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Characterization of refuse landfill leachates of three different stages in landfill stabilization process

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Abstract

Landfill leachates with different ages (mature leachate, 11 years; semi-mature leachate, 5 years; fresh leachate, under operation) were collected from Laogang Refuse Landfill, Shanghai to characterize the colloid size distribution and variations of leachate. These leachates were separated using micro-filtration and ultra-filtration into specific size fractions, i.e., suspended particles (SP) (> 1.2 μm), coarse colloids (CC) (1.2–0.45 μm), fine colloids (FC) (0.45 μm, 5 kDa/1 kDa molecular weight (MW)), and dissolved organic matters (DM, < 5 kDa/1 kDa MW). The specific colloids in each size fraction were quantified and characterized through chemical oxygen demands (COD), total solid (TS), pH, NH_4^+-N, total organic carbon (TOC) and fixed solid (FS). It was found that COD, NH_4^+-N and TS in leachate decreased significantly over ages, while pH increased. The dissolved fractions (< 5 kDa/1 kDa) dominated (over 50%) in three leachates in terms of COD, and the organic matter content in dissolved fraction of leachates decreased and the inorganic matter increased as the disposal time extended, with the TOC/COD ratio 30%–7%. Dissolved fractions decreased from 82% to 40% in terms of TOC as the disposal time extended, suggested that the organic matter remained in leachate would form into middle molecular weight substances during the degradation process.

Key words: characterization; landfill leachate; different ages; size-distribution

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Introduction

Landfills are adopted as a dominated way in waste management system (Chian, 1977; Trebovet *et al*., 2001). Millions of landfills are under operation, especially in developing countries.

The major concern with the landfill is the fate of the constituents in leachate. It has been known that leachate composition would vary significantly as the disposal time extended (Kjeldsen *et al*., 2002; Renou *et al*., 2008). It has been concluded that landfill leachate management is one of the complex tasks according to the practical experiences (Lou *et al*., 2007), and only 12% of leachate treatment process could meet the Class III in Standard for Pollution Control on the Landfill Site of Municipal Solid Waste (GB 16889-1997) in China.

It is clear that leachate treatment process would perform better if it is designed according to the leachate characteristics, especially for the track of the variation of leachate compositions in the entire time horizon of landfill. However, only small parts of organic matter could be determined, for example, a total equivalent COD of 10–20 mg/L (Jensen *et al*., 1999; Caron *et al*., 1996), in comparison with the COD of 1000–55000 mg/L in leachates (Christensen *et al*., 2001; Lou *et al*., 2007). The molecular weight distribution in aged raw leachate had been reported by several publications (Calace *et al*., 2001; Vaslllos *et al*., 1993; Wang *et al*., 2006), whereas the particle size distribution, percentages of colloidal and dissolved matters in leachate from different landfill stabilization time periods in East Asia, where the refuse contains high contents of food wastes, are still unknown. Hence, it is important to characterize the main components of leachate with different ages, including molecular weight and particle size distributions.

In this work, leachate samples with three different ages were separated sequentially using a series of micro- and ultra-membranes with different porosities, to evaluate the variation of leachate compositions as disposal time extended. This investigation confirmed the existence and the different size-distribution of macro-molecules substances and colloids in landfill leachate, and provided fundamental data about the distribution ratio of matters in leachate from landfill with high content of food waste.

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1 Materials and methods

1.1 Sampling

Laogang Refuse Landfill in Shanghai was constructed in 1989 along the shore of the East China Sea. The land was formed by the sedimentation of silt carried by Yangtze River and put into operation at the end of 1991. The mature leachate sampled from the cell compartment closed in 1991, and semi-mature leachate and fresh leachate were collected from the cell compartment closed in 1997 and the cell compartment under placement operation, respectively. The samples were collected using a bucket (with the volume 2 L) made of stainless steel for several times and immediately transferred into a 10-L polyethylene containers, which were rinsed twice with deionized water and conditioned two times with sample before collecting.

1.2 Ultra-filtration apparatus

The ultra-filtration apparatus used in this study is shown in Fig. 1. It consists of a methyl-methacrylate glass holder with a volume of 300 mL and the effective membrane area is 0.02 m^2. The samples were pressed through the filters by a pressure applied at the top of the barrel with the aid of N_2. The operation pressures of micro-filtration process and ultra-filtration process were maintained at 0.1 and 0.25 MPa, respectively.

Leachate samples were treated to separate and concentrate leachate colloids into size fractions, using a 1.2-μm membrane and subsequently 0.45-μm, 100 kDa, 50 kDa/30 kDa, 10 kDa, 5 kDa/1 kDa molecular weight (MW) membranes (1 Da = 1/16 O atomic mass unit) (Shanghai Institute of Nucleus Physics, Chinese Academy of Sciences). The micro-membranes were made of mixed cellulose, while the ultra-membrane was made of polyether sulfone (PES).

1.3 Analytical methods

Total organic carbon (TOC) was measured by TOC-V CPH/CPN (Shimadzu, Japan). Total solid (TS) and fixed solid (FS) in each fraction were measured by weighing the residues after 20 mL of each fraction was dried in porcelain crucibles at 105°C for 24 h and at 600°C for1 h, respectively. Chemical oxygen demand (COD), NH_4^+-N, turbidity, color were determined according to the standard methods recommended by USEPA.

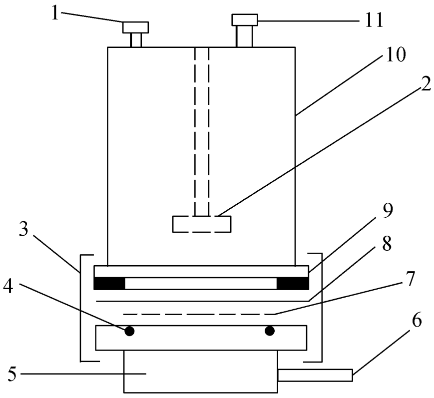

Fig. 1 Schematic diagram of SCM type of ultra-filter. (1) admitting pipe; (2) stirrer; (3) fixator; (4) O-ring seal packing; (5) seat; (6) outlet; (7) slow deflector; (8) ultra-membrane; (9) sealing plate; (10) ultrafilter cup; (11) feed inlet.

Potassium was determined using an atomic absorption spectrometer (AA-6501F, Shimadzu, Japan) after digestion by microwave-assisted acid digestion method with combined acid (HNO_3:H_2O_2:HCl, 6:0.25:3 (mL)). Contents of heavy metals were determined by inductively coupled plasma atomic emission spectrometer (ICP-AES) (Optima 2100DV, PerkinElmer, USA) after digestion.

2 Results

2.1 Fundamental chemical characteristics of leachates

General characteristics of leachate with different ages are summarized in Table 1. The great decrease of TOC from 9870 mg/L in fresh leachate to 182 mg/L in mature leachate was due to the degradation of the majority of organic matter. The concentrations of NH_4^+-N and Orthophosphate were reduced from 4632 to 1388 mg/L and from 20.20 to 0.36 mg/L, respectively as disposal time extended. It was found that fresh leachate contained amounts of black suspended substances with stronger odor, and semi-mature leachate seemed to be less black with strong odor, while mature leachate was yellowy without any odor.

Metal contents in three leachates are shown in Table 2. Contents of Ca and Mg in fresh leachate was much higher than that in other two leachates, meaning that Ca and Mg are lower in the methanogenic phase leachates, due to a high pH (enhancing sorption and precipitation) and low content of dissolved organic matter, which may complex the cations. Most of heavy metals could be found in all three leachates samples, and their contents were below the maximum permissible level recommended by the China Environmental Protection Agency (GHZB 1-1999), except Cr in fresh leachate and Pb in all leachates.

Table 1 Elemental analysis of leachate with different ages at Laogang Refuse Landfill, Shanghai

	TOC (mg/L)	NH_4^+-N (mg/L)	PO_4^{3-} (mg/L)	pH	TS (mg/L)
Fresh leachate	9870	4632	20.20	7.71	28400
Semi-mature leachate	809	2197	1.71	8.38	13205
Mature leachate	182	1388	0.36	8.60	6700

Sampling date: March 2003; around 15°C. TS: total solid.

Table 2 Heavy metal contents in leachate with different ages (mg/L)

	Fresh leachate	Semi-mature leachate	Mature leachate	Background value
Cu	0.05	< 0.05	0.348	< 0.05
Zn	0.522	0.244	0.417	0.108
Pb	< 0.2	< 0.2	< 0.2	< 0.2
Ni	0.14	0.1	0.16	< 0.01
Cr	0.154	0.004	< 0.004	< 0.004
Cd	< 0.05	< 0.05	< 0.05	< 0.05
Ca	529	45.2	17.1	7.45
Mg	272	110	102	0.239
K	1540	883	1040	10.1

The background value is the corresponding metal contents in local surface water.

2.2 Effect of membrane porosity on pH

The high pH in all three leachates (Table 1) revealed that landfill leachate in Laogang Landfill was alkalinity (Fig. 2). The increase pH sequence of fresh leachate < semi-mature leachate < mature leachate indicated that pH in leachate would increase up to a steady state as disposal time extended. pH of the leachate would not only depend on the concentration of the acid but also on the partial pressure of CO_2 in the landfill gas which is in contact with the leachate. It has been demonstrated that fatty acid matters with low molecular weight predominated in fresh leachate, and the majority matter would be some non-degradable matters in mature leachate, such as humic like and fulvic like compounds, which resulted in the pH increase in leachate as the time extended (Christensen *et al*., 2001; Lou *et al*., 2007). The decrease in the volatile fatty acid (VFA) concentration in leachate causes the rising of pH as the disposal time extended. Meanwhile, CO_2 concentration in landfill gas increased from < 40% to > 70% as the disposal time extended, and the corresponding H_2CO_3 would also increase, which contributes to the increase of pH in leachate (George *et al*., 2000).

As shown in Fig. 2, pH values in leachate filtrates increased slightly and then progressively level off with filtered sequentially by the series membranes used, which may resulted from the stripping of CO_2 during the filtration. It can be supported by the previous report, in which CO_2 concentrations (CO_3^{2-}) in the leachate decreased from the initial 6–15 mmol/L to 0.5–1.5 mmol/L during the size fraction operation, and the corresponding pH increased by 0.4–1.4 pH units (Jensen *et al*., 1999).

2.3 Effect of membrane porosity on COD

COD in fresh leachate were higher than those in semi-mature leachate and mature leachate. It decreased from 36653 mg/L to 2675 mg/L during the first 6 years after disposal, and then decreased to about 1500 mg/L in the following 5 years. Meanwhile, COD in mature leachate with 11 years was still in a high value, comparing to the requirements of the Chinese National Discharge Standard (COD < 300 mg/L, Class II of (GB 16889-1997)).

COD in leachate decreased after gradient separation using a series of membranes with differential pore sizes down to 5 kDa/1 kDa MW (Fig. 3), with a total removal rate of about 48%, 34% and 27% (data not shown), respectively, indicating that the dissolved matters predominated in all leachate samples.

2.4 Effect of membrane porosity on NH_4^+-N

Fresh leachate has a higher NH_4^+-N concentration than other two leachates implying that NH_4^+-N concentration in leachate would decrease over time (Fig. 4). The NH_4^+-N concentrations in three leachates were in high level (over 1300 mg/L), while most of C from that stage was recalcitrant matter (Imai *et al*., 1995; Wang *et al*., 2006), which result in the un-favorable ratio of C/N for the biological treatment. Therefore, the selection of mature leachate treatment process should be different from that of fresh leachate.

2.5 Effect of membrane porosity on TS

As shown in Fig. 5, TS in fresh leachate was much higher than that in semi-mature and mature leachates, indicating that solid particles in leachate would decrease dramatically in the first 6 years. There are more solid soils in fresh refuses than that in aged refuses, and these solid soils in refuses would be leaching out, and the corresponding TS content in leachate would decrease as the disposal time extended. The great difference (two times) between the TS contents in leaches indicated that fresh leachate contained amount of suspended substances and dissolved matters, and semi-mature leachate contained less suspended matters, while there were almost no suspended substances in mature leachate as observed in site.

The distribution of FS and TOC in each fraction of leachates is shown in Figs. 6a and 6b, respectively. Both of

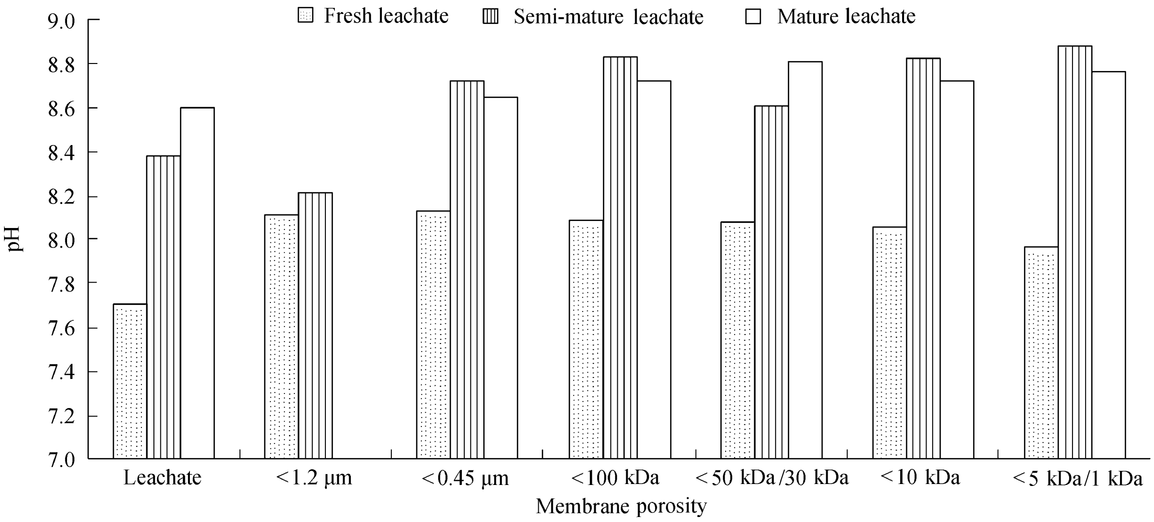

Fig. 2 Relationship between pH and membrane porosity. 50 kDa/30 kDa means that fresh leachate and semi-mature leachate were filtered by 30 kDa membranes, and mature leachate was filtered by 50 kDa membrane; 5 kDa/1 kDa means that fresh leachate and semi-mature leachate were filtered by 1 kDa membranes, and mature leachate was filtered by 5 kDa membrane.

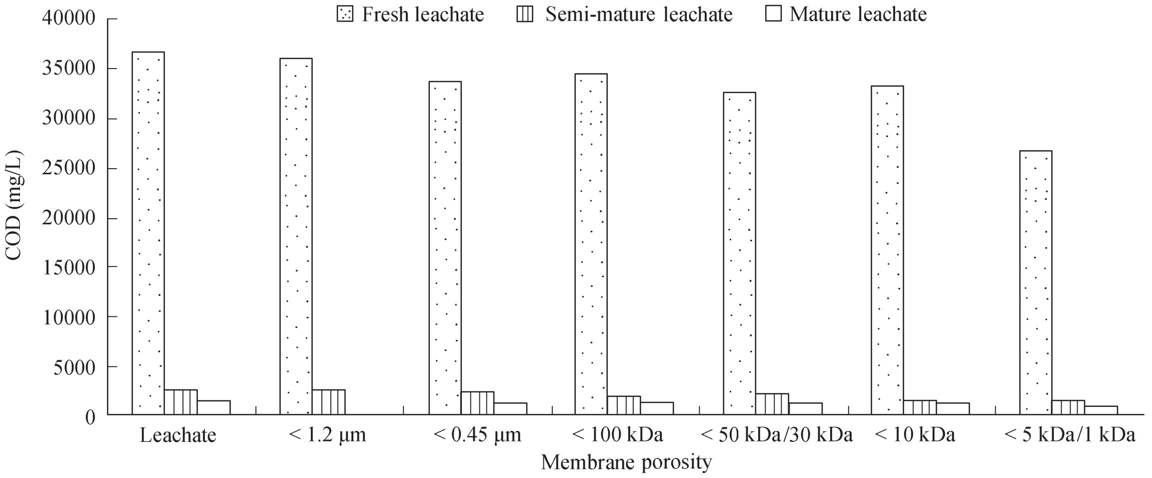

Fig. 3 Relationship between COD and membrane porosity.

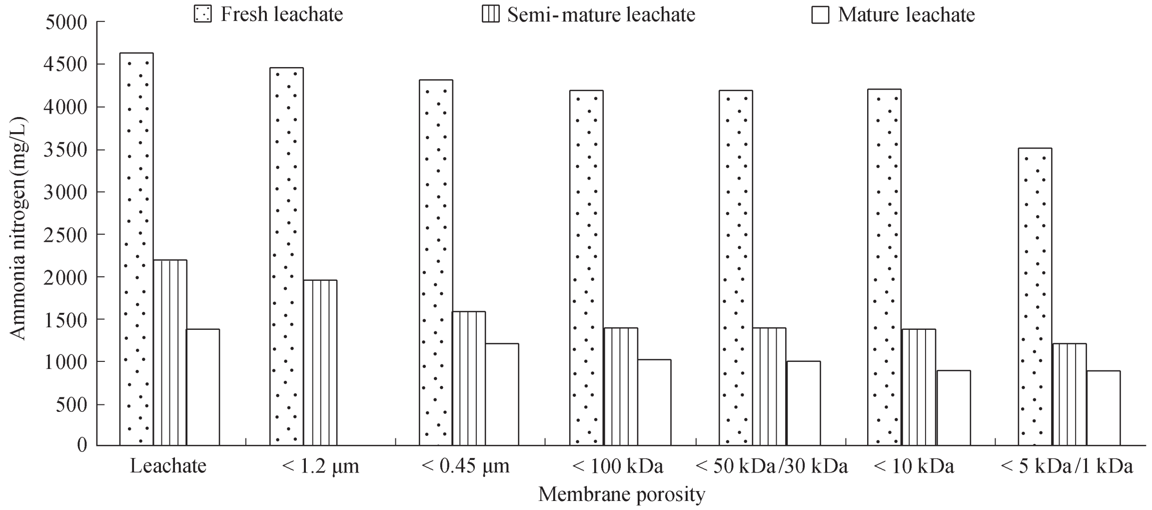

Fig. 4 Relationship between NH_4^+-N and membrane porosity.

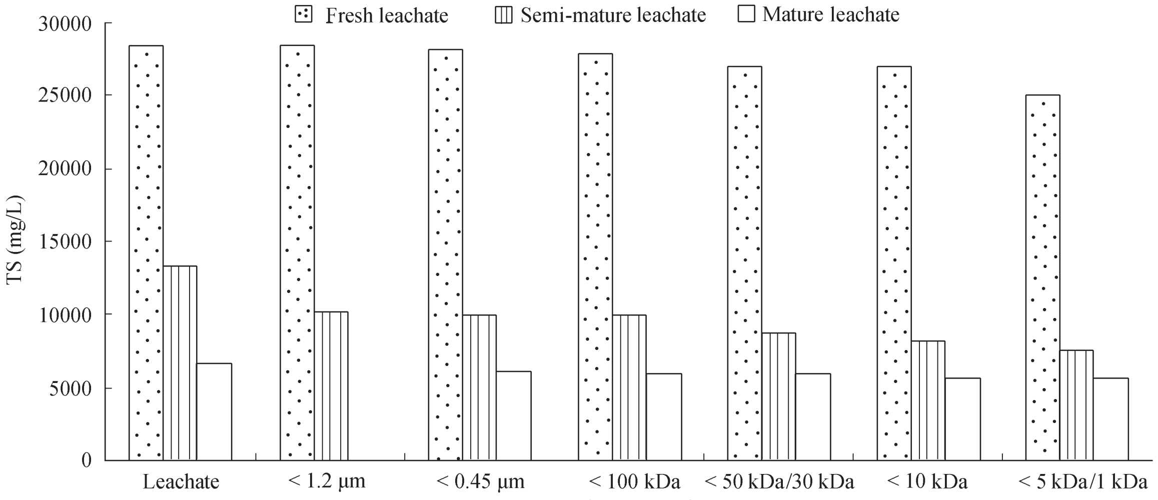

Fig. 5 Relationship between TS and membrane porosity.

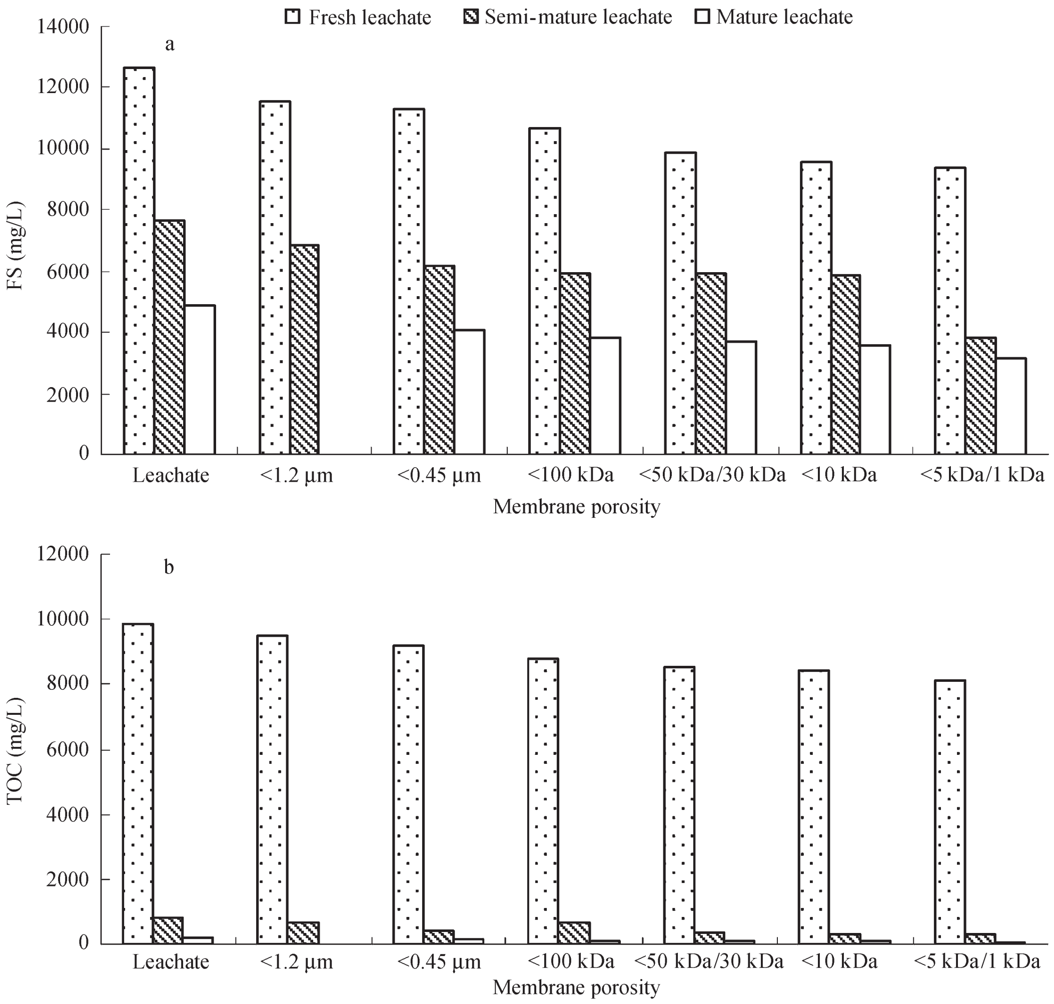

Fig. 6 Relationships between FS (a) or TOC (b) and membrane porosity.

FS and TOC were major components of the colloidal mass in all leachate samples, with the occupation percentage of 55%.

3 Discussion

The COD, NH_4^+-N and TS in fresh leachate were much higher than those in the other two leachates, indicating that landfill would be a bioreactor with an effectiveness natural attenuation process. Therefore, some landfill engineering practices, such as bioreactor and leachate recirculation, could be taken into account during the landfill design. Meanwhile, although concentrations of individual heavy metals in leachates were in a low level (< 1 mg/L), the total concentrations of all heavy metals in leachate are still high, and the combined toxic effect of heavy metals might do detrimental to micro-organism in biological treatment process. Consequently, the removal of heavy metals is still one of the important tasks for leachate pre-treatment process, with the stricter leachate discharge regulation.

The NH_4^+-N concentrations in all three leachate samples were in high level and were inhibitive to most biological treatment processes generally. As well known, the NH_4^+-N range of 50–200 mg/L would be beneficial for anaerobic treatment process, and the range 200–1000 mg/L would be detrimental slightly. NH_4^+-N would harm to the biological treatment process in high pH, when the concentration reached 1500 mg/L, and it would inhibit the growth of microorganism in treatment process greatly, with the value above 3000 mg/L (Lou *et al*., 2007). Hence, NH_4^+-N in leachate from Laogang Refuse Landfill should be pretreated before leachate was introduced into the biological treatment processes.

In addition, FS/TS in leachate increased with the disposal age increasing, i.e., the percentage of FS/TS was in the range of 35%–45% in fresh leachate, was 51%–72% in semi-mature leachate, and was 56%–73% in mature leachate, indicating that the inorganic matter content in leachate increased over disposal time. Meanwhile, the percentage of dissolved fractions decreased from 82% to 40% in terms of TOC as the disposal time extended, suggested that the organic matter remained in leachate would be formed as the large molecular weight substances during the degradation process, and could be removed by membranes used in this work. FS content was higher than the corresponding TOC value in each size fraction, suggesting that significant amounts of inorganic solids co-existed with the organic matter in these leachate samples. Additionally, organic compounds were the key constituents in the acid phase in leachate, and then the inorganic compounds were predominated in leachate from methanogenic phase. Therefore, the biological treatment process could be applied in the fresh leachate after pretreatment by the removal of high concentration of NH_4^+-N, such as stripping stage. The physical and chemical treatment could be used in the mature and semi-mature leachates, due to the increase of inorganic matter in leachate, such as flocculation, coagulation and reverse osmosis.

4 Conclusions

Landfill leachates contain high concentration of organic matter as well as inorganic matters (including heavy metals) in terms of TOC and FS, and the occupation ratio of inorganic matters in leachate would increase as the disposal time extended.

The dissolved fractions predominated in three leachates in terms of COD, which occupies over 50%, and some organic macro-molecular species in leachate could be isolated from leachate samples based on the membranes separation results. The organic matter content in dissolved fraction of leachates decreased and the inorganic matter increased as the disposal time extended, with the TOC/COD ratio from 30% to 7%, and the corresponding leachate treatment process should be improved according to the characteristics of landfill leachate as the landfill age extended.

Acknowledgments

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