analysis, 1 L of each water sample was extracted with a 6-ml (500 mg) Supelclean LC-18 SPE cartridge (Supelco, USA). The cartridge was prewashed with 5 ml of methylene chloride and conditioned with 5 ml of methanol followed by 5 ml of deionized water. After the extraction, the cartridge was then eluted using 10 ml of methylene chloride. For 4-NP analysis, 1 L of each water sample was first adjusted to pH 2 using 6 mol/L of HCl and then extracted using a 6-ml (500 mg) Oasis® HLB SPE cartridge (Waters Corp., USA). The cartridge was prewashed with 5 ml of methyl

tert-butyl ether (MTBE) and conditioned with 5 ml of methanol followed by 5 ml of deionized water. After the extraction, the cartridge was then eluted with 10 ml of methanol/MTBE mixture (10:90, V/V). All extracts were evaporated to near dryness under a gentle flow of nitrogen and dissolved in 1 ml of hexane before cleanup.

The OCP and PAH extracts were cleaned up using a silica gel/alumina composite chromatographic column, which was composed of 5 g of silica gel and 5 g of aluminum oxide. Seventy milliliter of methylene chloride/hexane mixture (30:70, V/V) elution was collected. The 4-NP extract was cleaned up using a silica gel chromatographic column, which was composed of 4 g of silica gel. Thirty milliliter of ethyl acetate/hexane mixture (25:75, V/V) elution was collected.

All the elution was evaporated to dryness in a rotary evaporator (Büchi Laboratory Equi., Switzerland). The residue of OCP and PAH sample was then dissolved in 1 ml of hexane and added with the internal standards. The residue of 4-NP sample was first dissolved in 200 μl of hexane, then silylated with 50 μl of derivatization reagent (BSTFA with 1% TMCS), reacted for 2 h at 60°C, and finally dissolved in 1 ml of hexane, which were added with the internal standard.

1.4 Chromatographic analysis

The analysis of OCPs was carried out using an Agilent 6890 series gas chromatograph equipped with a Ni⁶³ micro electron capture detector (GC/ μ -ECD). Analytes were separated on two different capillary gas chromatograph columns. A DB-5 (30 m \times 0.25 mm \times 0.25 μm) column served as the primary column for pesticide quantification, whereas an SPB-1701 (30 m \times 0.25 mm \times 0.25 μm) column was used to confirm the identified pesticides by relative retention times. Detailed instrument conditions are shown in Table 3.

PAHs and 4-NP were all analyzed on an Agilent 6890 GC connected to a 5973 mass spectrometry (GC/MS), equipped with a DB-5MS (60 m \times 0.25 mm \times 0.25 μm) capillary gas chromatograph column. Detailed instrument conditions are shown in Table 3. The mass spectrometry was operated in the selected ion monitoring mode for quantification, and at least two ions for each target analyte were monitored.

All the analytes were quantified by peak area using the internal standard method. Qualitative analysis and detection limit of each analyte are shown in Table 4. Mean recoveries of OCPs, PAHs, and 4-NP through entire analytical procedures were in the range of 61%–142%, 58%–121%, and 81%, respectively, which were determined with laboratory fortified blanks.

2 Results and discussion

2.1 Characteristics of leachate

Characteristics of the leachate are shown in Table 5. The concentrations of COD were measured as soluble COD (SCOD) in this study. The raw landfill leachate (L1) had a high BOD/COD ratio of 0.71, which suggested that

Table 3 Instrument conditions of chromatographic analysis

Analyte	Column	Oven	Inlet	Detector	Carrier gas
OCPs	DB-5	Initially 85°C for 2 min, and increased by 15°C/min to 160°C, then increased by 5°C/min to the final temperature 280°C (hold for 20 min)	250°C, splitless	ECD, 300°C	Nitrogen, 2.0 ml/min
	SPB-1701	Initially 60°C for 2 min, and increased by 20°C/min to 160°C, then increased by 4°C/min to the final temperature 260°C (hold for 20 min)	200°C, splitless	ECD, 280°C	Nitrogen, 0.9 ml/min
PAHs	DB-5MS	Initially 50°C for 2 min, and increased by 20°C/min to 200°C (hold for 2 min), increased by 5°C/min to 240°C (hold for 2 min), then increased by 3°C/min to the final temperature	290°C (hold for 15 min) 280°C, splitless	MS, 280°C	Helium, 1.0 ml/min
4-NP	DB-5MS	Initially 100°C for 1 min, and increased by 25°C/min to 180°C (hold for 15 min), then increased by 20°C/min to the final temperature 300°C (hold for 15 min)	280°C, splitless	MS, 280°C	Helium, 1.0 ml/min

OCP: organochlorine pesticides; PAH: polycyclic aromatic hydrocarbons; 4-NP: 4-nonylphenol.

Table 4 Qualitative analysis and detection limit of each investigated organic micropollutant

OCP	RT on DB-5 (min)	RT on SPB-1701 (min)	Detection limit (ng/L)	PAH and 4-NP	Qualifier ion	Detection limit (ng/L)
α -HCH	9.684	15.489	0.41	Naphthalene	128, 102	5.0
β -HCH	10.335	19.402	0.46	Acenaphthylene	152, 76	13.0
γ -HCH	10.477	16.845	0.57	Acenaphthene	154, 76	5.2
δ -HCH	11.107	20.321	0.71	Fluorene	166, 139	2.9
<i>p, p'</i> -DDT	19.163	27.268	0.99	Phenanthrene	178, 76	0.5
<i>p, p'</i> -DDD	17.951	26.472	1.85	Anthracene	178, 89	1.5
<i>p, p'</i> -DDE	16.606	23.434	1.57	Fluoranthene	202, 101	1.0
Methoxy-chlor	20.346	29.945	5.47	Pyrene	202, 101	0.9
Aldrin	13.336	18.833	0.81	Benzo[a]anthracene	228, 114	1.4
Dieldrin	16.488	23.907	0.60	Chrysene	228, 114	1.4
Endrin	17.152	24.728	0.82	Benzo[b]fluoranthene	252, 113	2.6
Endrin aldehyde	18.116	28.126	0.74	Benzo[k]fluoranthene	252, 113	4.1
Endosulfan I	15.655	22.471	0.89	Benzo[a]pyrene	252, 113	1.3
Endosulfan II	17.475	26.557	0.70	Indeno[1,2,3-cd]pyrene	276, 138	1.2
Endosulfan sulfate	18.415	29.420	0.47	Dibenzo[a,h]anthracene	278, 139	2.3
Heptachlor	12.366	17.807	1.38	Benzo[ghi]perylene	276, 138	4.1
Heptachlor epoxide	14.565	21.382	1.15	4-NP	292, 179	10

RT: retention time.

Table 5 Characteristics of the landfill leachate during the treatment process

Parameter	L1	L2	L3	L4
pH	8.0	8.3	8.4	8.4
SCOD (mg/L)	10,084	9,357	1,955	1,007
BOD (mg/L)	7,200	5,600	40	24
TOC (mg/L)	2,962	2,917	753	410
TN (mg/L)	2,445	2,468	874	848

SCOD: soluble COD; L1: raw landfill leachate; L2: leachate after anaerobic filtration; L3: supernatant of mixed liquor in MBR; L4: final effluent.

the leachate was collected from a young and biodegradable landfill. High removal efficiencies were achieved for SCOD, BOD, and TOC by the combined anaerobic-MBR treatment system due to the relatively high biodegradability of leachate, as indicated in Table 5.

2.2 Occurrence of organic micropollutants

The landfill leachate during all the treatment processes was screened for 34 organic micropollutants, including 17 OCPs, 16 PAHs, and technical 4-NP. Detected pollutants were present in much lower concentrations (at the level of ng/L) in the landfill leachate, compared with total organic constituents (at the level of thousands of mg/L), as shown

in Table 6.

The total concentration of OCPs (Σ OCPs) in the raw landfill leachate (L1) was only 203.5 ng/L, in which γ -HCH, *p, p'*-DDT, and *p, p'*-DDE were detected. During the treatment processes, *p, p'*-DDD, another metabolite of *p, p'*-DDT, was also checked out. Organochlorine pesticides residue has been seldom reported in landfill leachates.

Polycyclic aromatic hydrocarbons were present in concentrations higher than those of OCPs in the leachate. Twelve PAHs were detected during the treatment processes, and main components were low molecular-weight PAHs, which are listed in Table 6. The total concentrations of PAHs (Σ PAHs) were in the range of 485.2–1,188.2 ng/L. The main component of PAHs in the raw leachate (L1) was acenaphthylene, at a concentration of 595.2 ng/L. Contamination of PAH in this leachate was not very high, as the total amounts of PAHs have been reported in landfill leachates at the concentrations up to 114,273 ng/L (Herbert *et al.*, 2006).

4-Nonylphenol was detected during all the treatment processes at concentrations of 92–482 ng/L. Similarly, 4-NP has been identified in landfill leachates at levels of below detection limit to 7,000 ng/L in the literature (Baun *et al.*, 2004).

Table 6 Concentrations of organic micropollutants detected in the leachate during treatment process

Analyte	Concentrations (ng/L)				Mean RPD (%)	Blank
	L1	L2	L3	L4		
γ -HCH	138.7	ND	20.5	8.7	4	ND
<i>p, p'</i> -DDT	51.6	ND	ND	ND	8	ND
<i>p, p'</i> -DDD	ND	4.2	ND	ND	8	ND
<i>p, p'</i> -DDE	13.2	11.9	11.2	3.1	7	ND
Naphthalene	ND	71.3	34.4	72.9	4	5.1
Acenaphthylene	595.2	ND	20.1	54.9	6	8.7
Acenaphthene	ND	ND	3.9	ND	2	ND
Fluorene	ND	181.8	157.8	144.7	11	ND
Phenanthrene	ND	129.6	136.7	152.3	2	ND
Fluoranthene	122.6	ND	ND	ND	8	ND
Pyrene	194.8	ND	ND	ND	5	ND
Benzo[a]anthracene	129.0	106.1	137.8	39.8	8	ND
Chrysene	48.3	ND	13.9	15.6	15	ND
Benzo[b]fluoranthene	21.3	10.7	13.1	5.0	11	ND
Benzo[a]pyrene	30.4	ND	ND	ND	18	ND
Benzo[ghi]perylene	46.6	ND	ND	ND	13	ND
4-NP	400	482	99	92	5	ND

ND: not detected; RPD: relative percentage deviations for sample duplicates. L1, L2, L3, and L4 are the same as that in Table 5.

2.3 Removal of trace organic contaminants in leachate treatment process

Figure 1 shows the behaviors of investigated organic micropollutants (OCPs, PAHs, and 4-NP at levels of ng/L) and total organic constituents (SCOD, BOD, and TOC at levels of mg/L), after each treatment process in the combined leachate treatment systems.

The breakdown of OCPs was mainly achieved in the anaerobic process. A 94% removal of γ -HCH could be obtained in final, resulting in the decrease of concentration from 138.7 to 8.7 ng/L (Table 6). Previous work has demonstrated that β -HCH and δ -HCH are more persistent than α -HCH and γ -HCH (Langenhoff *et al.*, 2002; Phillips *et al.*, 2005; Rath *et al.*, 1998). However, none of other HCH isomers except γ -HCH were detected in the leachate, which indicated that there were no marked transformation processes between HCH isomers throughout the treatment processes. γ -HCH in the leachate was probably dechlorinated into more stable products, such as chlorobenzenes and chlorophenols (Langenhoff *et al.*, 2002). The removal of *p, p'*-DDTs was as high as 99% by the integrate treatment system. Dechlorinated metabolic

transformation of DDT under anaerobic conditions leads to the metabolite DDD, and evidence has presented that the preferential metabolic pathway via DDD can avoid the formation of DDE (Mitra and Raghu, 1998). In this study, *p, p'*-DDT preferred to degrade to *p, p'*-DDD, whereas the total amount of *p, p'*-DDTs was dissipated markedly after anaerobic treatment process. A possible reason could be the decrease of total DDTs because DDD was not the final metabolite and further degradation of DDD could occur under anaerobic conditions, which has been already confirmed (Mitra and Raghu, 1998). The metabolite DDE has been shown to be more persistent than either DDT or DDD (Kveseth *et al.*, 1979). Hence, *p, p'*-DDE was hardly removed throughout the treatment processes, and it was the only metabolite that could be found in final effluent (L4) (Table 6).

Most of PAHs in leachate were also removed after anaerobic process. Under anaerobic conditions, stability of PAHs makes it difficult to cleave the ring without oxygen. However, recent research has shown that unsubstituted low molecular polycyclic aromatic compounds can be degraded under nitrate-reducing, iron-reducing, sulfate-reducing, and methanogenic conditions (Bedessem *et al.*, 1997; Rockne and Strand, 1998; Sharak Genthner *et al.*, 1997). In this study, most of the decrease in low molecular weight PAHs in the leachate was probably attributed to this type of anaerobic biodegradation, which should be confirmed by further research to find out the electron acceptor conditions in the stimulated biodegradation of PAHs during this biological pretreatment process.

The removal of 4-NP was different with OCPs and PAHs, which was mainly achieved in the MBR treatment system. A significant drop of 4-NP was observed in the MBR systems, from 482 to 92 ng/L (Table 6). However, a slight increase in concentration of 4-NP was observed after the anaerobic treatment (from 400 to 482 ng/L, a minus removal efficiency of -21% as shown in Table 7). Nonylphenol has been reported as one of the degradation products of nonylphenol polyethoxylates (NPnEOs) (Hoai *et al.*, 2003), which was found to be hardly degraded under

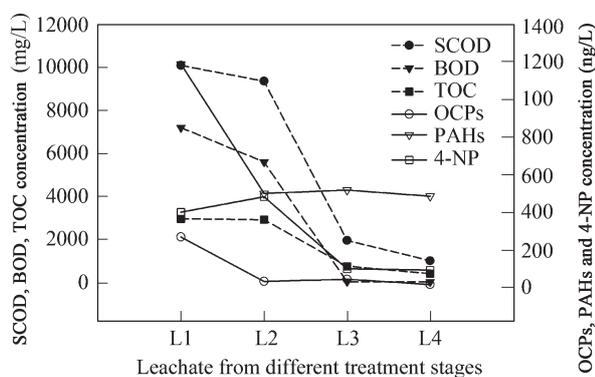


Fig. 1 Behavior of total organic constituents and trace organic contaminants in the treatment processes. L1, L2, L3, and L4 are the same as that in Table 5.

Table 7 Removal efficiency of different analytes during different treatment processes

Analyte	Removal efficiency (%)			
	Anaerobic	Bioreactor	Membrane	Integrate treatment
SCOD	7	73	9	89
BOD	22	77	0	99
TOC	2	73	12	87
∑OCPs	88	-4	10	94
∑PAHs	58	-2	3	59
4-NP	-21	96	2	77

Integrate treatment: treatment throughout all the processes.

anaerobic conditions (Angelidaki *et al.*, 2000).

The comparison of removal efficiencies between organic micropollutants and total organic constituents in the leachate after each treatment process by anaerobic-MBR technology is listed in Table 7, where the MBR treatment is divided into two processes, the bioreactor (aerobic) and membrane process (ultrafiltration).

In the landfill leachate used in this study, concentrations of organic micropollutants such as OCPs and PAHs were as low as only 10^{-7} – 10^{-5} percentage of TOC. Therefore, decrease of SCOD, BOD, and TOC could hardly indicate the reduction of these organic micropollutants. Main removals of them were performed after different processes in this combined treatment system. For total organic constituents, 73% of SCOD, 77% of BOD, and 73% of TOC in the raw leachate could be eliminated mainly in the bioreactor. Similarly, effective removal of 4-NP was also achieved in the bioreactor. However, 88% of OCPs and 58% of PAHs were mainly removed through the anaerobic process.

High removals of SCOD, BOD, and TOC were achieved by this combined anaerobic-MBR treatment system, with total removal efficiencies of 89%, 99%, and 87%, respectively. However, there still remained 1,007 and 410 mg/L of SCOD and TOC (Table 5), respectively, in the final effluent. It suggested that there were some biorefractory organics stick to the leachate, which could be hardly removed by both biological process and membrane process. Organochlorine pesticides had higher removal efficiencies than other two kinds of organic micropollutants investigated in this study. Hence, in general, the total removal efficiencies of organic micropollutants were in the order as follows: OCPs > 4-NP > PAHs.

3 Conclusions

We reported the removal efficiencies of trace organic contaminants, OCPs, PAHs, and 4-NPs, in the treatment of landfill leachate by combined anaerobic-MBR technology. Organochlorine pesticides, PAHs, and 4-NP were all detected in the raw leachate at levels of ND–595.2 ng/L, which were as low as only 10^{-7} – 10^{-5} percentage of TOC (at the level of 2,962 mg/L).

In general, high removals of both total organic constituents and trace organic contaminants could be achieved by the combined anaerobic-MBR technology. 94%, 59%, and 77% of OCPs, PAHs, and 4-NP, respectively, could be

removed efficiently throughout leachate treatment processes. Removals of SCOD, BOD, and TOC, in agreement with 4-NP, were mainly performed in the bioreactor. However, the effective treatment process of OCPs and PAHs was anaerobic pretreatment.

It can be concluded that to evaluate work efficiencies of treatment techniques more properly, behaviors of both total organic constituents and organic micropollutants with great environmental concerns should be considered and investigated carefully.

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