Management strategy of landfill leachate and landfill gas condensate

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Dissertation submitted to the Faculty of

Virginia Polytechnic Institute and State University

In partial fulfillment of the requirements for the degree of

DOCTOR of PHILOSOPHY

In

Civil Engineering

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August 27, 2012

Blacksburg, Virginia

Keywords: Landfill leachate, Size fractionation, Organic matter, Organic nitrogen, UV quenching, biological treatment, humic substance, hydrophilic, membrane separation, biodegradability, statistical analysis, physic-chemical treatment, protein, stabilization state.

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Abstract

Studies were conducted to evaluate the impact of landfill leachate discharge on the operation of waste water treatment plants (WWTPs). Two aspects of interferences were found: one is UV quenching substances, which are bio-refractory and able to penetrate the biological treatment processes, consequently interfere the UV disinfection in WWTPs. The other one is organic nitrogen, which can pass the nitrification-denitrification process and contribute to the effluent total nitrogen (TN). Also, treatability study was conducted for landfill gas (LFG) condensate.

In a laboratory study, leachate samples were fractionated into humic acids (HA), fulvic acids (FA) and Hydrophilic (Hpi) fractions, the specific UV254 absorbance (SUVA254) of the three fractions follows: HA > FA > Hpi. However, the overall UV254 absorbance of the Hpi fraction was important because there was more hydrophilic organic matter than humic or fulvic acids. It was found that the size distribution of the three fractions follows: HA > FA > Hpi. This indicates that membrane separation following biological treatment is a promising technology for the removal of humic substances from landfill leachates. Leachate samples treated in this manner could usually meet the UV transmittance requirement of the POTWs.

Also, nitrogen species in landfill leachates under various stabilization states were investigated. Although the effect of landfill stabilization state on the characteristics of organic matter and ammonia is well documented, there are few investigations into the landfill leachate organic nitrogen under different stabilization stages. Ammonia was found to leach out slower than

organic matter and can maintain a constant level within the first a couple of years (< 10 years). The concentration and biodegradability of organic nitrogen were found to decrease with landfill age. A size distribution study showed that most of organic nitrogen in landfill leachates is < 1 kDa. The protein concentration was analyzed and showed a strong correlation with the organic nitrogen. Different slopes of regression curves of untreated and treated leachates indicate that protein is more biodegradable than the other organic nitrogen species in landfill leachates. XAD-8 resin was employed to isolate the hydrophilic fraction of leachate samples, hydrophilic organic nitrogen was found to be more biodegradable/bioavailable than the hydrophobic fractions.

Furthermore, biological and physical-chemical treatment methods were applied to a landfill biogas (LFG) condensate to explore the feasible treatment alternatives for organic contaminant and arsenic removal efficiency. Sequencing batch reactor (SBR) showed effectiveness for the degradation of organic matter, even in an environment containing high levels of arsenic. This indicated a relatively low toxicity of organic arsenic as compared to inorganic arsenic. However, for arsenic removal, oxidation-coagulation, including biological oxidation, conventional oxidation and advanced oxidation followed by ferric salt coagulation, and carbon adsorption were not effective for what is believed to be tri-methyl arsenic. Among these, advanced oxidation-coagulation showed the best treatment efficiency (15.1% removal). Only reverse osmosis (RO) could reduce the arsenic concentration to an acceptable level to meet discharge limits. These results implied high stability and low toxicity of organic arsenic.

ACKNOWLEDGEMENTS

I would like to express my sincere respect and gratitude to my advisor, Dr. John T. Novak. For the four years of my PhD study, he is always available for my questions on the research and life. His rigorous attitude towards research and energetic attitude toward life will inspire me through my whole career and life.

I am also very grateful to my committee members Dr. Andrea M. Dietrich, Dr. Peter J. Vikesland at Virginia Tech, and Dr. C. Douglas Goldsmith at Alternative Natural Technologies, Inc. for their discussions and constructive suggestions on my research.

I am grateful to Betty Wingate, Julie Petruska, Jody Smiley and Beth Lucas for their guidance on my laboratory work. I would like to express special appreciation to Mr. Abhinav Gupta and Ms. Natalie Driskill for the discussion and collaboration in the research projects, you made my PhD study experience fruitful and bearable. I would like to thank all Novak's researchers, Chris Wilson, Jongmin Kim, Jennifer Miller, Ana, Nirupa, Loveenia, Nicole, Evan, Ritika, Kartik, Sudiher, Kuang, Ross, Palavi and other students in the EWR program, Simoni, Nicole, Becky, Hong, Yanjun, Jia, Anna, Gargi, Virginia. I would like to thank my many friends and

acquaintances that I was privileged to meet and interact with during an enjoyable four years of

my doctoral degree.

I would like to express my appreciation to my parents, Shuzhou Zhao and Juxiang Wang, and my

brother Rentong Zhao, thank you so much for you love and support for this long journey.

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Chapter 1. Executive Summary

Landfilling is one of the most widely employed methods of disposing of municipal solid waste (El-Fadel et al., 1997), although reduction, recycling and reuse of municipal refuse have become preferred practices (Chai et al., 2008). Leachate, which is generated by rainwater percolating through the waste layer in the landfill (US EPA, 2005), is a major problem in landfill operation and management, because of its high concentration and variation of contaminants. Since there is the possibility for leachate to enter the groundwater, risk of groundwater pollution due to leachate seepage has become a major environmental concern. Furthermore, even though a sound engineering design, including liners, piping and pumping systems, can prevent or minimize the leakage of leachate, the collected leachate has to be treated prior to discharge, so treatment of leachate plays an important role in the operation and management of landfills.

Landfills can be classified into an acidification stage and a methane fermentation stage. Leachates produced in these periods are usually called "young" and "old" leachate. Young leachate contains a high concentration of volatile fatty acids (Ehrig, 1984), which account for the bulk of chemical oxygen demand (COD) and results in a lower pH value (as low as 4). This acidic environment promotes an increasing concentration of heavy metals in the leachate (Erses et al., 2005). Young leachate is usually characterized by a high biological oxygen demand (BOD), high chemical oxygen demand (COD), a moderately high concentration of ammonia nitrogen and a high biodegradability (BOD/COD ratio ranges from 0.4-0.7) (Zouboulis et al., 2001, Morais et al., 2005). By contrast, with the degradation and stabilization of VFA by methane-forming organisms (Chen, 1996), most of the remaining organic materials are bio-

refractory compounds with a high molecular weight, such as humic substances (Weis et al., 1989). This, results in a moderately high level of COD and a low BOD/COD ratio of less than 0.1 and the pH rises to the alkaline range which drives the heavy metals to a low level.

Due to its low cost, biological treatment is usually the first option to remove the bulk of organic contaminants from landfill leachate. In some circumstances, leachate is combined with municipal sewage treatment plant influent. Biological treatment is usually effective for young leachate because a major portion of organics are volatile fatty acids (VFA) which have a high biodegradability. Stabilized old leachate cannot be effectively treated either by using biological processes such as activated sludge (AS), anaerobic filtration and anaerobic lagoons or by natural systems such as leachate recirculation or constructed wetland. Moreover, biological treatment is prone to toxic compounds and unbalanced nutrients that inhibit biomass activity in the biological process (Kurniawan et al., 2006). In recent years, the presence of bio-refractory compounds in the landfill leachate has gained major attention (Vilar et al., 2011; He et al., 2009). Humic substances (humic acids and fulvic acids) are believed to be the main components that show recalcitrant properties (He et al., 2006). Up to 60%-75% of the organic fraction in landfill leachates was reported to be contributed by humic substances (Zhang et al., 2009; Artiola-Fortuny and Fuller, 1982). In practice, landfill leachates discharged to WWTPs are reported to interfere their UV disinfection performance since landfill leachates from several landfills are found to quench strongly the UV light (Zhao et al., 2012). However, there have been limited investigations into the influence of bio-refractory organic matter, such as humic acids and fulvic acids on UV disinfection.

Moreover, unlike soluble carbon compounds, the release of soluble nitrogen from municipal solid waste into leachate lasts for several decades (Ehrig et al., 1989). Hydrolysis of the

polypeptide chain is slow in energetic terms and this is apparently the reason for the slow kinetics of protein hydrolysis, which in turn causes the slow release of ammonia (Jokela et al., 2002), so ammonia concentration in leachate will remain moderately high throughout the life of a landfill. As a source of nutrients, ammonia can cause eutrophication in receiving watercourses, so removal of nitrogen from landfill leachate is necessary. In addition, organic nitrogen has been recognized as a new emerging issue for the water environment. On one hand, there is a concern about stricter discharge limits for total nitrogen. With the wider use of nitrification/denitrification, organic nitrogen can account for up to 80% of dissolved nitrogen in the municipal WWTP nitrification-denitrification effluents (Qasim et al., 1999), impacting adversely many costal and estuarine ecosystems as well as certain freshwater ecosystems by eutrophication (Pehlivanoglu and Sedlak, 2004). On the other hand, dissolved organic nitrogen (DON) can be a potential source of nitrogenous disinfection by-products (NDBP) (Krasner at el. 2009; Mitch and Sedlak, 2004). Among the other nitrogen removal techniques, such as air stripping, membrane separation processes, chemical precipitation (Ozturk et al., 2003; Chianese et al., 1999; Palma et al., 2002; Zdybiewska et al., 1991; Altinbas et al., 2002), biological treatment for nitrogen removal is preferred in most cases because of it cost-effectiveness. So the impact of nitrogen species in landfill leachates on the biological treatment systems need to be investigated.

This research will primarily explore the impact of leachate on the receiving sewage treatment facilities, specifically includes: 1, Identification, source and treatability of UV quenching substances in landfill leachate;2, Characterization and bioavailability of N species in landfill leachate.

1. Evaluation of on-site biological treatment for landfill leachates and its impact: A size distribution study (Chapter 3) [Water Research 46(12):3837-48]

A cost effective and widely applied approach for landfill leachate disposal is to discharge it to a municipal wastewater treatment plant (WWTP). The recalcitrant nature of leachate organics and the impact on the downstream WWTPs were comprehensively investigated in this study. Size fractionation by ultrafiltration (UF) and microfiltration (MF) was employed in conjunction with various analyses (TOC, COD, nitrogen species and UV254 absorbance) on raw and biologically treated landfill leachates to provide insight into biological treatability. Overall, landfill leachate organics showed bio-refractory properties. Less than half of the organic matter, measured as total organic carbon (TOC), could be removed in the biological processes examined. Size distribution data showed that the < 1 thousand Daltons (kDa) fraction is dominant in most untreated and treated landfill leachates, indicating difficulties for membrane treatment. Also, most removal occurred for the < 1kDa fraction in the biological processes, while the intermediate size fractions increased slightly. This may be caused by bio-flocculation and/or partial degradation of larger molecular weight fractions. Organic nitrogen was investigated in this study as one of the first explorations for landfill leachates. Organic nitrogen in landfill leachates was more bio-refractory than other organic matter. UV quenching by landfill leachates was also investigated since it interferes with the UV disinfection at WWTPs. The combination of activated carbon and activated sludge (PACT) showed some effectiveness for reducing UV quenching, indicating that carbon adsorption is a potential method for removal of UV quenching substances. Fourier transform Infrared (FT/IR) data showed that aromatic groups are responsible for the UV quenching phenomenon.

2. Investigating the impact of landfill leachate on the ultraviolet (UV) disinfection in POTWs: source and countermeasure (Chapter 4) [prepared for submission to Water Research]

Landfill leachates were found to quench the UV light strongly, when they are discharged to the publicly owned treatment works (POTWs), landfill leachate interfere the UV disinfection severely. To investigate the UV quenching problem of landfill leachates, six landfill leachates with a variety of conditions (age and waste acceptance) were collected in this study. Biodegradability study shows that UV absorbing substances in landfill leachates are more bio-refractory than the other organic matter. Biological treatment processes cannot provide the retention time long enough to make the microorganisms capable of degrading/decomposing the UV absorbing substances survive. UV absorbing substances can penetrate the biological processes and impact on the subsequent UV disinfection system in the POTWs. Leachates samples were fractionated into humic acids (HA), fulvic Acids (FA) and hydrophilic (Hpi) fractions to investigate the source of UV absorbing materials. Results show that for all leachates examined, the specific UV_{254} absorbance ($SUVA_{254}$) of the three fractions follows: HA > FA > Hpi, while the overall UV_{254} absorbance of Hpi fraction is the highest among all three fractions. Size distribution was also investigated to provide implication for the landfill leachates' treatability in terms of UV absorbance before they are discharged to the POTWs. It was found that, for all leachates examined, the size distribution of the three fractions follows: HA > FA > Hpi. This result proposes the membrane separation and coagulation-sedimentation promising technologies for the treatment of humic substances in landfill leachates. Membrane separation and biological process were combined to complement each other's advantage for the leachate treatment. The 1 kDa nanofiltration (NF) was found to be eligible to make the biologically

treated leachate samples meet the UV transmittance requirement of the POTWs (UV transmittance = 60%). The 1 kDa NF was observed to remove most of the humic substances in landfill leachates, while 500 Da NF can further remove the organic matter in the Hpi fractions.

3. Nitrogen species in landfill leachates under various stabilization states (Chapter 5) [working paper]

Biological nutrient removal (BNR) process can remove most of the inorganic nitrogen species in waste water treatment plants (WWTP), leaving the organic nitrogen accounts for a large portion of the total nitrogen in the waste water effluent. When it is discharged to the WWTPs, the landfill leachate becomes an important source of the nitrogen loading to the sewer system and subsequently the surface waters. Although the effect of landfill stabilization state on the characteristics of organic matter and ammonia is well documented, there are few investigations into the landfill leachate organic nitrogen under different stabilization stages. In this study, nitrogen species in landfill leachates under various stabilization states were investigated. Ammonia was found to leach slower than organic matter and can maintain a high level within the first a couple of years (< 10 years). Concentration and biodegradability of organic nitrogen were found to decrease with the landfill age. Size distribution study showed that most of organic nitrogen in landfill leachates is < 1 kDa. Protein concentration was analyzed and showed a strong correlation with the organic nitrogen. Different slopes of regression curves of untreated and treated leachates indicate that protein is more biodegradable than the other organic nitrogen species in landfill leachates. XAD-8 resin was employed to isolate the hydrophilic fraction of leachate samples, hydrophilic organic nitrogen was found to be more biodegradable/ bioavailable than the hydrophobic fractions.

4. Treatment of Organic Matter and Methylated Arsenic in Landfill Biogas Condensate (working paper; Appendix)

Biological and physical-chemical treatment methods were used to treat a landfill biogas (LFG) condensate to explore the feasible treatment alternatives for organic contaminant and arsenic removal efficiency. The treatment using a sequencing batch reactor (SBR) showed that biological treatment was effective for the degradation of organic matter, even in a toxic environment with high levels of arsenic. This indicated a relatively low toxicity of organic arsenic as compared to inorganic arsenic. However, for arsenic treatment, oxidation-coagulation, including biological oxidation, conventional oxidation and advanced oxidation followed by ferric salt coagulation, and carbon adsorption were not effective for what is believed to be tri-methyl arsenic. Among these, advanced oxidation-coagulation showed the best treatment efficiency (15.1% removal). Only reverse osmosis (RO) could reduce the arsenic concentration to an acceptable level to meet discharge limits. These results implied high stability and low toxicity of organic arsenic.

Reference:

Altinbas, M., Yangin, C., Ozturk, I., 2002. Struvite precipitation from anaerobically treated municipal and landfill wastewaters, Water Sci. Technol. 46, 271–278.

Artiola-Fortuny, J., Fuller, W.H., 1982. Humic substances in landfill leachates: I. Humic acid extraction and identification. J. Environ. Qual. 11. 663–668.

Chai, X.L., Takayuki, S., Guo, Q., Zhao, Y.C., 2008. Characterization of humic and fulvic acids extracted from landfill by elemental composition, 13C CP/MAS NMR and TMAH-Py-GC/MS. Waste Management 28, 896–903.

Chen, P.H., 1996. Assessment of leachates from sanitary landfills: impact of age, rainfall, and treatmen,t, Environ. Int. 22 (2), 225–237.

Chianese, A., Ranauro, R., Verdone, N., 1999. Treatment of landfill leachate by reverse osmosis, Water Res. 33, 647–652.

Ehrig, HJ. Leachate quality. In: Christensen TH, Cossu R, Stegmann R, editors. Sanitary landfilling: Process, technology and environmental impact. London: Academic Press, 1989. p. 213–30.

Ehrig, H.J., 1984. Treatment of sanitary landfill leachate: biological treatment, Waste Manage. Res. 2, 131–152.

El-Fadel, M., Findikakis, A.N., Leckie, J.O., 1997. Environmental impacts of solid waste landfilling. J. Environ. Manage. 50, 1–25.

Erses, A.S., Fazal, M.A., Onay, T.T., Craig, W.H., 2005. Determination of solid waste sorption capacity for selected heavy metals in landfills. J. Hazard. Mater. 121 (1–3), 223–232.

He, P.J., Zheng, Z., Zhang, H., Shao, L.M., Tang, Q.Y., 2009. PAEs and BPA removal in landfill leachate with Fenton process and its relationship with leachate DOM composition. Science of the Total Environment 407, 4928-4933.

He, P., Xue, J., Shao, L., Li, G., Lee. D.J., 2006. Dissolved organic matter (DOM) in recycled leachate of bioreactor landfill. Water Research 40, 1465 – 1473.

Jokela, J.P.Y., Kettunenb, R.H., Sormunena, K.M., Rintala. J.A., 2002. Biological nitrogen removal from municipal landfill leachate: low-cost nitrification in biofilters and laboratory scale in-situ denitrification. Water Research 36, 4079–4087.

Krasner, S.W., Westerhoff, P., Chen, B., Rittmann, B., Nam, S., Amy, G., 2009. Impact of Wastewater Treatment Processes on Organic Carbon, Organic Nitrogen, and DBP

Precursors in Effluent Organic Matter. Environmental Science and Technology 43 (8), 2911-2918.

Kurniawan, T. A., Lo, W., Chan, G.Y.S., 2006. Physico-chemical treatments for removal of recalcitrant contaminants from landfill leachate. Journal of Hazardous Materials B129, 80–100.

Mitch, W.A., Sedlak, D.L., 2004. Characterization and fate of N-nitrosodimethylamine precursors in municipal wastewater treatment plants. Environmental Science and Technology 38(5), 1445-1454.

Morais, J.L., Zamora, P.P., 2005. Use of advanced oxidation process to improve the biodegradability of mature landfill leachate, J. Hazard. Mater. B 123, 181–186.

Ozturk, I., Altinbas, M., Koyuncu, I., Arikan, O., Gomec-Yangin, C., 2003. Advanced physico-chemical treatment experiences on young municipal landfill leachates, Waste Manage. 23, 441–446.

Palma, L.D., Ferrantelli, P., Merli, C., Petrucci, E., 2002. Treatment of industrial landfill leachate by means of evaporation and reverse osmosis, Waste Manage. 22, 951–955.

Pehlivanoglu, E., Sedlak, D.L., 2004. Bioavailability of wastewater-derived organic nitrogen to the alga *Selenastrum Capricornutum*. Water Research 38(14-15), 3189-3196.

Qasim, S.R., 1999. Wastewater treatment plants: Planning, design, and operation. Technomic, Pennsylvania.

US EPA (Environmental Protection Agency), Urban Watershed Management Research Terminology, 2005 (http://www.epa.gov/ednnrmrl/terminology.html).

Vilar, V.J., Rocha, E.M., Mota, F.S., Fonseca, A., Saraiva, I., Boaventura R.A., 2011. Treatment of a sanitary landfill leachate using combined solar photo-Fenton and biological immobilized biomass reactor at a pilot scale. Water Research 45(8), 2647-2658.

Weis, M., Abbt-Barun, G., Frimmel, F.H., 1989. Humic-like substances from landfill leachates—characterization and comparison with terrestrial and aquatic humic substances. Sci. Total Environ. 81/82 , 343–352.

Zdybiewska, M.W., Kula, B., 1991. Removal of ammonia nitrogen by the precipitation method, on the example of some selected wastewaters, Water Sci. Technol. 24, 229–234.

Zhang, L., Li, A., Lu, Y., Yan, L., Zhong, S., Deng. C., 2009. Characterization and removal of dissolved organic matter (DOM) from landfill leachate rejected by nanofiltration. Waste Management 29 (3), 1035–1040.

Zhao, R.Z., Novak, J.T., Goldsmith, C.D., 2012. Evaluation of on-site biological treatment for landfill leachates and its impact: a size distribution study. Water Research 46(12), 3837-3848.

Zouboulis, A.I., Loukidou, M.X., Christodoulou, K., 2001. Enzymatic treatment of sanitary landfill leachate. Chemosphere 44, 1103–1108.

Chapter 2. Literature Review

1. Fractionation

The first step for intensive leachate research is fractionation, based on size distribution and chemical characteristics (acid-base properties and hydrophilic-hydrophobic properties). Humic substances are a major portion of refractory organics in landfill leachate so isolation methods for humic substances are an important part of leachate fractionation.

1.1 Size fractionation

With membrane filtration, gel filtration or other separation techniques, leachate can be fractionated into a series of portions based on size. These sizes can undergo further characterization and analysis to provide detailed component information.

Harmsen (1983) studied the organic components in two different types of leachate from waste tips in the acidification stage and methane fermentation stages respectively. The leachate was fractionated into volatile acids, <1k Da fraction (aliphatic, aromatic and polar substance), 1-50 k Da fraction and >50k Da fraction, the last two fractions were known as high molecular weight compounds. The results showed that the organic load of leachate decreased drastically from the acidification stage to the methane fermentation stage, represented by a TOC of 20000 mg/L and 2100 mg/L, respectively. Furthermore, for the acidification stage leachate, only 0.5% of TOC was attributable to >50k Da fraction and 0.8% to the 1-50 k Da fraction, while for methane fermentation leachate, 12% of the TOC could be attributed to >50k Da fraction and 20% to 1-50 k Da fraction.

A series of studies on size-fractionation and characterization were done by Lou et al. (2007; 2009a; 2009b). Leachates were separated into fractions by size, such as suspended particles (> 1.2um), coarse colloids (1.2-0.45um), fine colloids (0.45um- 1kDa MW), and dissolved organic matter (< 1kDa MW). By comparing leachates before and after a series of anaerobic anoxic and aerobic biological treatment, the researchers found that organic matter in the dissolved fraction (< 1k Da MW) was dominant in both raw and biologically treated leachates, with a content of 78% and 47 % respectively. After treatment in the biological process, the organics (in terms of TOC) in the fine colloid fraction (0.45um-1 k Da MW) increased from 6% to 38% while those in the dissolved fraction (<1k Da MW) decreased from 78% to 47%. By comparing leachates in different stability stages (mature leachate, semi-mature leachate and fresh leachate), it was found that the dissolved fractions (< 5kDa) was always greater than 50% of the total for all the stability stages.

It was also found by size fractionation that, both TN and NH_3-N were dominant in soluble form, 30-40% in fresh leachate and around 66% in anaerobic lagoon leachate (Lou et al., 2009a; Lou et al., 2009b). NH_4^+ occupied 80-90% of total N (Lou et al., 2009b).

As reported by Li et al. (2009), Dong et al (2008) and Slater et al. (1985), it was confirmed that the organic matter of all raw and treated leachate samples primarily existed in the dissolved fraction (< 1kDa or < 0.5 KDa) and moderate sized organic matter appeared to increase throughout all the biological treatment processes (Li et al., 2009). Moreover, also by fractionation, it was also found that most of the heavy metals existed in the colloidal fraction (0.45um- 1kDa MW) (Li et al., 2009).

1.2 Hydrophobicity fractionation

Based on their chemical characteristics, i.e. hydrophobic/hydrophilic and acid, base, neutral, leachates can also be fractionated into hydrophobic acid, base, neutral (Hpo-A, Hpo-B, Hpo-N) and hydrophilic acid, base, neutral (Hpi-A, Hpi-B and Hpi-N) employing XAD-8 resin and cation and anion exchange resins (Leenheer, 1981). This fractionation method can provide a different perspective for understanding the component of leachate and other water samples.

The properties of leachate from landfill sites containing municipal solid waste incineration residues were investigated by characteristic fractionation (Seo et al., 2007). The leachate was divided into Hpo-A, Hpo-B, Hpo-N and Hpi portions. It was found that the hydrophobic fraction was the major portion in the dissolved organic matter (DOM) of leachate and accounted for around 80-90% of total DOM. The proportion of Hpo-N was found to increase with the landfill operation time. Furthermore, leachate from landfill sites containing abundant amounts of non-combustible wastes had a higher proportion of Hpo-B and Hpo-N than Hpi and Hpo-A (Seo et al., 2007).

Another study was done with leachate from municipal refuse landfill and fractionation of dissolved organic matter was divided into 6 fractions, i.e. Hpo-acid, base, neutral and Hpi- acid, base, neutral (Lou et al., 2009c). It was found that the hydrophobic fraction accounted to more than 50% in all leachate. The authors developed a ranking for different fractions as: Hpo-A>Hpi-A>Hpi-B>Hpo-B>Hpi-N>Hpo-N, among which, Hpo-A, Hpi-A and Hpi-B dominanted in leachate while the rest occupied less than 15%. Also, the percentage of Hpo-A in leachate was found to decrease as the landfill operation time increased (Lou et al., 2009c).

1.3 Humic substance

DOM is often regarded as a group of organic molecules that can be filtered by 0.45um membranes, including low molecular weight substances like amino acids, carbohydrates, organic acids, and some high molecular weight substances like humic substances (Kalbitz et al., 2000). The existence of DOM is widespread in aquatic environments and exhibits highly stable and microbially refractory properties. The fractionation and characterization method recommended by the International Humic Substances Society (IHSS, http:// www.ihss.gatech.edu) is an effective method for describing the chemical features of DOM (Alberts et al., 2004; McDonald et al., 2004).After fractionation, employing acid precipitation and XAD-8 resin (Thurman and Malcolm, 1981;Christensen et al., 1998) DOM can be isolated into much purer humic acid (HA), fulvic acid (FA) and hydrophilic (HyI) fractions for further analysis(Zhang et al., 2009). It was reported that HA and FA accounted for around 60% of DOM in methanogenic phase leachate (Artiola-Fortuny et al., 1982).

On the other hand, the interaction of HS with many refractory organic compounds, which is important in the understanding of treatment for landfill leachate, will be affected significantly by the amount and characteristics of HS. Terefore, the information of HS present in landfill leachate can be used for optimization of leachate treatment and leachate-contaminated groundwater remediation (Kang et al., 2002).

The humic substance in leachate collected from three landfills in Korea with different landfilling ages were extracted and compared with commercial humic substances (Kang et al., 2002). By a series of analysis, it was found that, leachate HS were comprised of molecules of smaller size and were less aromatic compared with commercial humic acid. By comparing leachate HS with different landfilling age, it was found that the aromatic components and molecular size of the HS

increased with increasing landfilling age, which suggested that the degree of humification increased as the landfilling age increased (Kang et al., 2002).

A similar study on humic substance was carried out for leachates from three different landfills in Oklahoma with different age and redox conditions (Nanny and Ratasuk, 2002). In this study, the acid-precipitated (AP) and acid-soluble (AS) fractions of the combined hydrophobic neutral and hydrophobic acid dissolved organic carbon (DOC) were isolated from leachate, which are equivalent to HA and FA. It was found that the AP (HA) and the AS (FA) combined hydrophobic neutral and acid DOC comprised 6-15% and 51-66% respectively, of the leachate NPOC. Moreover, results showed that the AP (HA) and the AS (FA) combined hydrophobic neutral and acid DOC were highly aliphatic, and less oxidized than most terrestrial and aquatic humic substances (Nanny and Ratasuk, 2002).

Recycled leachates of bioreactor landfill under different aeration modes were studied by He et al (He et al., 2006). It was found that their HA fraction comprised mainly large molecules (> 10k Da), while the FA and Hyl were composed of smaller molecules (< 50k Da and < 4k Da, respectively). With the presence of oxygen, FA and Hyl fractions of molecular weight lower than 4k Da decreased because of degradation, while the organic matter remaining was poorly biodegradable (He et al., 2006).

The landfill leachate rejected by nanofiltration was fractionated into humic acid, fulvic acid and hydrophilic fractions (Zhang et al., 2009). It was reported that, humic substances(HA and FA) composed 75% of the total DOM, chemical analysis showed that HA and FA exhibited lower condensed aromatic functional group but more acidic groups compared with other aquatic DOMs (Zhang et al., 2009).

2. Characterization

In addition to regular water quality analysis for whole leachate and leachate fractions, such as COD, BOD, TOC, TKN, NH4+-N, pH and TS, etc., chemical, spectroscopic and chromatographic separation and analysis, for example elemental analysis, UV-visible, and fluorescence spectrometry, FT/IR, NMR and TMAH-Py-GC/MS, can provide more detailed information of different leachate fractions on elemental composition, functional groups and chemical structures.

2.1 Elemental analysis

Kang et al. (2002) analyzed the elemental composition for humic substances isolated from three different landfill leachate and compared them with literature average values. By calculating ratios of H/C and O/C, it was found that: the high H/C rations in the leachate HS imply that the structures contain significant portions of aliphatic functional groups, on the other hand, O/C ratios were relatively lower than those found in the literature (Visser et al., 1983; Steelink, 1985), which means lower contents of oxygen-possessing carbohydrate.

Landfill leachate rejected by nanofiltration was also fractionated into HA, FA and Hyl then analyzed (Zhang et al., 2009). The H/C ratios here are higher than those reported in the literature (Christensen et al., 1998; Kang et al., 2002 ; Ma et al., 2001) (usually < 1.3), which implied that the structure contains significant portions of aliphatic functional groups. On the other hand, O/C ratios are similar to those for other DOMs. Moreover, the O/C ratio of FA is slightly higher than that of HA. According to Ma et al. (2001), aquatic FA generally has a higher H/C and O/C ratio

than HA. This is consistent with a deeper humification process in HA than FA, which would produce a more condensed aromatic structure and fewer acidic groups (Zhang et al., 2009).

2.2 Spectroscopic characteristics analysis

2.2.1 UV-visible

The adsorption coefficient at 280nm (e_{280}) is generally used as an indicator for the aromaticity of a sample's structure (Chin et al., 1994); the ratio of adsorption coefficients ant 465nm and 665nm (e_4/e_6) is generally known to be inversely proportional to molecular weight and proportional to acidity (Chin et al., 1994). The SUVA$_{254}$ (specific UV adsorption at wavelength of 254nm) is positively relative to the aromatic extent of organic matters (Tchobanoglous et al., 2003).

In Kang et al. (2002)'s study, e_{280} and e_4/e_6 were measured for leachate HS and Aldrich HA, the values of e_{280} were lower in the leachate HS than that of AHA, and showed an increasing trend with landfilling age; while the values of e_4/e_6 were measured higher in leachate HS than Aldrich HA, but showed no trend with landfill age.

A similar study was done with landfill leachate rejected from nanofiltration (Zhang et al., 2009), e_4/e_6 values were measured for HA, FA and Hyl fractions of leachate and Aldrich HA. By comparing the results of molecular weight and acid-base titration analysis, it was confirmed that the value of e_4/e_6 is generally inversely proportional to molecular weight and proportional to acidity (Ma et al., 2001).

However, different results were found by Ma *et al.* (2001). By measuring and comparing e_4/e_6 and elemental content (C, O, N, S and their ratios), no significant correlation was observed. The authors concluded that the e_4/e_6 ratio has no direct relationship with the nature of water-soluble humic substances.

By analyzing the leachates and leachate fractions recycled in three lab-scale bioreactor landfills, He et al. (2006) found that HA and FA had much higher $SUVA_{254}$ than Hyl portion, and aerobic processes had higher $SUVA_{254}$, implying that humic substance (HA and FA) contained more bio-refractory compounds and aerobic processes removed most easily degradable, non-aromatic , organic compounds.

2.2.2 Fourier Transform Infrared spectra (FTIR)

Infrared (IR) spectroscopy is usually used for analysis of specific molecular structures and various functional groups. Correlation has been developed between adsorption wavelengths (in cm^{-1}) and molecular structures or functional groups, such as: absorption band 3400-3200 cm^{-1} corresponds to intermolecular O-H stretching or H-bounded OH; 2980-2850 cm^{-1} corresponds to asymmetrical and symmetrical stretching, respectively, of methyl and methylene C-H bond; 2900 cm^{-1} corresponds to aliphatic C-H stretching; a shoulder at 1650 cm^{-1} represents stretching of C=C bonds in aromatic or asymmetric alkenes conjugated with C=O or carboxylate, 1540 cm^{-1} corresponds to C=N stretching, amide II band, 1240 cm^{-1} represents C-O stretching(Seo et al., 2007; Kang et al., 2002; Nanny and Ratasuk, 2002; Zhang et al., 2009; Fan et al., 2006).

The infra-red spectra of different leachate fractions were found to be similar, with insignificant difference (Seo et al., 2007; Kang et al., 2002; Nanny and Ratasuk, 2002; Zhang et al., 2009): almost all leachates and leachate fractions exhibited adsorption band at 3400-3200 cm^{-1} due to

intermolecular O-H stretching or H-bounded OH and adsorption band at 1690-1710 cm^{-1} due to C=O stretching of COOH and ketonic C=O. For the humic substances fraction of leachate (HA and FA), Kang et al found the order of adsorption intensity at 1630 cm^{-}1(attributed to the C=C bonds in benzene ring) that Aldrich HA > leachate HA > leachate FA, which was confirmed by Zhang et al, who found higher adsorption intensity at 1630 cm^{-1} for leachate HA than leachate FA; Nanny et al found that all leachate AP and AS (equivalent to HA and FA) fractions lack C-O absorption bands in the region of 1200-1000 cm^{-1}, especially at 1050 cm^{-1} which is assigned as C-O stretching in polysaccharides. Similar results were found by Artiola-Fortuny et al. (1982) and Calace et al. (1997). For leachates as a whole sample, Fan et al. (2006) found that, the absorption at 2900 cm^{-1} which corresponds to aliphatic groups appeared to be more in active landfills than closed landfill.

2.2.3 Nuclear magnetic resonance (NMR)

Proton NMR (1H NMR) is the application of nuclear magnetic resonance in NMR spectroscopy with respect to hydrogen-1 nuclei within the molecules of a substance, in order to determine the structure of its molecules (Silverstein et al., 1991); 13C NMR is the application of nuclear magnetic resonance in NMR spectroscopy with respect to carbon. It is analogous to proton NMR (1H NMR) and allows the identification of carbon atoms in an organic molecule. By ^{1}H NMR analysis for fractions of leachate, Kang et al. (2002) found that, as landfilling age increased, the leachate HS signal peak became broader, which may be caused by an increase of molecular size. Ma et al. (2001) found that, hydrophilic portion of landfill leachate had almost no aromatic proton, in aliphatic region, hydrophilic fractions contained more sharp peaks than FA fraction, which indicated that hydrophilic fractions contained more simple compounds.

By ^{13}C NMR analysis, a high signal in 50-60 ppm region, which representing amino acid carbon, was found to be caused by high level of nitrogen in the leachate HS, moreover, the signal intensity in 0.4-1.7 ppm region (assign to alkyl-C) became higher in older leachate than that of younger leachate, which may result from methanogenesis process in older leachate (Kang et al., 2002). Also, FA fraction of leachate was found to contain more alcohol and ether (65-72ppm) and carboxylic acid (170-190ppm) functional group than HA fraction, which meant that FA fractions were more oxidized; absence of signal at 56ppm, which assign to methoxy groups, in both HA and FA indicated a lack of lignin (Nanny and Ratasuk, 2002).

3. Treatment

3.1 Biological treatment

Biological treatment is commonly used for removal of leachate with high BOD/COD ratio, which can degrade organics compounds to carbon dioxide under aerobic condition and to biogas (mainly CO_2 and CH_4) under anaerobic condition. The advantages of biological treatment include high removal efficiency for soluble and colloidal organic substances, cost-effectiveness compared with physico-chemical methods, good settling properties and simplicity for handling of treatment byproducts (sludge). Due to its characteristics, biological processes are very effective in removing organics from immature leachates which contain a larger portion of biodegradable organics.

3.1.1 Aerobic processes

Aerobic biological processed can be used in suspended-growth biomass systems, attached-growth systems, membrane bioreactors, or combined membrane separation and aerobic bioreactors. An aerobic process should allow a partial removal of biodegradable organic pollutants and should achieve nitrification of ammonia.

Activated sludge. This method is extensively applied for sewage and also for combined influent of leachate and domestic wastewater. However, in recent decades, this method has been found to be inadequate for treatment of landfill leachate because of the disadvantages (Lin et al., 2000) including long aeration times and high energy demand (Loukidou et al., 2001), excess sludge production (Hoilijoki et al., 2000) and sensitivity to toxins including ammonia (Lema et al., 1988).

Sequencing batch reactors. This system can provide an ideal operation regime to operate concurrent organics oxidation and ammonia nitrification so is compatible for nitrification-denitrification processes. A wide application for landfill leachate treatment by SBR was reported (Uygur and Kargi, 2004; Lin and Chang, 2000), COD removal up to 80% was widely reported. Based on the wide variation of landfill leachate in both quantity and quality, SBR system with great flexibility should be taken into consideration (Kennedy and Lentz, 2000).

Trickling filters. This method has shown a good performance for biological nitrification from municipal landfill leachate, with high treatment efficiency and resistance to environment conditions. In a recent work, up to 90% nitrification was achieved in both lab scale and pilot scale with loading rates 100-130 mg NH4/L·day at 25°C and 50 NH4/L·day at temperature as low as 5°C, respectively (Jokela et al., 2002).

Moving-bed biofilm reactor (MBBR). The major advantages of this method are: higher biomass concentrations, short sludge-settling periods and lower sensitivity to toxic compounds (Loukidou et al., 2001). Nearly 90% nitrogen removal was reported while the COD removal was only 20% (Welander et al., 1998). Imai et al. (1998) developed an efficient biological activated carbon process, nearly 70% refractory organics were removed by coupling biodegradation and adsorption.

3.1.2 Anaerobic processes

Contrary to aerobic processes, anaerobic digestion conserves energy by producing biogas and generates less sludge, but is sensitive to temperature and has low reaction rates. Anaerobic treatment is particularly suitable for leachates with high concentration of organic effluents, especially those from young landfills (Pokhrel and Viraraghavan, 2004).

Up-flow anaerobic sludge blanket (UASB). UASB process has advantageous properties including high treatment efficiency and good performance at low temperature. It has shown higher removal efficiency compared with other anaerobic processes when submitted to high volumetric organic loading rates (Garcia et al., 1996). The average COD reduction efficiency was always higher than 70% at ambient temperature (20-23°C) and 80% at 35°C. Up to 92% COD removal was observed at low and intermediate organic loading rates (Knox, 1985). Leachate treatment was observed at low temperature (Kettunen and Rintala, 1998). A pilot-scale reactor was used for the leachate with COD 1500 -2000mg/L at 13-23 °C, 65-75% of COD and up to 95% of BOD was removed. It was concluded that COD removal efficiency was not affected by temperature between 15-35°C (Garcia et al., 1996).

Anaerobic filter. In anaerobic filter, biomass is retained as biofilm attached on support materials (Nedwell and Reynolds, 1996), it was observed that up to 90% COD was reduced in anaerobic filter for different ages of landfill (Henry et al., 1987).

3.2 Physico-Chemical treatment

Biological treatment is not sufficient for all these stabilized leachates to meet the regulations so physic-chemical techniques are necessary to be applied either as pretreatment or post-treatment. Physico-chemical treatment includes coagulation-flocculation, adsorption, oxidation and membrane separation.

3.2.1 Coagulation-flocculation

This method is usually used to get rid of bio-refractory organic compounds and heavy metals (Tatsi et al, 2003; Kargi and Pamukoglu, 2003). It employs coagulants (ferric or alum salts) to overcome the repulsive forces between the colloidal particles, then the unstable particles are flocculated so that they can settle more easily. An application of coagulation-flocculation was applied for landfill leachate in Greece. The initial COD of which was 5690 mg/L.The highest COD removal was 56% with an $FeCl_3$ dose 0.8g/L, which was better than the 39% of for $Al_2(SO_4)_3$ (Diamadopoulos, 1994). Another similar study was conducted by Amokrane et al (Amokrane et al., 1997), with an initial COD of 4100mg/L and doses of 0.035 mol Fe or Al /L. Ferric salt was found to perform better with 55% organic removal compared with 42% for the aluminum salt. So, it can be found that ferric salt is more effective than alum salt in coagulation-flocculation treatment.

3.2.2 Advanced oxidation processes (AOP)

AOP has been reported as one of the most powerful techniques to degrade various refractory compounds from stabilized leachate thanks to the highly reactive hydroxyl free radical ($\cdot$OH) (Parsons and Williams, 2004), which can be produced by O_3, O_3/H_2O_2, O_3/UV, H_2O_2/UV, H_2O_2/Fe^{2+}, and $H_2O_2/Fe^{2+}/UV$ (Wang et al., 2003). AOP adapted to old and stabilized leachate, are applied to: a) oxidize organic substances to highest oxidation state (CO_2 and H_2O); b) enhance the biodegradatility of refractory organic substances to be suitable for subsequent economical biological treatment (Renou et al., 2008).

With single step of ozonation, 30% COD removal was observed (Rivas et al., 2003). The removal efficiency can be enhanced significantly by combining oxidants or irradiation, up to 90% of organics removal were observed for O_3/H_2O_2 (Schulte et al., 1995), 45-75% and 70-78% organic substance removal were reported for Fenton and photo-Fenton processes (Kim et al, 2001,Lopez et al., 2004). In terms of biodegradability enhancement, BOD/COD ration has been increased from 0.1 to 0.45 by the H_2O_2/UV process (Qureshi et al, 2002), and a BOD/COD ration close to 0.5 was also reported for Fenton process (Lopez et al., 2004).

3.2.3 Adsorption

Activated carbon adsorption has been used to compensate biological treatment for effective treatment of landfill leachate, bio-refractory organics could be reduced to acceptable levels for biological treatment effluent (Cecen et al., 2003, Cecen and Aktas, 2004). PAC was found to be most effective in lowering of non-biodegradable organic matter from landfill leachate compared with different resins, with 85% COD reduction and a 200 mg/L residual COD (Rodriguez et al, 2004). Also, simultaneous adsorption and biological treatment has been evaluated in recent years.

For example, biological treatment and adsorption was used for pre-treated leachate, up to 87% and 77% COD reduction was achieved with 2 g/L PAC and zeolite, respectively (Kargi and Pamukoglu, 2004). The main disadvantage of adsorption is frequent regeneration of columns and high consumption of adsorbents, such as powered active carbon.

3.2.4 Membrane separation

Nanofiltration (NF) membranes are usually made of polymeric films with a molecular cut-off between 200-2000 Da. NF is seldom used for landfill leachate treatment, about 60-70% COD and 50% ammonia removal could be achieved with different membrane material and a trans-membrane pressure between 6 and 30 bar (Marttinen et al., 2002; Trebouet et al., 2001; Trebouet et al., 1999). When combined with physical methods, COD lowering was up to 70-80% (Trebouet et al., 2001).

Reverse Osmosis (RO) seems to be the most effective method for landfill leachate treatment, up to 98 and 99% removal efficiency for COD and heavy metal respectively were reported (Ozturk et al., 2003; Chianese et al., 1999; Ahn et al., 2002). The operating pressure ranges between 30-60 bar and specific energy demand is less than 5 kWh/m^3.

The major drawbacks for membrane separation processes, especially RO, is membrane fouling. A wide spectrum of substances can contribute to membrane fouling, including dissolved organic matter and colloidal and suspended particles (Trebouet et al., 2001) which results in short runs and low process productivity and the generation of a concentrate which is not suitable for discharging and needs further treatment (Rautenbach et al., 2000).

Reference:

Ahn, W.Y., Kang, M.S., Yim, S.K., Choi, K.H., 2002. Advanced landfill leachate treatment using integrated membrane process. Desalination 149, 109–114.

Alberts, J.J., Takács, M., 2004. Total luminescence spectra of IHSS standard and reference fulvic acids, humic acids and natural organic matter: comparison of aquatic and terrestrial source terms. Organic Geochemistry 35 (3), 243–256.

Amokrane, A., Comel, C., Veron, J., 1997. Landfill leachates pretreatment by coagulation–flocculation. Water Res. 31, 2775–2782.

Artiola-Fortuny, J., Fuller, W.H., 1982. Humic Substances in Landfill Leachates: 1. Humic Acid Extraction and Identification. J. Environ. Qual., 11(4), 663-669.

Calace, N., Petronio, B.M., 1997. Characterization of high molecular weight organic compounds in landfill leachate: humic substances. J Environ Sci Health A 32(8), 2229–2244.

Cecen, F., Aktas, O., 2004. Aerobic co-treatment of landfill leachate with domestic wastewater. Environ. Eng. Sci. 21 , 303–312.

Cecen, F., Erdincler, A., Kilic, E., 2003. Effect of powdered activated carbon addition on sludge dewaterability and substrate removal in landfill leachate treatment. Adv. Environ. Res. 7 , 707–713.

Cheung, K.C., Chu, L.M., Wong, M.H., 1997. Ammonia stripping as a pretreatment for landfill leachate. Water Air Soil Pollut. 94, 209–221.

Chianese, A., Ranauro, R., Verdone, N., 1999. Treatment of landfill leachate by reverse osmosis. Water Res. 33, 647–652.

Chin, Y.P., Alken, G., O'Loughlin. E., 1994. Molecular Weight, Polydispersity, and Spectroscopic Properties of Aquatic Humic Substances. Environ Sci. Technol. 28, 1853-1858.

Chistensen, J.B., Jnsen, D.L., Gron, C., Filip, Z., Chistensen. T.H., 1998.Characterization of the Dissolved Organic Carbon in Landfill Leachate-Polluted Groundwater. Wat.Res. 32(1), 125-135.

Diamadopoulos, E., 1994. Characterization and treatment of recirculationstabilized leachate. Water Res. 28, 2439–2445.

Fan, H., Shu, H.Y., Yang, H.S., Chen. W.C., 2006. Characteristics of landfill leachates in central Taiwan. Science of the Total Environment 361, 25– 37.

Garcia, H., Rico, J.L., Garcia, P.A., 1996. Comparaison of anaerobic treatment of leachates from an urban-solid-waste landfill at ambient temperature and at 35 ◦C. Bioresour. Technol. 58, 273–277.

Ha, D., Cho, S., Kim, Y., Leung, S.W., 2008. A New Approach to Characterize Biodegradation of Organics by Molecular Mass Distribution in Landfill Leachate. Water Environ. Res. 80, 748-756.

Harmsen, J., 1983. Identification of organic compounds in leachate from a waste tip. Water Res. 17(6), 699-705.

He, P., Xue, J., Shao, L., Li, G., Lee. D., 2006. Dissolved organic matter (DOM) in recycled leachate of bioreactor landfill. Water Research 40, 1465 – 1473.

Henry, J.G., Prasad, D., Young, H., 1987. Removal of organics from leachates by anaerobic filter. Water Res. 21, 1395–1399.

Hoilijoki, T.H., Kettunen, R.H., Rintala, J.A., 2000. Nitrification of anaerobically pretreated municipal landfill leachate at low temperature. Water Res. 34, 1435–1446.

Imai, A., Onuma, K., Inamori, Y., Sudo, R., 1998. Effects of pre-ozonation in refractory leachate treatment by the biological actived carbon fluidized bed process. Environ. Technol. 19, 213–221.

Jokela, J.P.Y., Kettunen, R.H., Sormunen, K.M., Rintala, J.A., 2002. Biological nitrogen removal from municipal landfill leachate: low-cost nitrification in biofilters and laboratory scale in-situ denitrification. Water Res. 36, 4079–4087.

Kalbitz, K., Solinger, S., Park, J.H., Michalzik, B., Malzner, E., 2000. Controls on the dynamics of dissolved organic matter in soils: a review. Soil Sci. 165, 277–304.

Kang, K., Shinb, H., Park. H., 2002. Characterization of humic substances present in landfill leachates with different landfill ages and its implications. Water Research 36, 4023–4032.

Kargı, F., Pamukoglu, M.Y., 2003. Powdered activated carbon added biological treatment of pre-treated landfill leachate in a fed-batch reactor. Biotechnol. Lett. 25, 695–699.

Kargi, F., Pamukoglu, M., 2004. Repeated fed-batch biological treatment of pretreated landfill leachate by powdered actived carbon addition. Enzyme Microb. Technol. 34, 422–428.

Kennedy, K.J., Lentz, E.M., 2000. Treatment of landfill leachate using sequencing batch and continuous flow upflow anaerobic sludge blanket (UASB) reactors, Water Res. 34, 3640–3656.

Kettunen, R.H., Rintala, J.A., 1998. Performance of an on-site UASB reactor treating leachate at low temperature, Water Res. 32, 537–546.

Kim, J.S., Kim, H.Y., Won, C.H., Kim, J.G., 2001. Treatment of leachate produced in stabilized landfills by coagulation and Fenton oxidation process. J. Chinese Inst. Chem. Eng. 32, 425–429.

Knox, K., 1985. Leachate treatment with nitrification of ammonia, Water Res. 19, 895–904.

Leenheer, J.A., 1981. Comprehensive Approach to Preparative Isolation and Fractionation of Dissolved Organic Carbon from Natural Waters and Wastewaters. Environmental Science & Technology15 (5), 578-587.

Lema, J.M., Mendez, R., Blazquez, R., 1988. Characteristics of landfill leachates and alternatives for their treatment: a review. Water Air Soil Pollut. 40, 223–250.

Li, R., Yue, D., Liu, J., Nie. Y., 2009. Size fractionation of organic matter and heavy metals in raw and treated leachate. Waste Management 29, 2527–2533.

Li, X.Z., Zhao, Q.L., 2001. Efficiency of biological treatment affected by high strength of ammonium-nitrogen in leachate and chemical precipitation of ammonium-nitrogen as pretreatment. Chemosphere 44, 37–43.

Lin, C.Y., Chang, F.Y., Chang, C.H., 2000. Co-digestion of leachate with septage using a UASB reactor. Bioresour. Technol. 73, 175–178.

Lin, S.H., Chang, C.C., 2000. Treatment of landfill leachate by combined electro-Fenton oxidation and sequencing batch reactor method, Water Res. 34, 4243–4249.

Lopez, A., Pagano, M., Volpe, A., Di Pinto, A., 2004. Fenton's pre-treatment of mature landfill leachate. Chemosphere 54, 1005–1010.

Lou, Z., Zhao, Y., Yuan, T., Song, Y., Chen, H., Zhu, N., Huan, R., 2009. Natural attenuation and characterization of contaminants composition in landfill leachate under different disposing ages. Science of the Total Environment 407, 3385–3391.

Lou, Z., Zhao, Y., 2007. Size-fractionation and characterization of refuse landfill leachate by sequential filtration using membranes with varied porosity. Journal of Hazardous Materials 147, 257–264.

Lou, Z., Chai, X., Niu, D., Ou, Y., Zhao, Y., 2009a. Size-fractionation and characterization of landfill leachate and the improvement of Cu2+ adsorption capacity in soil and aged refuse. Waste Management 29, 143–152.

Lou, Z., Dong, B., Chai, X., Song Y., Zhao, Y., Zhu, N., 2009b. Characterization of refuse landfill leachates of three different stages in landfill stabilization process. Journal of Environmental Sciences 21,1309–1314.

Loukidou, M.X., Zouboulis, A.I., 2001. Comparaison of two biological treatment process using attached-growth biomass for sanitary landfill leachate treatment. Environ. Pollut. 111, 273–281.

Ma, H., Allen, H.E., YIN, Y., 2001. Characterization of isolated fractions of dissolved organic matter from natural waters and a wastewater effluent. Wat. Res. 35(4), 985-996.

Marttinen, S.K., Kettunen, R.H., Sormunen, K.M., Soimasuo, R.M., Rintala, J.A., 2002. Screening of physical–chemical methods for removal of organic material, nitrogen and toxicity from low strength landfill leachates. Chemosphere 46, 851–858.

McDonald, S., Bishop, A.G., Prenzler, P.D., Robards, K., 2004. Analytical chemistry of freshwater humic substances. Analytica Chimica Acta 527 (2), 105–124.

Nanny, M. A., Ratasuk, N., 2002. Characterization and comparison of hydrophobic neutral and hydrophobic acid dissolved organic carbon isolated from three municipal landfill leachates. Water Research 36, 1572–1584.

Nedwell, D.B., Reynolds, P.J., 1996. Treatment of landfill leachate by methanogenic and sulphate-reducing digestion, Water Res. 30, 21–28.

Ozturk, I., Altinbas, M., Koyuncu, I., Arikan, O., Gomec-Yangin, C., 2003. Advanced physico-chemical treatment experiences on young municipal landfill leachates. Waste Manage. 23, 441–446.

Parsons, S.A., Williams, M., 2004. Introduction, in: S.A. Parsons (Ed.), Advanced Oxidation Processes forWater andWastewater Treatment. IWA Publishing, London, 1–6.

Pokhrel, D., Viraraghavan, T., 2004. Leachate generation and treatment—a review, Fresenius Environ. Bull. 13, 223–232.

Qureshi, T.I., Kim, H.T., Kim, Y.J., 2002. UV-catalytic treatment of municipal solid-waste landfill leachate with hydrogen peroxide and ozone oxidation. J. Chem. Eng. 10, 444–449.

Rautenbach, R., Linn, T., Eilers, L., 2000. Treatment of severely contaminated waste water by a combination of RO and NF—potential and limits of the process. J. Membr. Sci. 174, 231–241.

Renou, S., Givaudan, J.G., Poulain, S., Dirassouyan, F., Moulin, P., 2008. Landfill leachate treatment: Review and opportunity. Journal of Hazardous Materials 150, 468–493.

Renou, S., Givaudan, J.G., Poulain, S., Dirassouyan, F., Moulin, P., 2008. Landfill leachate treatment: Review and opportunity. Journal of Hazardous Materials 150, 468–493.

Rivas, F.J., Beltran, F., Gimeno, O., Acedo, B., Carvalho, F., 2003. Stabilized leachates: ozone-actived carbon treatment and kinetics. Water Res. 37, 4823–4834.

Rodriguez, J., Castrillon, L., Maranon, E., Sastre, H., Fernandez, E., 2004. Removal of non-biodegradable organic matter from landfill leachates by adsorption. Water Res. 38, 3297–3303.

Schulte, P., Bayer, A., Kuhn, F., Luy, T., Volkmer, M., 1995. H_2O_2/O_3, H_2O_2/UV and H_2O_2/Fe^{2+} processes for the oxidation of hazardous wastes. Ozone Sci. Eng. 17, 119–134.

Seo, D., Kim, Y., Hama, S., Lee, D., 2007. Characterization of dissolved organic matter in leachate discharged from final disposal sites which contained municipal solid waste incineration residues. Journal of Hazardous Materials 148, 679–692.

Silva, A.C., Dezotti, M., Sant'Anna Jr., G.L., 2004. Treatment and detoxication of a sanitary landfill leachate. Chemosphere 55, 207–214.

Silverstein, R. M., Bassler G. C., Morrill, T. C., 1991.Spectrometric Identification of Organic Compounds, 5th Ed., Wiley.

Slater, C.S., Uchrin, C.G., Ahlert. R.C., 1985. Ultrafiltration Process For The Characterization and Separation of Landfill Leachates. J. Environ. Sci. Health, A 20(1), 97-111.

Steelink, C., 1985. Implications of elemental characteristics of humic substances. In: Aiken GR, McKnight DM, Warshaw RL, editors. Humic substances in soil, sediment, and water. New York: Wiley, 457–476.

Tatsi, A.A., Zouboulis, A.I., Matis, K.A., Samaras, P., 2003. Coagulation– flocculation pretreatment of sanitary landfill leachates. Chemosphere 53, 737–744.

Tchobanoglous, G., Burton, F. L., Stensel, H. D., Wastewater Engineering Treatment and Reuse. 4th. Ed., McGraw-Hill Companies, Inc. New York, NY.

Thurman, E.M., Malcolm, R.L., 1981. Preparative Isolation of Aquatic Humic Substances. Environmental Science & Technology 15(4), 463-466.

Trebouet, D., Schlumpf, J.P., Jaouen, P., Quemeneur, F., 2001. Stabilized landfill leachate treatment by combined physicochemical–nanofiltration process. Water Res. 35, 2935–2942.

Trebouet, D., Schlumpf, J.P., Jaouen, P., Maleriat, J.P., Quemeneur, F., 1999. Effect of operating conditions on the nanofiltration of landfill leachates: pilotscale studies. Environ. Technol. 20, 587–596.

Uygur, A., Kargi, F., 2004. Biological nutrient removal from pre-treated landfill leachate in a sequencing batch reactor. J. Environ. Manage. 71, 9–14.

Visser, S.A., 1983. Comparative study on the elementary composition of fulvic and humic acids of aquatic origin and from soils and microbial substrates. Wat. Res. 17(10), 1393–1396.

Wang, F., Smith, D.W., El-Din, M.G., 2003. Application of advanced oxidation methods for landfill leachate treatment. J. Environ. Eng. Sci. 2, 413–427.

Welander, U., Henrysson, T., Welander, T., 1998. Biological nitrogen removal from municipal landfill leachate in a pilot scale suspended carrier biofilm process. Water Res. 4, 95–102.

Zhang, L., Li , A., Lu, Y., Yan, L., Zhong, S., Deng. C., 2009. Characterization and removal of dissolved organic matter (DOM) from landfill leachate rejected by nanofiltration. Waste Management 29, 1035–1040.

Chapter 3. Evaluation of On-site Biological Treatment for Landfill Leachates and Its Impact: A Size Distribution Study

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Evaluation of on-site biological treatment for landfill leachates and its impact: a size distribution study

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Abstract

A cost effective and widely applied approach for landfill leachate disposal is to discharge it to a municipal wastewater treatment plant (WWTP). The recalcitrant nature of leachate organics and the impact on the downstream WWTPs were comprehensively investigated in this study. Size fractionation by ultrafiltration (UF) and microfiltration (MF) was employed in conjunction with various analyses (TOC, COD, nitrogen species and UV_{254} absorbance) on raw and biologically treated landfill leachates to provide insight into biological treatability. Overall, landfill leachate organics showed bio-refractory properties. Less than half of the organic matter, measured as total organic carbon (TOC), could be removed in the biological processes examined. Size distribution data showed that the < 1K Daltons (Da) fraction is dominant in most untreated and treated landfill leachates, indicating difficulties for membrane treatment. Also, most removal occurred for the < 1K Da fraction in the biological processes, while the intermediate size fractions increased slightly. This may be caused by bio-flocculation and/or partial degradation of larger molecular weight fractions. Organic nitrogen was investigated in this study as one of the first explorations for landfill leachates, Organic nitrogen in landfill leachates was more bio-refractory

than other organic matter. UV quenching by landfill leachates was also investigated since it interferes with the UV disinfection at WWTPs. The combination of activated carbon and activated sludge (PACT) showed some effectiveness for reducing UV quenching, indicating that carbon adsorption is a potential method for removal of UV quenching substances. Fourier transform Infrared (FT/IR) data showed that aromatic groups are responsible for the UV quenching phenomenon.

Keywords: landfill leachate; size fractionation; organic matter; organic nitrogen; UV disinfection; biodegradation

1. INTRODUCTION

Although recycling, composting and incineration are being encouraged, landfilling is still the most widely employed method for municipal solid waste disposal throughout the world (El-Fadel et al.,1997; Wiszniowski et al., 2006). In the USA, about 54% of the 243 million tons of MSW generated in 2009 was discarded to landfills (US EPA, 2010).

Landfill leachate is produced by rainwater percolation and waste decomposition in the landfill (Vilar et al., 2011). Since there is a possibility for leachate to enter groundwater, sound engineering facilities, such as liners, pipes and pumps, are installed in most of the sanitary landfills to prevent or minimize the seepage of leachate and collect the leachate for treatment (Kurniawan et al., 2006). Based on the widespread use of landfills, there is a large amount of landfill leachate collected that needs to be treated.

The most common and cost effective treatment method is on-site activated sludge coupled with necessary pretreatment (Renou et al., 2008). The effluent from on-site treatment facilities is

rarely of sufficient quality for direct discharge so is often discharged to municipal sewer systems and then transported to the local sewage treatment plants. The impact of biological treated leachate on the downstream sewage treatment plant is a critical issue for both landfills and the receiving sewage treatment plants. The biological treatment of landfill leachate plays an important role in both wastewater treatment and solid waste management, and evaluation of on-site biological treatment for landfill leachate is necessary.

Although the composition of landfill leachates varies considerably, depending on the type of waste accepted, landfill age, location and climate, operation technology and etc. (Renou et al., 2008), there are some common characteristics of municipal landfill leachates that impact the downstream WWTPs.

Nutrient imbalances in landfill leachates (especially stabilized leachates) make it difficult to maintain effective biological treatment (Chian and De Walle, 1976; Renou et al., 2008). The high concentration of ammonia nitrogen coupled with relatively low phosphorous and bioavailable carbon is a constraint for both on-site and downstream biological systems (Berge et al., 2006). Struvite precipitation (Ozturk et al., 2003; Calli et al., 2005 and Li et al., 1999), air stripping (Cheung et al., 1997; Marttinen et al., 2002) and nitrification-denitrification coupled with addition of external phosphorous and carbon sources, have been tried and have shown some success for inorganic nitrogen (Jokela et al., 2002; Xu et al., 2010; He et al., 2006b).

In recent years, with the increased use of nitrification/denitrification, organic nitrogen has been recognized as a new emerging issue for WWTPs. For nitrification-denitrification effluents from municipal WWTP, organic nitrogen accounts for up to 80% of dissolved nitrogen (Qasim et al., 1999). On one hand, dissolved organic nitrogen (DON) would be a potential source of

nitrogenous disinfection by-products (Krasner at el. 2009); on the other hand, there is concern about stricter discharge limits for total nitrogen in discharges. However, little is known about organic nitrogen and its treatability in landfill leachates. Because landfill leachates are discharged to WWTPs, evaluation of total amount, characteristics and treatability of organic nitrogen in landfill leachates is necessary.

The presence of bio-refractory substances in landfill leachates, such as humic-like acids, fulvic-like acids, and xenobiotic organic compounds (XOCs) (Kjeldsen et al., 2002) is another challenge for biological treatment because these recalcitrant substances can pass through biological treatment processes and increase the organic level in the effluent. Some pre/post treatments, such as coagulation (Tatsi et al., 2003), adsorption (Rodriguez et al., 2004) and oxidation (Kurniawan et al., 2006), have been employed to reduce the organic level to meet discharge limits.

Preliminary studies (Zhao et al., unpublished results) show that landfill leachates from different landfills quench UV light severely, which interferes with disinfection processes at WWTPs where UV light is employed. The UV quenching compounds are bio-refractory and can pass through the biological treatment processes. Also, the extent of UV quenching is fairly strong. A significant amount of UV light will be blocked by leachate even if the leachate makes up only 2-5% of the total municipal flow.

Organic size fractionation has been used to characterize organics in water (Xu et al., 2011), wastewater (Leiviskä et al., 2009) and landfill leachate, in conjunction with measurements of general constituents such as BOD and COD and specific compounds. To characterize landfill leachates, size fractionation was conducted by means of ultra-filtration and microfiltration (Slater

et al., 1985; Calace et al., 2001; Lou et al., 2007; Lou et al., 2009a; Li et al., 2009) to explore the size distribution of the organics. It has been demonstrated in experiments that 47-92% (in terms of TOC) and up to 50% (in terms of COD) of organic substances are from the < 1K Dalton (Da, 1 Da=1/16 O atomic mass unit) fraction, which has significant implications for landfill leachate treatment because these small molecular weight organics are difficult to remove physically or chemically. However, most research focused on analyzing COD, organic carbon, total nitrogen, ammonia and heavy metal, to investigate the occurrence or fate and transport of organic matter, inorganic nitrogen species (Jokela et al., 2002; He et al., 2006b) and heavy metals (Calace et al., 2001; Li et al., 2009) in the landfill leachate treatment. Very little information has reported about the size distribution and fate of organic nitrogen and UV_{254} absorbance during on-site landfill leachate treatment processes.

The objective of this research was to evaluate the treatment efficiency of two biological treatment processes for landfill leachate organics and investigate the potential for these leachates to impact the receiving wastewater treatment facilities. In this study, based on the characteristics of landfill leachate discharged and new emerging issues in WWTPs, organic matter (in terms of COD and TOC), organic nitrogen, UV_{254} absorbance and specific UV_{254} absorbance ($SUVA_{254}$) were measured in conjunction with size fractionation for untreated and treated leachates from two on-site treatment plants. In particular, the research work focused on:

(1) Size distribution of organic matter in terms of TOC and COD for raw and treated leachates from two on-site landfill leachate treatment plants;

(2) The characteristics of organic nitrogen for raw and treated leachates from a landfill treatment plant using a sequencing batch reactor activated sludge system with nitrification and denitrification;

(3) Comparison of treatment efficiency between the two different wastewater treatment plants for organic matter and UV_{254} absorbance.

2. MATERIALS AND METHODS

2.1. Leachate Sampling

The leachate samples were collected from on-site MSW landfill leachate treatment plants from Pennsylvania (PA) and New Hampshire (NH), USA. Leachates before and after treatment were collected for comparison purpose. The leachate samples were shipped in polyethylene containers directly from the landfills to our lab, and stored at 4°C in the dark immediately after being received to reduce microbial activity. Before sampling for fractionation and analysis, containers were shaken well to resuspend settled particles.

2.2. On-site biological treatment process

The leachate treatment process of the PA landfill is a sequencing batch reactor (SBR) activated sludge system with a capacity of 30,000 gallon per day (gpd), and a HRT of 6-7 days. Both nitrification and denitrification are accomplished, with around 95% total nitrogen removal. The SBR system receives landfill leachate from a 1973 vintage landfill receiving 1,500 tons of municipal waste per day. Treated landfill leachate from this SBR system is discharged to a sewer and goes to a nearby municipal wastewater treatment plant.

The leachate treatment process at the NH landfill is a PACT system (a combination of activated sludge and powdered activated carbon system that has only nitrification) with a design capacity of 40,000 gpd and a permitted capacity of 80,000 gpd, a HRT of 3.5 days and a SRT of 50 - 100 days. Activated carbon is added to activated sludge with a ratio of approximately 10% of MLSS;

more carbon is added to compensate for the loss due to sludge wastage. Ammonia is nitrified from 1200 ppm to less than 1ppm, all converted to nitrate. The PACT system receives landfill leachate from three separate solid waste landfills (TLR-I operated 1983-1992; TLR-II operated 1990-1997; and TLR-III began operation in 1995 and continues to operate) receiving currently approximately 3,000 tons of municipal waste per day. Treated effluent from this PACT system goes to a nearby municipal wastewater treatment plant.

2.3. Fractionation

Size fractionation was carried out using dead end batch ultrafiltration and microfiltration apparatus. The ultra-filtration apparatus used in this study consists of a 200 mL stirred ultrafiltraion cell (model 8200, [Amicon, Belford, MA]), a nitrogen gas tank (pressure: 120 KPa) and membrane discs (Millipore, Billerica, MA) with diameter of 63.5mm. In each ultrafiltration process, about 180 mL of leachate sample was pressed through the membrane disc driven by pressure from N_2 tank. The MW cutoffs of membrane discs used in this study were: 0.5k, 1k, 3k, 5k, 10k, 30k, 100k, and 300k (YC05,YM1,PLBC,PBCC,YM10,PLTK,PLHK and PBMK, Millipore, Billerica, MA). The microfiltration apparatus used in this study consists of a 300 mL filtration cell (GELMAN, Ann Arber, MI), a vacuum pump and membrane discs of 0.2µm (47mm, Millipore, Bedford, MA), 0.45µm (47mm, Sartorius Stedim Biotech, France) and 1.5 µm (55mm, Florham park, NJ). In each ultrafiltration/microfiltration process, about 180 mL of leachate sample was filtered and collected in a glass bottle, then stored at 4°C for further analysis. Various analyses (COD, TOC, nitrogen species and UV_{254} absorbance) were applied to the filtrate.

To compare ultrafiltration and microfiltration results (Fig. 1, 2 and 3), molecular weight (in K Da) and pore size (in µm) were converted to each other with the equation (Erickson, 2009):

$R = 0.66MW^{1/3}$

Where R is the pore size in nanometer and MW is the molecular weight in Dalton.

2.4. Analysis

All chemicals used in this study were analytical grade. All the glassware was washed with soapy water, soaked in 10% nitric acid, rinsed with deionized water and baked for 4 h at 450ºC. Total organic carbon (TOC) was analyzed using high temperature combustion with a TOC analyzer (Shimadzu TOC-5000A, Japan). Chemical oxidation demand (COD) was analyzed according to standard methods (APHA, 1998). Ultraviolet absorbance at 254nm (UV_{254} absorbance) was measured with a Beckman DU640 spectrophotometer, leachate samples and filtrates were diluted in order to yield appropriate reading. Five dilution factors (20, 30, 40, 50, and 100) were used for each sample. UV readings were multiplied by the corresponding dilution factor to give the final UV absorbance values. Average and standard deviation were made based on the five final UV absorbance values for statistical purpose. Specific ultraviolet absorbance at 254nm ($SUVA_{254}$) was calculated as UV_{254} absorbance divided by TOC. The pH of each leachate sample was measured by a pH probe (Model No.13-620-287, Accumet, Petaling Jaya, Malaysia). The pH meter (Model No.910, Accumet, Cambridge, MA) was standardized against reference solution of pH 4 and pH 7. Metal analysis was conducted for PA and NH leachate samples using a Thermo Electron X-Series inductively coupled plasma with mass spectrometer (ICP-MS) per Standard Method 3125-B (APHA, 1998). ICP-MS Samples and calibration standards were prepared in a matrix of 2% nitric acid by volume.

Organic nitrogen (ON) was estimated by subtracting inorganic nitrogen (IN) from total nitrogen (TN) (Pehlivanoglu and Sedlak, 2004; Westgate and Park, 2010). IN consists of nitrate, nitrite and ammonia nitrogen. This method yields less accurate results when inorganic nitrogen

concentrations are high. In untreated PA leachate, the ammonia nitrogen concentration was 700-800mg-N/L and interfered with organic nitrogen analysis so untreated PA leachate and its size fractions were pretreated to strip out ammonia nitrogen. Twenty mL of each leachate sample was transferred to a glass vial, sodium hydroxide pellets were added and the pH value was adjusted to around 10 ± 0.5 and purged with N_2 gas for 5 hours. After N_2-purging, the pH was adjusted back to around 7 with concentrated hydrochloric acid. The evaporation loss during N_2 gas purging was compensated for by adding deionized water. The ammonia nitrogen concentration was 23-146 mg-N/L after N_2-purging. NH leachates were not analyzed for organic nitrogen because there was no denitrification installed for the PACT system. High level of inorganic nitrogen species (approximately 450mg/L of nitrate and 350mg/L of nitrite) interferes with the organic nitrogen analysis and makes accurate analysis difficult.

Total nitrogen concentrations of PA leachates and their size fractions were determined by the persulfate digestion method (Hach, Loverland, CO) and confirmed by a TN analyzer (Astoria micro-Segmented Flow Analyzer, Astoria-Pacific, Inc. Clackamas, OR). Nitrate and nitrite concentrations of PA leachates and their size fractions were measured by an ion chromatograph (DX120, Dionex, Sunnyvale, CA) equipped with an AS9-HS column (Model No. 051786, Dionex, Sunnyvale, CA); the elute was 9.0 mM Na_2CO_3 and the flowrate was 1.0mL/min. NH_4^+/NH_3 concentrations of PA leachates and their size fractions were measured with salicylate method (Hach, Loverland, CO) instead of ion chromatography because the co-elution of sodium and NH_4^+ interfered with the detection. In most cases, organic nitrogen was measured at least three times for statistical purpose.

For FT/IR analysis, PA and NH leachates were freeze dried under -75 ºC, 0.03Mbar pressure. FT-IR spectroscopy (Bruker Equinox 55 FTIR) measurements were performed on pressed KBr pellets of freeze dried PA and NH untreated and treated leachates (1:50 sample/KBr).

3. RESULTS

To evaluate the biological treatment of landfill leachate organics, leachate samples were collected before and after the on-site treatment processes from two landfills, one located in Pennsylvania, USA (PA landfill), the other located in New Hampshire, USA (NH landfill). Size fractionation (including ultrafiltration and microfiltration) was first applied on all the leachate samples, followed by characterization by COD, TOC, nitrogen species and UV_{254} analysis. Thus, size distributions of leachate components across the on-site biological treatments for the two different landfills were obtained, and the on-site biological treatments were evaluated. This allowed comparison of the differences between the two biological processes (SBR and PACT).

3.1. Organic matter

Fig. 1(a, b) and Fig. 2(a, b) show the organic matter size distributions (in terms of TOC and COD) for untreated and treated leachates from the PA and NH landfills. Data shown in Fig. 1(a) and Fig. 2(a) are cumulative values; data shown in Fig. 1(b) and Fig. 2(b) are distributive values. As shown in Fig.1 (A) and Fig.2 (A), organic matter (in terms of TOC and COD) is primarily in the less than 1K Da fraction. Almost all of the TOC and COD pass a 10 K Da ultrafilter.

A comparison between the organic matter size distribution and the pore size of commonly used membrane separation technologies, shown in able 2, provide some insight into the use of

membrane technologies for the treatment of landfill leachates. As shown in (Fig.1 part A), for PA treated leachate, nanofiltration with MWCO of 1K Da will 53.0% of organic matter in terms of COD and 36.1% in terms of TOC. As shown in (Fig.2 A), for the NH treated leachate, nanofiltration with MWCO of 1K Da will 25.6% and 50.8% in terms of COD and TOC, respectively. UF and MF with cutoffs of 50-300 K Da and 0.2µm, respectively, would be expected to remove very little organic matter. Of all the membrane separation technologies listed in Table 2, only RO, with a cutoff of 10-100 Da can provide a high degree (>90%) of organic removal.

The distributive data (Fig.1 part B) show that most organic matter exists in the < 1K Da fraction, contributing 68.2 % TOC and 65.7% COD for untreated PA leachate and 61.6% TOC and 47.0% COD for treated PA leachate. This result is consistent with other studies (Harmsen et al., 1983, He et al., 2006a, Ha et al., 2008, Lou et al., 2009, Li et al., 2009). Organics with MWCO less than 1k are the dominant species in not only raw leachates but also biological treated leachates, and this study confirmed that.

By comparing the total organic matter and distribution in untreated and treated PA leachates, the biological treatment (SBR) can be evaluated as follows: the overall organic matter treatment efficiency was 43.0 % in terms of TOC and 33.6 % in terms of COD (Table 1). Most removal was for the < 1K Da fraction and the > 0.45µm fraction, 48.6 % TOC and 52.5 % COD was removed at < 1K Da fraction and 85.0 % TOC and 99.0 % COD was removed for the > 0.45 µm fraction. The intermediate size fraction increased after biological treatment (SBR). The 100K - 0.45 µm fraction increased by 646.4 % and 218.8 % in terms of TOC and COD, the 1K -100K Da fraction increased by 45.5% in terms of COD. This increase in the intermediate size fraction

during treatment may be caused by partial degradation of larger size material and/or bio-coagulation of the smaller fraction in the activated sludge process.

For NH landfill leachate samples, the overall organic matter treatment efficiency was 56.5 % in terms of TOC and 34.0 % in terms of COD (Table 1). Similar to the PA leachates, the < 1K Da fraction was dominant among all size fractions in NH leachates (Fig.2 B). In untreated NH leachate 83.4 % TOC and 85.6 % COD were contributed by the < 1K Da fraction. In biologically treated (PACT) NH leachate, 49.1 % TOC and 74.4 % COD was contributed by the < 1K Da fraction. Most treatment occurred for the < 1K Da fraction; 74.4 % TOC and 42.6 % COD were removed for this fraction, which is similar to the PA leachate.

Different from the PA landfill, the > 0.45 μm fraction increased by 53.0 % and 212.1% in terms of TOC and COD after PACT treatment in NH landfill. The existence of powdered activated carbon in the PACT treatment process might have contributed to this increase.

It should be noted that the BOD of the biologically treated leachates was fairly low (15.3 mg/L and 9.66mg/L for PA and NH treated leachates respectively, shown in Table 1), implying the bio-recalcitrant nature of organic matter in treated leachates.

3.2. Organic nitrogen

Fig.3 shows the organic nitrogen concentration in different size fractions of untreated and treated leachates from the PA landfill. Fig. 3 part A shows the cumulative data and Fig. 3 part B shows the distributive data.

As shown in Fig.3 part A, organic nitrogen concentration increased with increasing MW/pore size. However, for both untreated and treated leachates, a significant fraction of the organic nitrogen is between 1K Da and 100 K Da, which is different from the COD and TOC.

A comparison between organic nitrogen size distribution and pore size of commonly used membrane separation technologies provides some useful information for the potential use of membrane treatment for landfill leachates. As shown in Fig.3 part A, for the PA treated leachate, nanofiltration with MWCO of 1K Da can remove 57.9% organic nitrogen. UF and MF will remove much less organic nitrogen than NF. Of all the membrane separation technologies listed in Table 2, only RO can provide a high degree of organic nitrogen removal.

The distributive data (Fig.3 part B) show that the < 1 K Da fraction is dominant in terms of organic nitrogen size distribution; 53.8 % and 42.1 % of organic nitrogen is contributed by < 1K Da fraction in untreated and treated PA landfill leachates respectively. By comparing the total amount and size distribution of organic nitrogen in untreated and treated PA leachates, the on-site biological treatment process (SBR) can be evaluated. Most organic nitrogen removal was by the smallest size fraction (< 500Da fraction) and second largest fraction (100K Da-0.45 μm fraction). 68.5 % and 5.6 % organic nitrogen was removed in the < 500 Da fraction and 100K-0.45μm fraction. Organic nitrogen in the intermediate size fractions increased after SBR treatment. The 500-1K Da fraction and the 1K-100K Da fraction increased by 42.4 % and 13.4 % respectively. The increase might be caused by partial degradation or bio-coagulation.

Different from the TOC and COD, organic nitrogen in the largest fraction (>0.45μm) was not removed by biological treatment (SBR). The organic nitrogen concentration was 6.8 mg/L in the

influent and 6.6mg/L in the effluent, indicating that removal of the > 0.45 μm was non-nitrogen-containing organic matter, such as polysaccharides and lipids.

Correlations between organic nitrogen and organic matter (TOC and COD) of PA landfill leachates are shown in Fig. 4. As shown in this figure, concentrations of organic matter (in terms of TOC and COD) are directly proportional to organic nitrogen, in both untreated and treated PA leachates. (R^2 values were 0.9425 and 0.8726 for TOC and COD in untreated leachates, 0.8747 and 0.9599 for TOC and COD in treated leachates respectively.)

As shown in Fig.4 part A, the higher slope of the regression line for organic nitrogen versus TOC in treated PA leachate than untreated PA leachate indicates that, more organic carbon got removed than organic nitrogen during the biological treatment (SBR). As calculated from the regression line slopes, the C/N ratio in the organic matter was reduced from 8.9 to 5.8, indicating that organic nitrogen is more bio-refractory than other organic matter.

Both regression lines in Fig.4 part A have a similar intercept on the horizontal axis, 14.43mg/L for untreated samples and 12.07mg/L for treated samples, indicating the existence of non-nitrogen organic compounds in < 500 Da fraction for both untreated and treated leachates samples, and this fraction did not get removed by biological treatment.

The correlation between organic nitrogen and COD in leachate fractions before and after treatment is shown in Fig.4 part B. The slopes did not change much for the untreated and treated leachates, and intercepts on X-axis were very close to zero, indicating the oxidation state or nitrogen containing organic matter was altered very little by the SBR treatment. These data also suggest that COD is a better surrogate for organic nitrogen than TOC.

3.3. UV$_{254}$ absorbance and SUVA$_{254}$

UV quenching of landfill leachate is a concern for the UV disinfection process in the downstream WWTPs. UV_{254} absorbance and $SUVA_{254}$ were analyzed to evaluate the treatment efficiency for UV quenching substances and the potential impact on the receiving WWTPs. Fig. 5 shows the UV_{254} absorbance of the unfiltered sample and size fractions of untreated and treated leachates from PA and NH landfills. First, for the unfiltered leachate samples, UV_{254} absorbance was reduced by different amounts in the two treatment plants. PA leachate UV absorbance was reduced from 15.3 to 13.9 cm^{-1} (9.2 % removal), while the NH leachate was reduced from 19.7 to 9.0 cm^{-1} (54.3 % removal), indicating a better performance of PACT (NH landfill) than the conventional biological process (PA landfill) for UV materials.

By comparing UV_{254} absorbance in size fractions before and after treatment, it can be seen that for PA leachate (SBR treated), most treatment of UV_{254} absorbance occurred for the smaller size fractions, while NH leachate (PACT treated) mostly occurred for the larger size fractions. As shown in Fig.5 part A (PA leachate), UV_{254} absorbance of < 500 Da and > 100K Da fractions was reduced by 69.9 % and 36.2 %, respectively, while the 500 Da-1K Da and 1K -100K Da fractions increased by 25.7 % and 33.8 % after treatment, which coincides with the organic matter and organic nitrogen results. As shown in Fig.5 part B (NH leachate), UV_{254} absorbance of all size fractions was reduced. The 1K Da- 100K Da and > 100 K Da fractions contribute to most of the removal (5.13 cm^{-1} and 5.26 cm^{-1} respectively).

Size distribution results in Fig.5 provide significant implication for the membrane treatment of UV quenching substances. When nanofiltration with a MWCO of 1K is applied to the biologically treated leachates, UV_{254} absorbance can be reduced to 4.88 cm^{-1} and 4.16 cm^{-1} for PA and NH leachates respectively, which means that, when 5% of biologically treated leachate is mixed with WWTP wastewater, the UV_{254} transmittance will be up to 57.02% and 61.94% for

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the PA and NH leachates, respectively. It appears that nanofiltration can be an effective treatment technology as a polishing step for biologically treated landfill leachates to reduce interference with UV disinfection in the receiving WWTPs.

SUVA$_{254}$ data for PA and NH leachates and leachate size fractions are shown in Fig.6. In Fig.6 part A, it is shown that SUVA of PA leachate increased from 2.08 to 3.44 after the SBR treatment, indicating the bio-refractory property of UV quenching substance compared with other organic matter. On the other hand, NH leachates did not show a SUVA increase during the PACT treatment (from 2.7 to 2.8), implying a different treatment mechanism for UV quenching substances. The existence of powdered activated carbon in the PACT process is the major difference between SBR and PACT. The UV quenching substances showed some bio-refractory properties so it appears that carbon absorption is likely to be responsible for the UV quenching substance removal in the PACT process. Also, it is suspected that, lignin and lignin derivatives originating from paper, cardboard and other wood products in the landfill are responsible for the UV quenching.

3.4. FT/IR

FT/IR spectra obtained from freeze dried leachate samples are shown in Fig.7 and Fig.8. It should be noted that, only the wavenumbers of the peaks and not the magnitudes of the peaks can be compared directly for the FT/IR spectra. Interpretation of the FT/IR spectra of leachates samples was based on a structural spectroscopy textbook (Lambert et al., 1998) and literature data for landfill leachates (Calace et al., 2001) and humic substances (Leenheer et al., 1981; Zhang et al., 2009).

As shown in Fig.7, the FT/IR spectra of untreated and treated PA leachates are similar. Both spectra have the absorption bands at 1400-1310 cm^{-1} and this may be attributed to COO- groups in carboxylic salts (Calace et al., 2001). The absorbance band at 1150-1070 cm^{-1} was assigned to C-O-C in aliphatic ethers. It should be noted that the absorbance band at 1620-1610cm^{-1} was assigned to the aromatic C=C stretch (Lambert et al., 1998, Bu et al., 2010), the absorption around 1030-950 cm^{-1} was resulted from the carbon rings in cyclic compounds and the two peaks at 890-805 cm^{-1} may be attributed to the CH in trisubstituted benzenes (Lambert et al., 1998). All the peaks at 1620-1610cm^{-1}, 1030-950 cm^{-1}, and 890-805 cm^{-1} may be attributed to the aromaticity and strong UV$_{254}$ absorption in both untreated and treated PA leachates. Complex absorption bands around700- 650cm^{-1} are related to halogenated compounds (Zhang et al., 2009). Amide groups are not shown because of the interference of hydroxyl groups which absorb in the same region (Leenheer et al., 1981).

Fig.8 shows the FT/IR spectra of untreated and treated NH leachates. The spectrum of untreated NH leachate is similar to those of PA leachates, except the lack an absorption band around 1150-1070cm^{-1}, indicating the absence of C-O-C in aliphatic ethers. The FT/IR spectrum of NH treated leachate is different from the untreated sample. No conspicuous signal appeared around the 1080-950cm-1 and 890-805cm-1 regions, which are usually assigned to aromatic groups. This result is in agreement with the lower UV$_{254}$ absorption of NH treated leachate.

4. Discussion

Size distribution in conjunction with a variety of analysis was applied to leachate samples before and after on-site biological treatment systems in two landfills, so that the treatment was evaluated from a size-distribution standpoint.

A number of studies have been done on the size fractionation of landfill leachate. Harmsen (1983) , Li et al. (2009) and Lou et al. (2009b) did the identification and characterization of organic matter in leachates at different stabilization stages; Slater et al. (1985), Gourdon et al. (1989), Lou and Zhao (2007), and Lou et al. (2009a) examined the amount and properties of organic matter in leachates under different biological treatment conditions (aerobic, anaerobic etc.). There is an agreement that <1K Da fraction is predominant among all size fractions for a variety of leachate samples under different stabilization conditions and through different biological treatments. The results of this study confirmed this conclusion.

Also, this study agrees with the previous results (Li et al., 2009) that biological treatment is effective for low molecular weight organic matter. Intermediate and large size fraction increased after biological treatment, even though the total amount of organic matter decreased, which could be explained by bio-flocculation of smaller size fractions and partial degradation of larger size fractions.

Commonly used membrane separation technologies were compared with the organic matter size distribution data of biologically treated leachates. Even though slight polymerization was observed in biological treatment, it was found that microfiltration and ultrafiltration cannot provide enough removal to allow biologically treated leachate to be discharged directly. In practice, MF and UF are usually used in partnership with other treatments, such as pre-treatment for RO (Syzdek and Ahlert, 1984; Piatkiewicz et al., 2001) and post-treatment for biological processes (Bohdziewicz et al., 2001). NF shows some effectiveness for removing macromolecules and particles, but it really depends on the characteristics of material constituting the membrane, especially the molecular weight cut off. In this study, assuming the typical molecular weight cut off of NF is 1 K Da, the data showed 53.0 % COD and 36.1 % TOC

removal for PA treated leachate and 25.6 % COD and 50.8 % TOC removal for the NH treated leachate. These data are within the range previously reported for landfill leachate treatment by NF with different membrane materials and geometry (Rautenbach and Mellis., 1994; Trebouet et al., 1999; Marttinen et al., 2002). However, it is still not enough for NF to work independently to prepare leachate for direct discharge to receiving waters. When combined with physical treatment, NF was reported to remove 70-80% of the COD (Trebouet et al., 2001). Reverse osmosis is one of the most promising and efficient methods among all membrane separation technologies. As reported previously (Baumgarten et al., 1996; Bohdziewicz et al., 2001; Ahn et al., 2002; Linde et al., 1995), up to 98% removal was achieved for organic matter (in terms of COD) and heavy metals in landfill leachates. Drawbacks for RO were found to be membrane fouling and the large amount of reject liquid (Renou et al., 2008).

Based on the cost effectiveness, discharging of on-site treated leachates to WWTPs is widely used. Therefore, the impact of the distinctive characteristics of leachates on the downstream WWTPs is unavoidable. Two aspects of these impacts from leachate components were explored in this study, one is organic nitrogen, and the other is UV quenching substances.

This study is one of the first to investigate the occurrence, abundance and characteristics of organic nitrogen in landfill leachates. Previous studies show that organic nitrogen, which cannot be removed by nitrification/denitrification, has been recognized as an important issue for WWTPs because it might cause eutrophication (Westgate and Park, 2010) and might be the precursor of nitrogen containing disinfection by-products (Mitch and Sedlak, 2004). Landfill leachates discharged to WWTPs can be one of the major sources of organic nitrogen. Results of this study show that organic nitrogen in the < 1K Da fraction is dominant (53.8 % and 42.1 % in untreated and treated samples respectively) for PA landfill leachates, which is similar to

wastewater result (67±24%) (Pehlivanoglu-Mantas and Sedlak 2008). This size distribution pattern indicates some difficulties for membrane treatment. Moreover, organic nitrogen showed more bio-refractory properties than other organic matter. The treatment efficiency for organic nitrogen in the on-site biological process (25.1 %) was lower than TOC (43.1 %) and COD (33.6 %) as shown in Table 1. Also, the C: N ratio before and after biological treatment (Fig.4 part A) confirmed that less organic nitrogen was removed in the biological process (SBR) than organic carbon. All above information indicates the challenge brought by the organic nitrogen in landfill leachates to the receiving WWTPs. Regarding the source of organic nitrogen in landfill leachates, a portion of organic nitrogen in landfill leachates is thought to be associated with humic substances, based on their abundance in landfill leachates, their elemental composition and refractory properties.

Another impact of leachate content on WWTPs is UV quenching. Landfill leachates from different sources showed severe UV quenching even when diluted. Preliminary results show that a wastewater containing 5% biologically treated landfill leachate can block 65-80% UV_{254} light. This number increases up to 98% for untreated young leachate. The results in this study show that UV quenching substances are not readily degradable in biological processes (Fig. 5 part A). Also, an increase in the $SUVA_{254}$ value after biological treatment (Fig.6 part A) indicates that organic matter responsible for UV quenching is resistant to biodegradation. However, the combination of biological treatment and activated carbon (PACT process in NH landfill) showed some success in removing UV quenching substances (Fig. 5 part B). Also in the PACT process, there was no obvious change on $SUVA_{254}$ observed in treatment (Fig.6 part B), indicating UV quenching substances were removed proportionally along with other organic matter. Moreover, size distribution data showed that UV quenching substance treatment in the PACT process was

mostly contributed by the removal of the > 100 K Da fraction, which is believed to be the target size fraction of activated carbon treatment. All the above evidence implies that activated carbon is effective for UV quenching substance removal. Regarding the functional groups responsible for UV quenching, FT/IR data (Fig.8) shows the presence and absence of aromatic groups in untreated and treated NH leachates. Based on their molecular structure and abundance in municipal solid waste of landfills, lignin and lignin derivatives (including humic substance) are thought to be the major source of these aromatic groups.

5. Conclusion

This study evaluated the on-site biological treatment for landfill leachates and provided insight into the potential impact of landfill leachates on the receiving WWTPs. The main conclusions that can be drawn from this study are as follows:

(1) Generally, landfill leachates showed refractory properties in the biological processes examined. No more than half of organic contaminants could be removed in the on-site biological treatment facilities, while most BOD was removed, leaving the landfill leachates effluent a potential impact on the downstream WWTPs.

(2) < 1K Da fraction, represented by TOC, COD and organic nitrogen, was found to be predominant in most untreated and treated landfill leachates, indicating difficulties for membrane treatment (except RO) .

(3) In the on-site biological processes, most removal happened at < 1K Da fraction, while, intermediate fractions increased after treatment, which might be caused by bio-flocculation and partial degradation.

(4) Organic nitrogen in landfill leachates showed more bio-refractory properties than other organic matter. Different from sewage, organic nitrogen in landfill leachate is presumed to be more associated with humic substances than proteinaceous compounds.

(5) FT/IR data showed that aromatic groups might be responsible for the UV quenching phenomenon. Combination of activated sludge and activated carbon (PACT) showed better treatment performance on UV quenching substance, indicating carbon absorption may be the mechanism for UV quenching substance removal.

(6) NF with an appropriate MWCO can reduce the UV quenching substances in landfill leachates and decrease the interferences on the downstream WWTPs UV disinfection.

Reference:

Ahn, W.Y., Kang, M.S., Yim, S.K., Choi, K.H., 2002. Advanced landfill leachate treatment using an integrated membrane process. Desalination 149 (1-3), 109–114.

APHA, 1998. Standard Methods for Examination of Water and Wastewater. In: Clesceri, L.S., Greenburg, A.E., Eaton, A.D. (Eds.), 20th Ed. American Public Health Association, Washington, D.C.

Baumgarten, G., Seyfried, C.F., 1996. Experiences and new developments in biological pretreatment and physical post-treatment of landfill leachate. Water Science and Technology 34 (7-8), 445–453.

Berge, N.D., Reinhart, D.R., Dietz, J., Townsend, T., 2006. In situ ammonia removal in bioreactor landfill leachate. Waste Management 26(4), 334-343.

Bohdziewicz, J., Bodzek, M., Gorska, J., 2001. Application of pressure-driven membrane techniques to biological treatment of landfill leachate. Process Biochemistry 36 (7), 641-646.

Boulton, R.B., Singleton, V.L., Bisson, L.F., Kunkee, R.E., 1996. Principles and Practices of Winemaking. Chapman & Hall, New York.

Bu, L., Wang, K., Zhao, Q.L., Wei, L.L., Zhang, J., Yang, J.C., 2010. Characterization of dissolved organic matter during landfill leachate treatment by sequencing batch reactor, aeration corrosive cell-Fenton, and granular activated carbon in series. Journal of Hazardous Materials 179 (1-3), 1096-1105.

Calace, N., Liberatori, A., Pertonio, B.M., Pietroletti, M., 2001. Characteristics of different molecular weight fractions of organic matter in landfill leachate and their role in soil sorption of heavy metals. Environmental Pollution 113 (3), 331-339.

Calli, B., Mertoglu, B., Inanc B., 2005. Landfill leachate management in Istanbul: applications and alternatives, Chemosphere 59 (6), 819–829.

Cheung, K.C., Chu, L.M., Wong, M.H., 1997. Ammonia stripping as a pretreatment for landfill leachate, Water, Air, & Soil Pollution 94 (1-2), 209–221.

Chian, E.S.K., DeWalle, F.B., 1976. Sanitary landfill leachates and their treatment. Journal of the Environmental Engineering Division 102 (2), 411-431.

Di Palma, L., Ferrantelli, P.,Merli, C., Petrucci, E., 2002.Treatment of industrial landfill leachate by means of evaporation and reverse osmosis. Waste management 22 (8), 951-955.

El-Fadelf1, M., Findikakis, A.N., Leckie, J.O., 1997. Environmental impacts of solid waste landfilling, Journal of Environmental Management 50(1), 1–25.

Erickson, H.P., 2009. Size and Shape of Protein Molecules at the Nanometer Level Determined by Sedimentation, Gel Filtration, and Electron Microscopy. Biological Procedures Online, 11(1), 32-51.

Gourdon, R., Comel, C., Vermande, P., Veron, J., 1989. Fractionation of the Organic-matter of a landfill leachate before and after aerobic or anaerobic biological treatment. Water Research 23(2), 167-173.

Ha, D.Y., Cho, S.H., Kim, Y.K., Leung, S.W., 2008. A New Approach to Characterize Biodegradation of Organics by Molecular Mass Distribution in Landfill Leachate. Water Environment Research 80 (8), 748-756.

Harmsen, J., 1983. Identification of organic compounds in leachate from a waste tip. Water Research 17(6), 699-705.

He, P.J., Xue, J.F., Shao, L.M., Li, G.J., Lee, D.J., 2006a. Dissolved organic matter (DOM) in recycled leachate of bioreactor landfill. Water Research 40 (7), 1465-1473.

He, P.J., Shao, L.M., Guo, H.D., Li, G.J., Lee, D.J., 2006b. Nitrogen removal from recycled landfill leachate by ex situ nitrification and in situ denitrification. Waste Management 26(8), 838-845.

Hedges, J.I., Mann, D.C., 1979. The characterization of plant tissues by their lignin oxidation products. Geochimica et Cosmochimica Acta 43 (11), 1803-1807.

Jokela, J.P.Y., Kettunen, R.H., Sormunen, K.M., Rintala, J.A., 2002. Biological nitrogen removal from municipal landfill leachate: low-cost nitrification in biofilters and laboratory scale in-situ denitrification. Water Research 36(16), 4079-4087.

Kjeldsen, P., Barlaz, M.A., Rooker, A.P., Baun, A, Ledin, A., Christensen,T.H., 2002. Present and Long-Term Composition of MSW Landfill Leachate: A Review. Critical Reviews in Environmental Science and Technology 32(4), 297-336.

Krasner, S.W., Westerhoff, P., Chen, B., Rittmann, B., Nam, S., Amy, G., 2009. Impact of Wastewater Treatment Processes on Organic Carbon, Organic Nitrogen, and DBP Precursors in Effluent Organic Matter. Environmental Science and Technology 43 (8), 2911-2918.

Kurniawan, T.A., Lo, W., Chan, G.Y.S., 2006. Radicals-catalyzed oxidation reactions for degradation of recalcitrant compounds from landfill leachate. Chemical Engineering Journal 125 (1), 35-57.

Lambert, J.B., Shurvell, H.F., Lightner, D.A., Cooks, R.G., 1998. Organic Structural Spectroscopy. Prentice-Hall, New Jersey.

Leenheer, J.A., 1981. Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural water and wastewaters. Environmental Science and Technology 15(5), 578-587.

Li, R., Yue, D., Liu, J., and Nie, Y., 2009. Size fractionation of organic matter and heavy metals in raw and treated leachate. Waste Management 29 (9), 2527-2533.

Li, X.Z., Zhao, Q.L., Hao, X.D., 1999. Ammonium removal from landfill leachate by chemical precipitation. Waste Management 19 (6), 409–415.

Linde, K., Jonsson, A.S., Wimmerstedt, R., 1995. Treatment of three types of landfill leachate with reverse osmosis. Desalination 101(1), 21–30.

Lou, Z., Zhao, Y., 2007. Size-fractionation and characterization of refuse landfill leachate by sequential filtration using membranes with varied porosity. Journal of Hazardous Materials 147 (1-2), 257-264.

Lou, Z., Chai, X., Niu, D., Ou, Y., Zhao, Y., 2009a. Size-fractionation and characterization of landfill leachate and the improvement of Cu2+ adsorption capacity in soil and aged refuse. Waste Management 29 (1), 143-152.

Lou, Z., Dong, B., Chai, X., Song, Y., Zhao, Y., Zhu, N., 2009b. Characterization of refuse landfill leachates of three different stages in landfill stabilization process. Journal of Environmental Sciences (China) 21 (9), 1309-1314.

Marttinen, S.K., Kettunen, R.H., Sormunen, K.M., Soimasuo, R.M., Rintala, J.A., 2002. Screening of physical–chemical methods for removal of organic material, nitrogen and toxicity from low strength landfill leachate, Chemosphere. 46 (6), 851–858.

Mitch, W.A., Sedlak, D.L., 2004. Characterization and fate of N-nitrosodimethylamine precursors in municipal wastewater treatment plants. Environmental Science and Technology 38(5), 1445-1454.

Ozturk, I., Altinbas, M., Koyuncu, I., Arikan, O., Gomec-Yangin, C., 2003. Advanced physico-chemical treatment experiences on young municipal landfill leachates, Waste Management 23 (5), 441–446.

Pehlivanoglu, E., Sedlak, D.L., 2004. Bioavailability of wastewater-derived organic nitrogen to the alga Selenastrum Capricornutum. Water Research 38 (14-15), 3189-3196.

Pehlivanoglu-Mantas, E., Sedlak, D.L., 2008. Measurement of dissolved organic nitrogen forms in wastewater effluents: Concentrations, size distribution and NDMA formation potential. Water Research 42 (14), 3890-3898.

Piatkiewicz, W., Biemacka, E., Suchecka, T., 2001. A polish study: treating landfill leachate with membranes. Filtration+ Separation 38 (6), 22-26.

Qasim, S.R., 1999. Wastewater treatment plants: Planning, design, and operation. Technomic, Pennsylvania.

Rautenbach, R., Mellis, R., 1994. Waste water treatment by a combination of bioreactor and nanofiltration. Desalination 95 (2), 171–188.

Renou, S., Givaudan, J.G., Poulain, S., Dirassouyan, F., Moulin, P., 2008. Landfill leachate treatment: Review and opportunity. Journal of Hazardous Materials 150 (3), 468-493.

Slater, C.S., Uchrin, C.G., Ahlert, R.C., 1985. Ultrafiltration processes for the characterization and separation of landfill leachates. Journal of Environmental Science and Health, Part A 20(1), 97-111.

Syzdek, A.C., Ahlert, R.C., 1984. Separation of landfill leachate with polymeric ultrafiltration membranes. Journal of Hazardous Materials 9 (2), 209-220.

Trebouet, D., Schlumpf, J.P., Jaouen, P., Quemeneur, F., 2001. Stabilized landfill leachate treatment by combined physicochemical–nanofiltration process, Water Research 35 (12), 2935–2942.

Trebouet, D., Schlumpf, J.P., Jaouen, P., Maleriat, J.P., Quemeneur, F., 1999. Effect of operating conditions on the nanofiltration of landfill leachates: pilotscale studies. Environmental Technology 20 (6), 587–596.

US EPA, 2010. Municipal Solid Waste Generation, Recycling, and Disposal in the United States: Facts and Figures for 2009. EPA-530-F-010-012, Washington, DC.

Vilar, V., Rocha, E., Mota, F., Fonseca, A., Saraiva, I., Boaventura, R., 2011. Treatment of a sanitary landfill leachate using combined solar photo-Fenton and biological immobilized biomass reactor at a pilot scale. Water Research 45 (8), 2647-2658.

Westgate, P.J., Park, C., 2010. Evaluation of Proteins and Organic Nitrogen in Wastewater Treatment Effluents. Environmental Science and Technology 44 (14), 5352-5357.

Wiszniowski, J., Robert, D., Surmacz-Gorska, J., Miksch, K., Weber, J.V., 2006. Landfill leachate treatment methods: A review. Environmental Chemistry Letters 4 (1), 51–61.

Xu, Z.Y., Zeng, G.M., Yang, Z.H., Xiao, Y., Cao, M., Sun, H.S., Ji, L.L., Chen, Y., 2010. Biological treatment of landfill leachate with the intergration of partial nitrification, anaerobic ammonium oxidation and heterotrophic denitrification. Bioresource Technology 101(1), 79-86.

Zhang, L., Li, A., Lu, Y., Yan, L., Zhong, S., Deng, C., 2009. Characterization and removal of dissolved organic matter (DOM) from landfill leachate rejected by nanofiltration. Waste Management 29 (3), 1035-1040.

Table 3-1. Characteristics of PA and NH leachates.

Parameter	Unit	PA untreated	PA treated	NH untreated	NH treated
TOC	mg/L	734.26±208.38	418.47±100.52	722.38±21.39	313.53±27.59
COD	mg/L	2240.00±998.58	1488.00±219.31	2713.00±16.97	1792.00±146.64
BOD	mg/L	378.0±14.4	15.30±0.08	n.a.[a]	9.66±2.04
UV$_{254}$ Abs.	cm-1	15.31±0.46	13.85±0.25	19.75±0.23	9.03±0.27
TN	mg/L	850.00	75.83±0.24	1305±21.21	801.67±17.68
NO$_2$	mg/L	n.d.[b]	n.d.	n.d.	368.26
NO$_3$	mg/L	0.21	1.41	n.d.	475.67
NH$_3$	mg/L	796.00	13.49±0.27	1138±16.97	6.41±0.17
pH	—	7.61	6.76	6.88	6.47
PO$_4$	mg/L	0.08	0.04	1.73	n.d.
SO$_4$	mg/L	72.11	81.34	22.97	42.31
Na	g/L	1.92±0.08	1.95±0.11	2.15±0.38	2.13±0.43
Mg	mg/L	92.64±4.75	97.25±0.22	117.1±2.7	111.14±5.60
Si	mg/L	33.08±2.45	30.17±3.21	42.7±0.0	23.93±1.84
P	mg/L	7.10±0.92	5.1629±0.64	6.9±0.4	3.83±0.62
S	mg/L	221.84±56.66	228.38±37.51	207.2±45.0	159.10±2.12
Cl	g/L	2.5±0.22	2.59±0.21	4.78±0.42	4.15±0.44
K	mg/L	487.58±33.55	496.41±26.00	795.6±38.1	627.70±24.89
Ca	mg/L	59.72±4.25	102.56±4.44	115.1±3.6	226.88±9.79
Cr	mg/L	0.77±0.03	0.66±0.04	0.3±0.0	0.13±0.01
Fe	mg/L	5.18±0.82	3.89±0.88	3.1±0.9	1.98±0.85
Mn	mg/L	0.24±0.05	0.33±0.09	0.2±0.0	0.44±0.08
Cu	mg/L	0.11±0.01	0.08±0.01	0.0±0.0	0.01±0.00

Zn	mg/L	0.38±0.00	0.47±0.01	0.0±0.0	0.05±0.04

a not available

b not detected

Table 3-2. Commonly used membrane separation technologies and corresponding molecular weight cut off.

| Membrane separation	MW cut-off	Material	Reference
MF	0.2µm	Polypropylene	(Piatkiewicz et al.,2001)
UF	300 K Da	Polysulfone	(Bohdziewicz et al., 2001)
	50-80 K Da	Polysulfone	(Piatkiewicz et al., 2001)
NF	1 K Da	Zirconium oxide	(Trebouet et al.,2001)
	450 Da	Polyacrylonitrile	(Trebouet et al.,1999)
	200-300 Da	Polymer	(Marttinen et al., 2002)
RO	10-100 Da[a]	Cellulose acetate	(Bohdziewicz et al., 2001)
	10-100 Da[a]	Polyamide	(Di Palma et al., 2002)

a MWCO of RO is referred to Boulton et al. (1998)
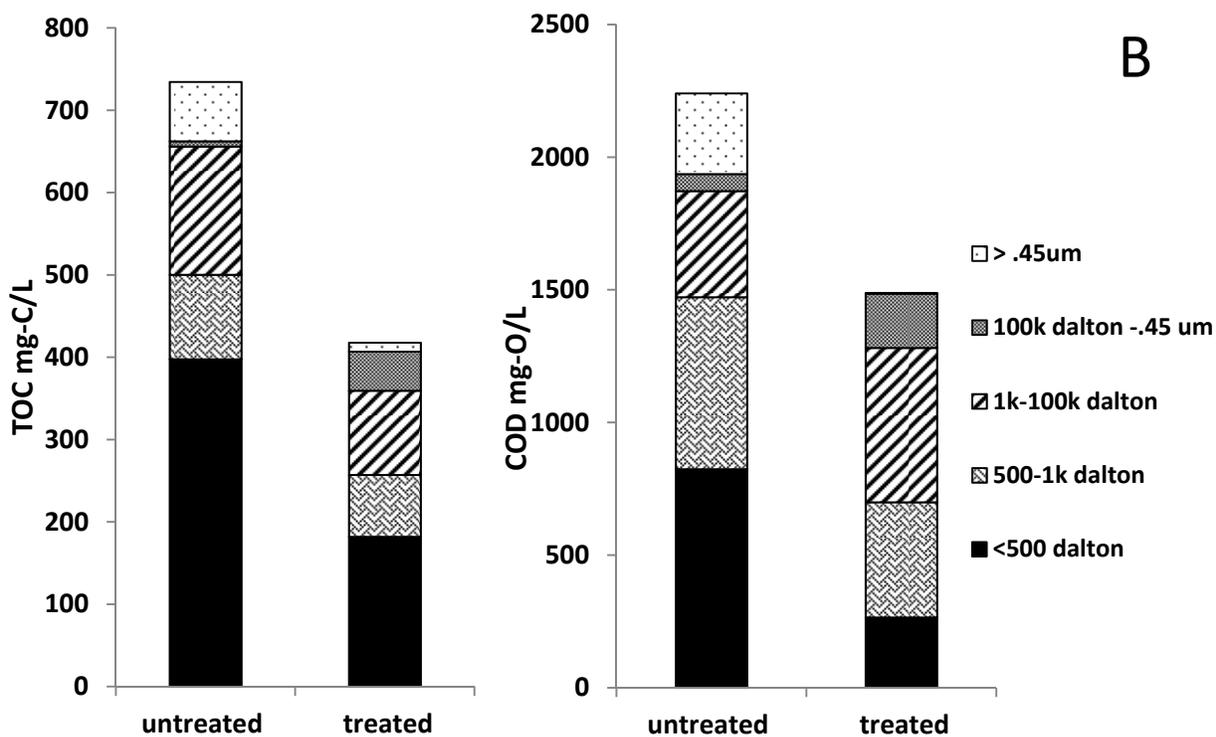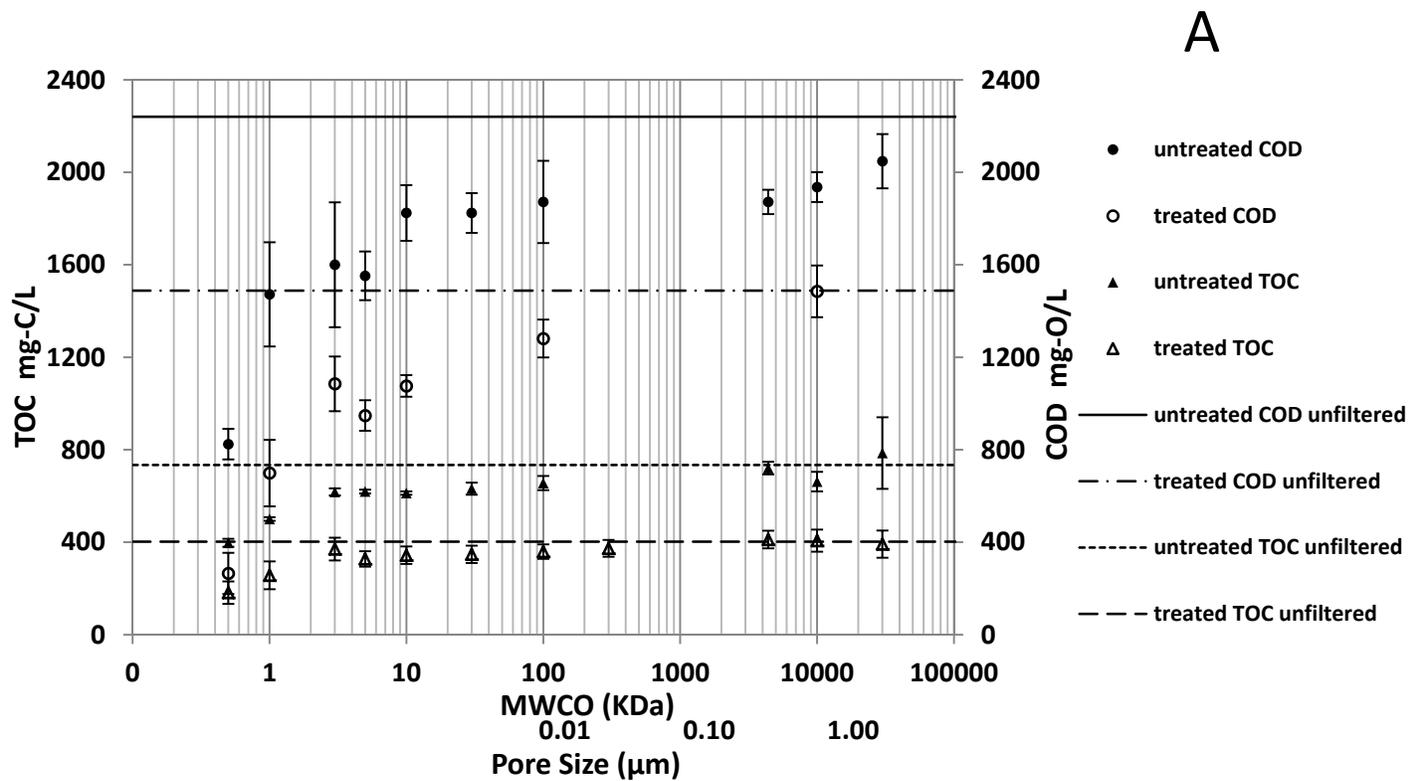
Fig. 3-1. Size distribution of organic matter in treated and untreated PA leachates in terms of TOC and COD shown as (A) accumulative data and (B) distributive data. TOC was measured 3 to 6 times; COD was measured 3 to 5 times for statistical purpose. Error bar indicates standard deviation.
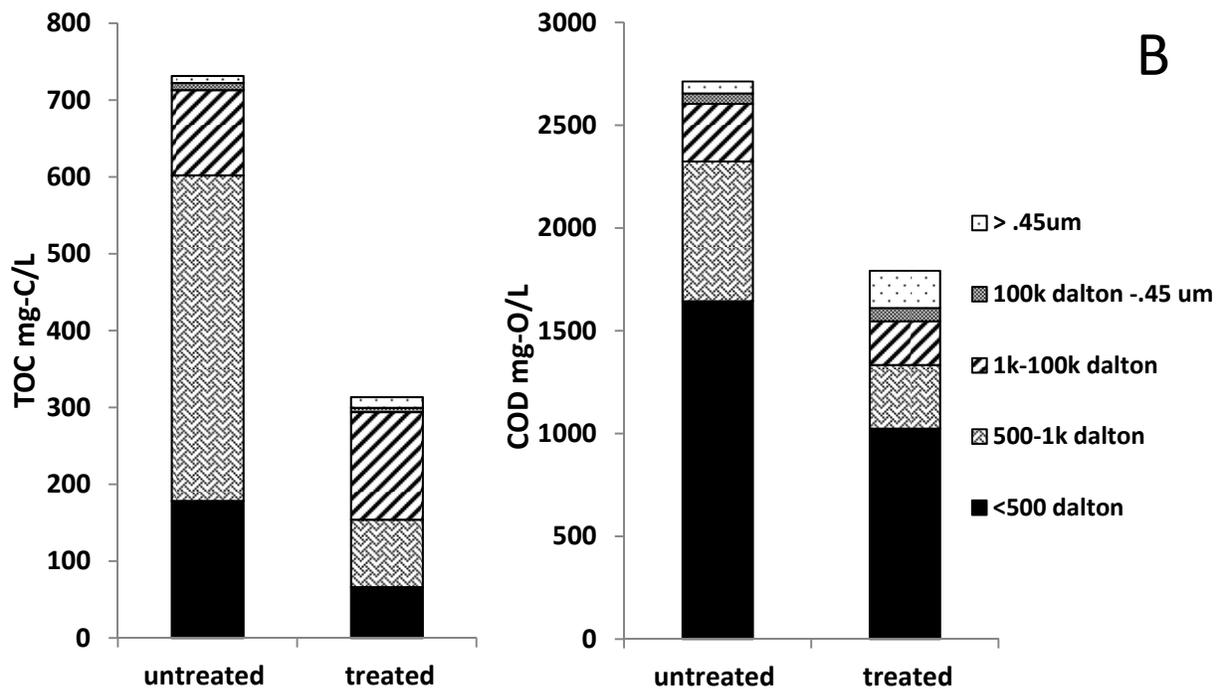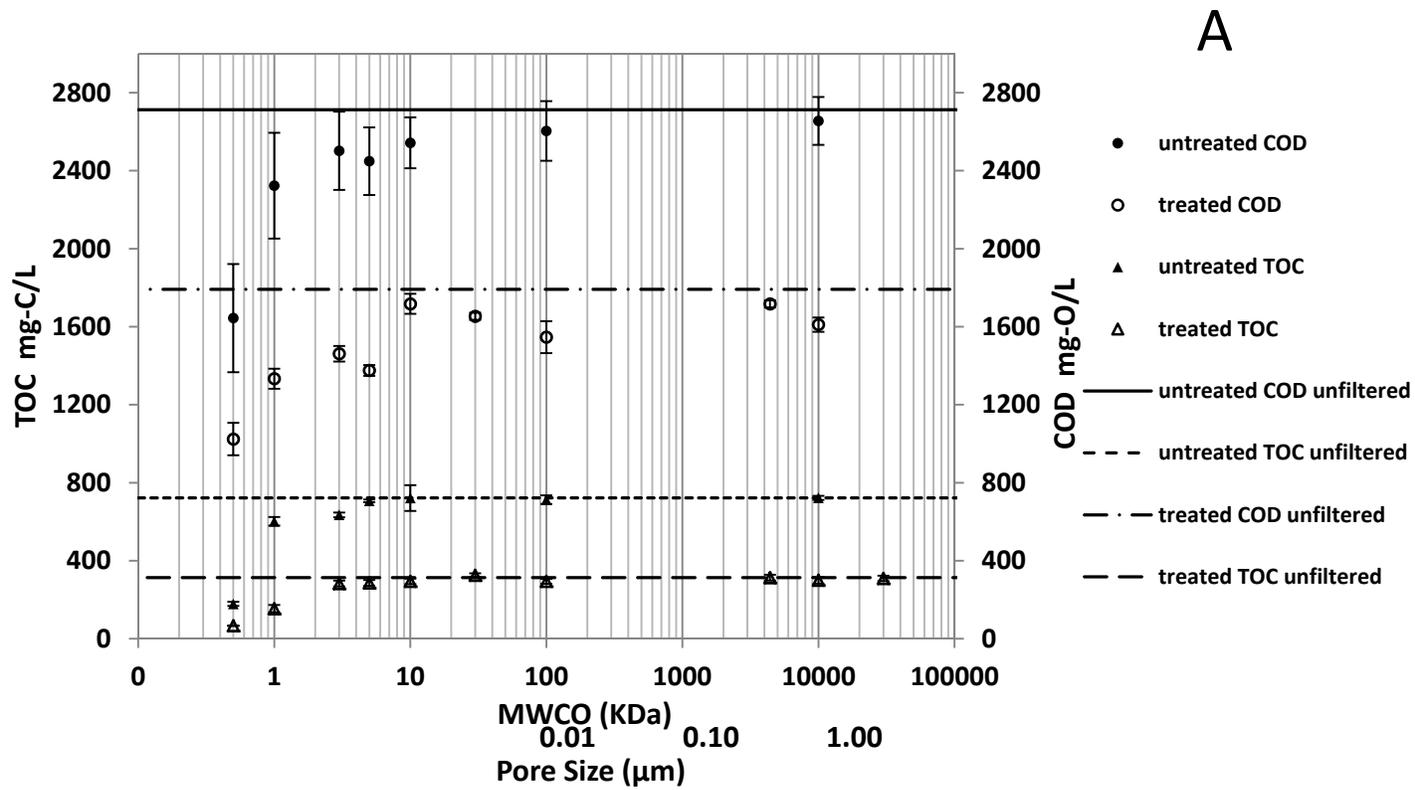
Fig. 3-2. Size distribution of organic matter in treated and untreated NH leachates in terms of TOC and COD shown as (A) accumulative data and (B) distributive data. TOC was measured 3 to 6 times; COD was measured 3 to 5 times for statistical purpose. Error bar indicates standard deviation.
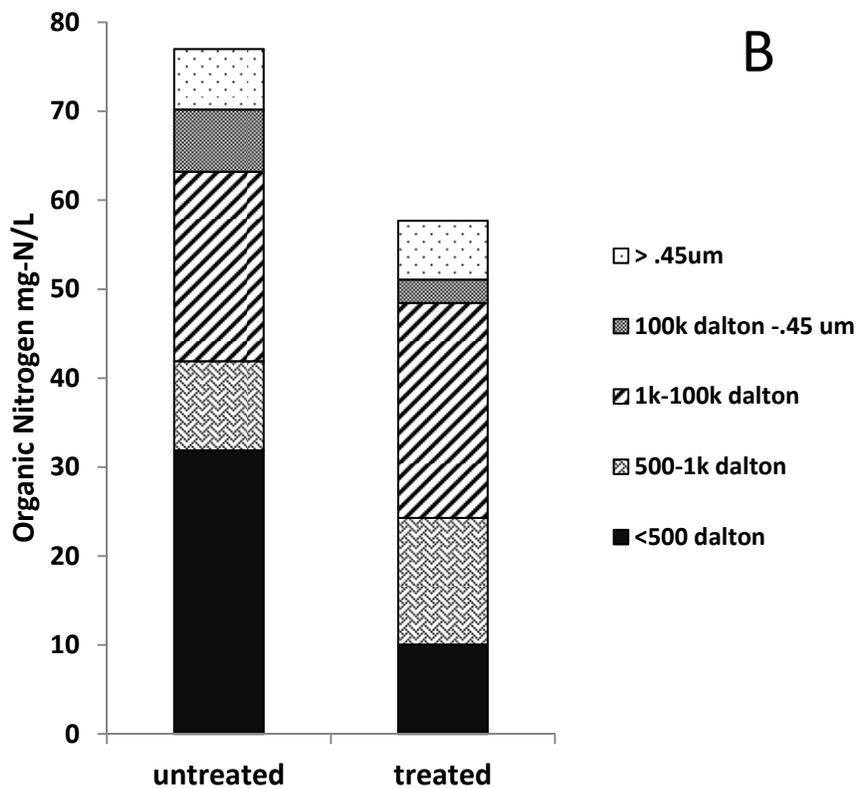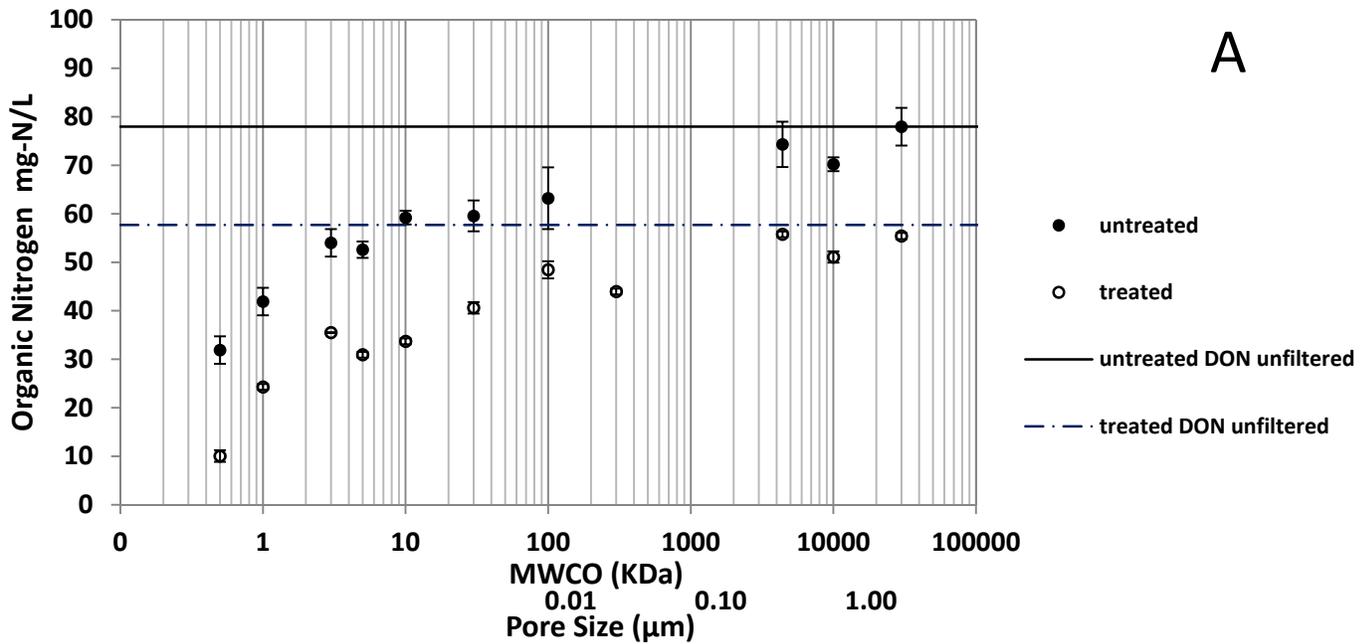
Fig. 3-3. Size distribution of organic nitrogen in treated and untreated PA leachates shown as (A) accumulative data and (B) distributive data. Organic nitrogen was measured 3 times for statistical purpose. Error bar indicates standard deviation.
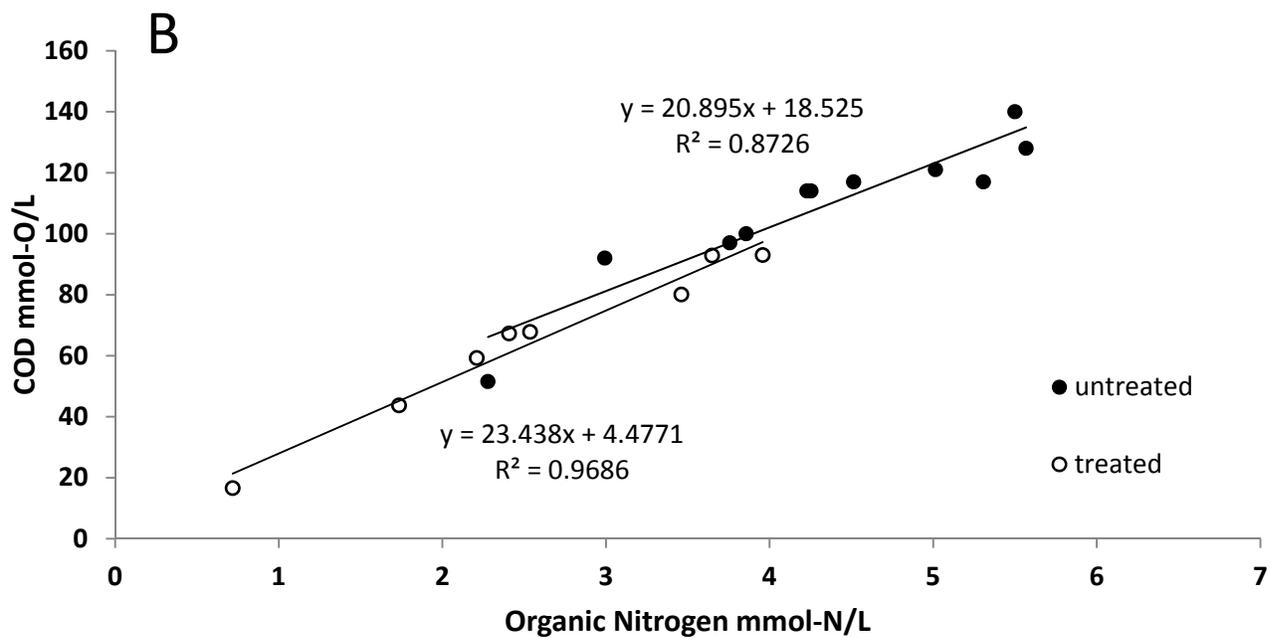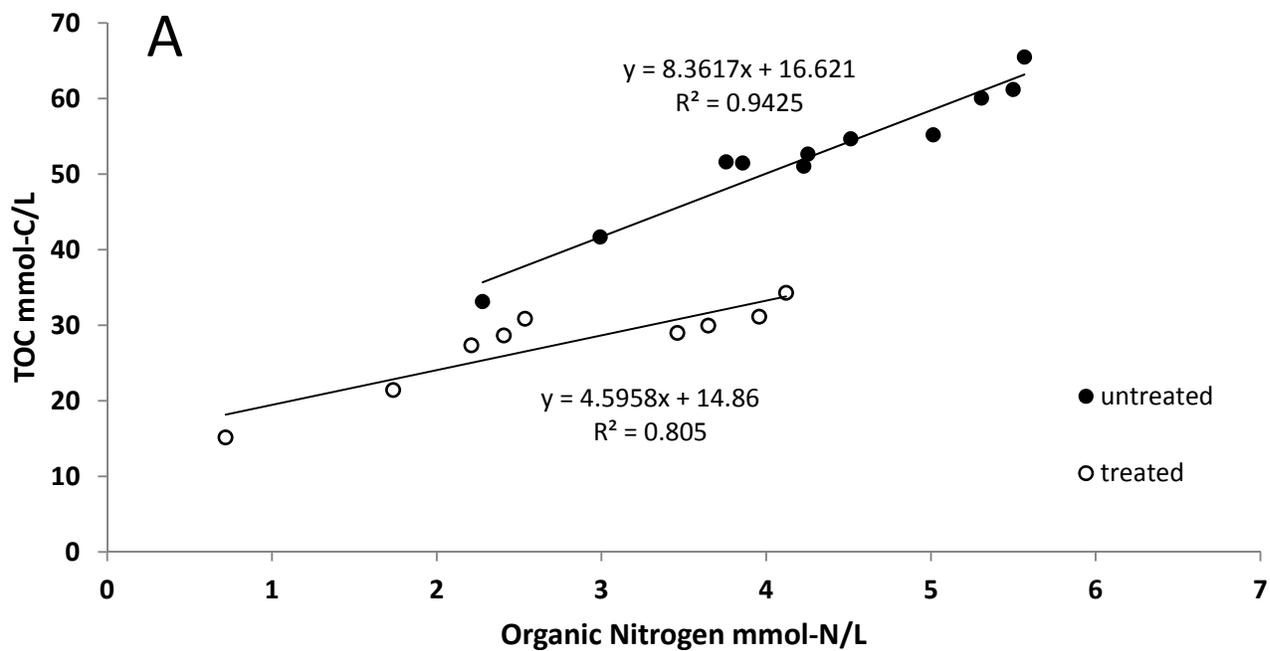
Fig. 3-4 Correlation between organic nitrogen and (A) TOC and (B) COD in size fractions of untreated and treated leachates from PA landfill.
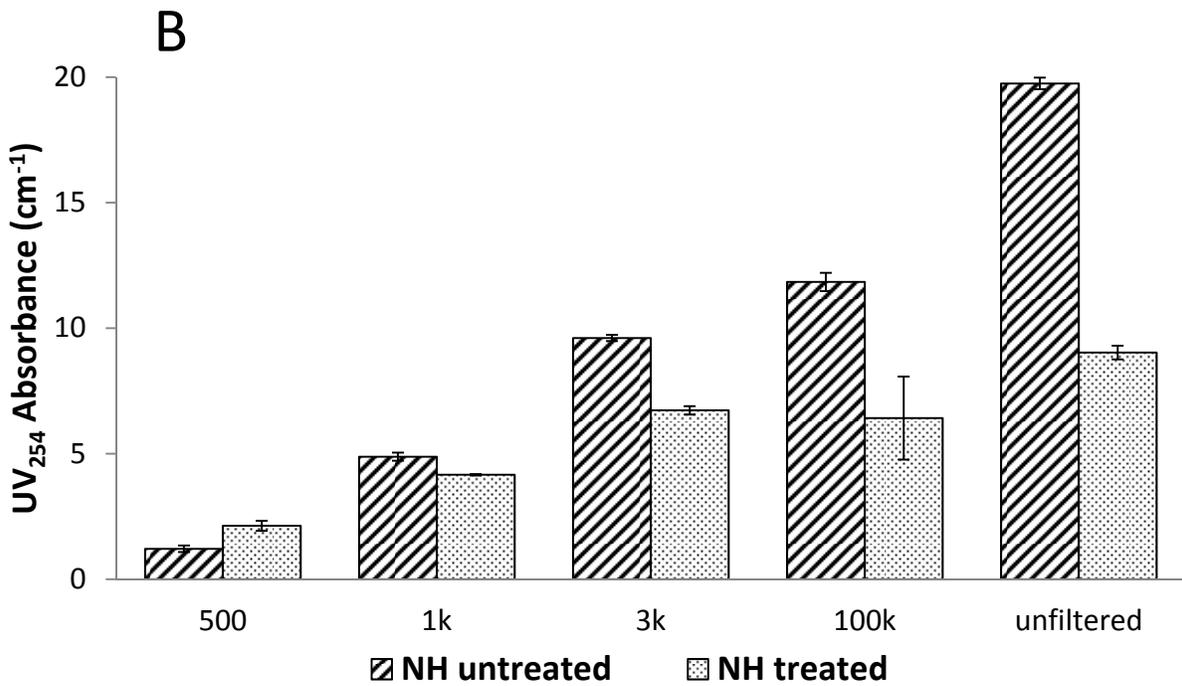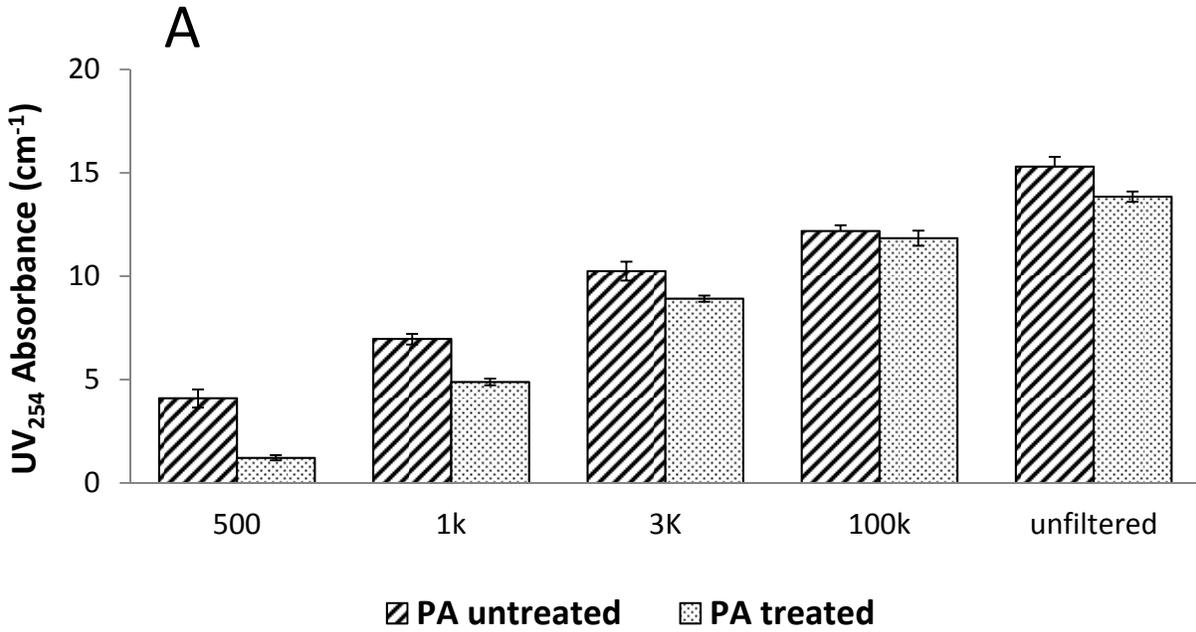
Fig. 3-5 UV$_{254}$ absorbance of size fractions and whole leachate sample from (A) PA landfill and (B) NH landfill. (Error bar indicates standard deviation).
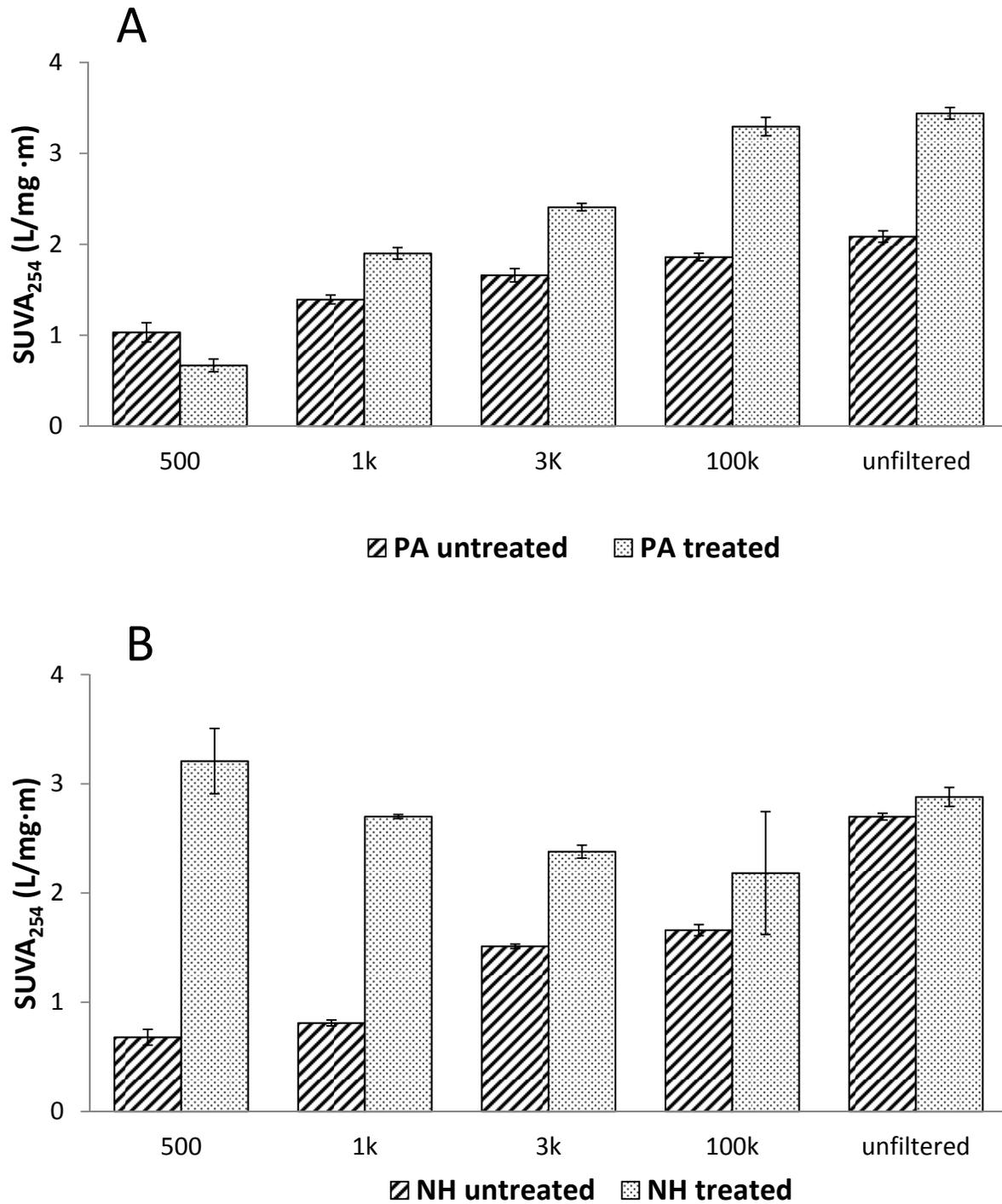
Fig. 3-6 SUVA$_{254}$ of size fractions and whole leachate sample from (A) PA landfill and (B) NH landfill. (Error bar indicates standard deviation).
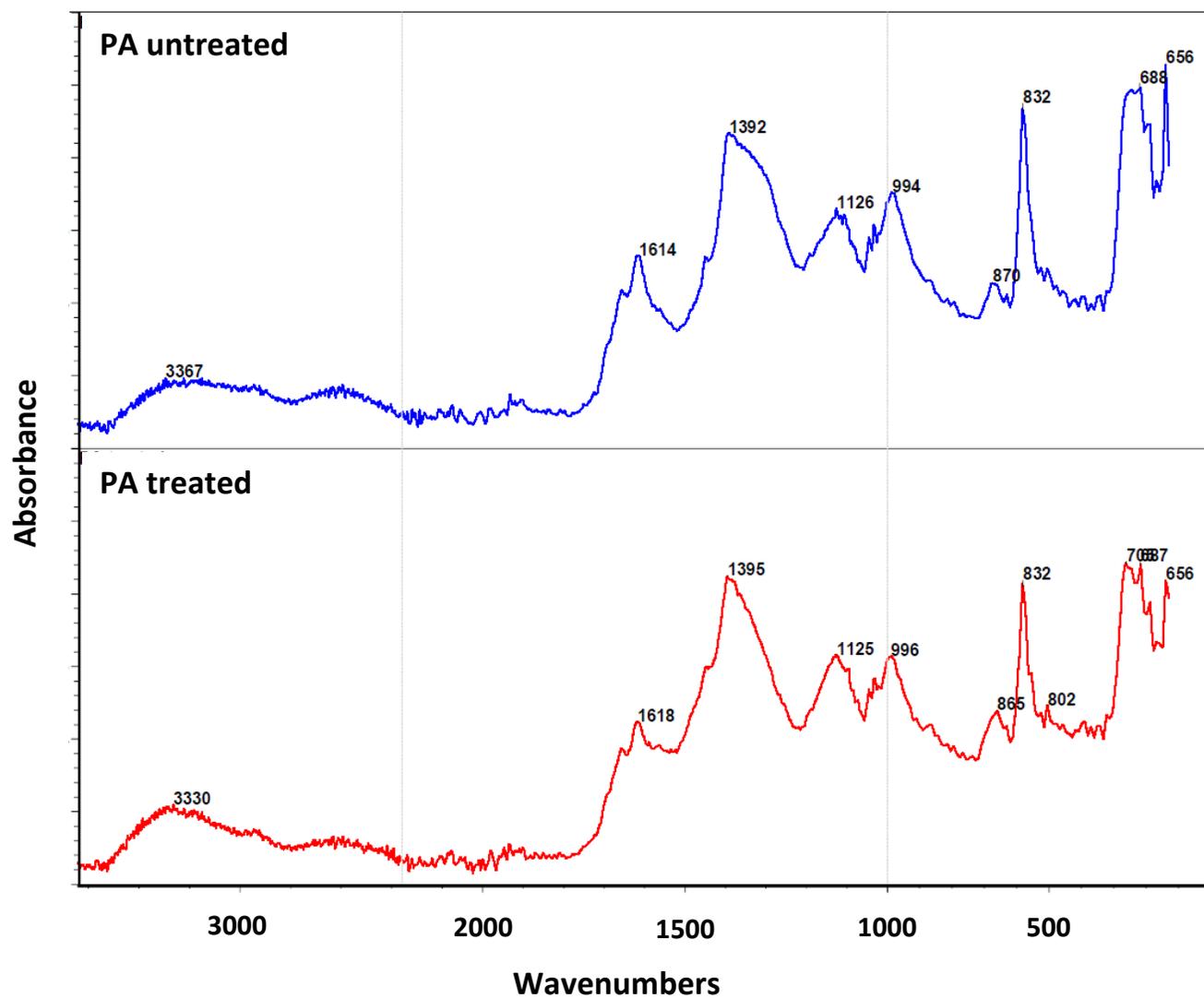
Fig. 3-7 FT/IR spectra of PA leachates
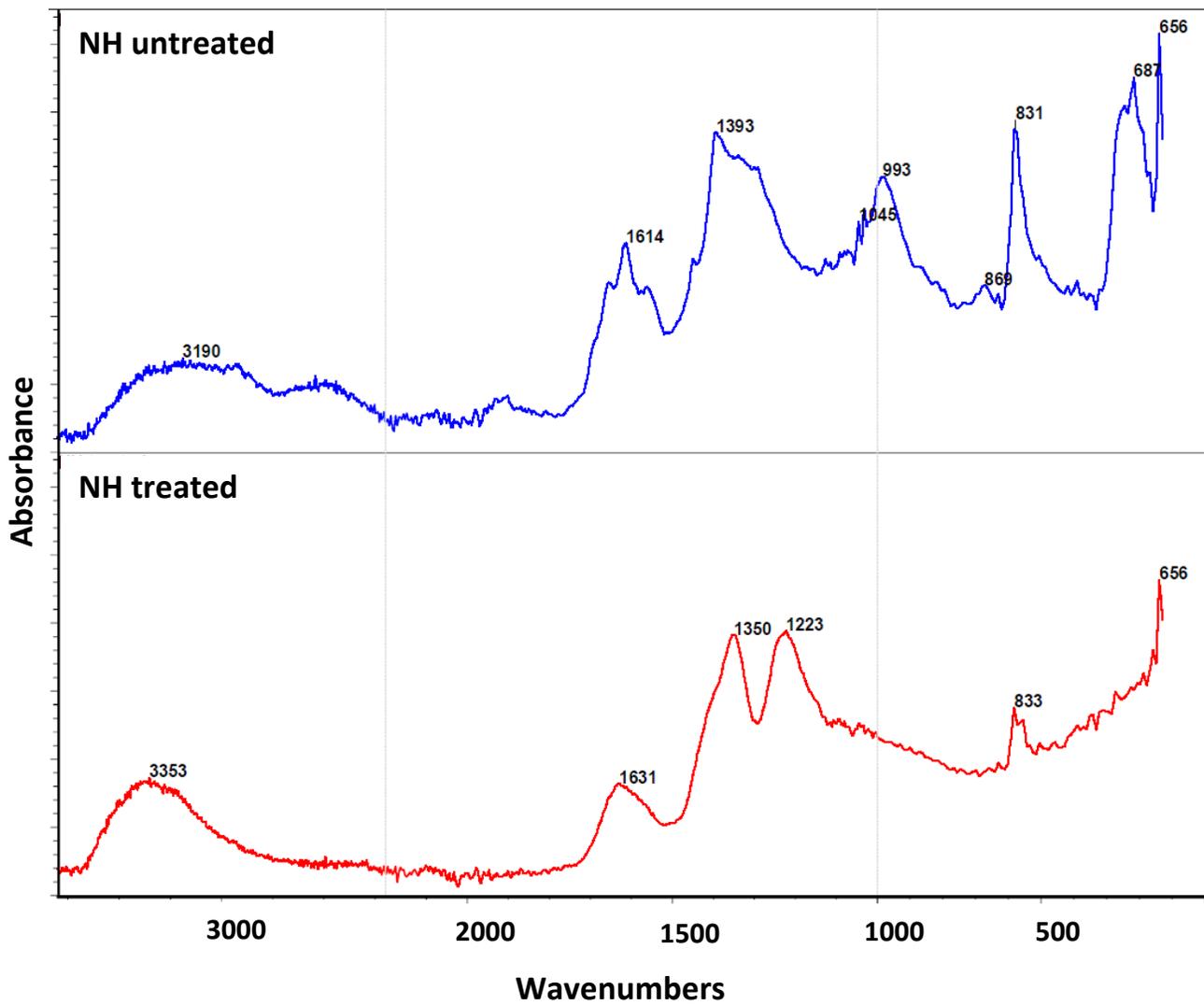
Fig. 3-8 FT/IR spectra of NH leachates

Chapter 4. Characterization of organic constituents in landfill leachate that influence UV light penetration

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Characterization of organic constituents in landfill leachate that influence ultraviolet (UV) light penetration

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ABSTACT

Landfill leachates strongly quench UV light. When leachate is discharged to publicly owned treatment works (POTWs), it can interfere with UV disinfection, depending on the ratio of leachate to municipal wastewater. To investigate the UV quenching problem of landfill leachates, eight landfill leachates with a range of ages, landfilling conditions, locations and treatments were collected and characterized. The UV blocking component of these materials was found to be resistant to biological degradation so they pass through wastewater treatment plants and impact the subsequent UV disinfection system in the POTWs. Leachate samples were fractionated into humic acids (HA), fulvic Acids (FA) and hydrophilic (Hpi) fractions to investigate the source of UV absorbing materials. Results show that for all leachates examined, the specific UV_{254} absorbance ($SUVA_{254}$) of the three fractions follows: HA > FA > Hpi. However, the overall UV_{254} absorbance of the Hpi fraction was important because there was more hydrophilic organic matter than humic or fulvic acids. The organic size distribution was also investigated to provide

information about the potential for membrane treatment of the leachate organic fractions. It was found that the size distribution of the three fractions follows: HA > FA > Hpi. This indicates that membrane separation following biological treatment is a promising technology for the removal of humic substances from landfill leachates. Leachate samples treated in this manner could usually meet the UV transmittance requirement of the POTWs.

KEYWORDS: UV disinfection, POTW, biological treatment, fractionation, humic substance, hydrophilic fraction, size distribution, membrane separation, nanofiltration, biodegradability, XAD resin, statistical analysis.

1. INTRODUCTION

Due to industrial and commercial development, the generation of municipal solid waste (MSW) is rapidly growing in many countries. Among all methods, including recycling, composting and incineration, sanitary landfilling is still the most common and widely accepted method of MSW disposal and new landfills are under construction due to their economic advantages and practical convenience (Renou et al., 2008; Anglada et al., 2009). In 2010, about 135.5 million tons out of 249.9 million tons of MSW generated in the USA were disposed to landfills (US EPA, 2011). Once landfilled, MSW decomposes through a series of biological and physical-chemical processes (Kurniawan and Lo et al., 2009). Soluble waste fractions and decomposition products are carried away by rainwater percolation and infiltration, generating a highly contaminated landfill leachate, which threatens the surrounding surface and ground water. In modern sanitary landfills, impermeable liners and collection systems are installed to prevent the escape of landfill leachate. It is estimated that 1 ton of landfilled MSW will produce 0.2 m^3 of leachate

(Kurniawan and Lo et al., 2009). Hence, a large amount of collected landfill leachate must be treated before being discharged. Due to the complex composition of the solid waste accepted and diverse conditions of landfills, landfill leachate constituents varies significantly, but generally contain large amounts of organic matter (biodegradable and recalcitrant), ammonia-nitrogen, metals and chloride salts (Renou et al., 2008). Accordingly, governments of many countries and regions apply strict regulation for the discharge of landfill leachate (Table 4-1).

Generally, the collected landfill leachate shall either be treated on-site, and then discharged directly to water bodies, discharged or transported to an off-site waste water treatment facility, or pretreated on-site, then discharged or transported to a publicly owned treatment works (POTW) or other waste water treatment facilities. A variety of treatment technologies have been applied to landfill leachate, such as coagulation-sedimentation (Monje-Ramirez and Orta de Velásquez, 2004), advanced oxidation (He et al., 2009; Deng and Ezyske, 2011; Batarseh et al., 2007), membrane separation (Chianese et al., 1999), and activated carbon (Singh et al., 2012). Among those treatment processes, biological treatment (on-site and off-site) is commonly used for the removal of bulk organic compounds, based on its reliability, simplicity and cost effectiveness (Kargı and Uygur, 2004). Usually leachates are pretreated to avoid an impact on the downstream biological treatment process. Hence, transporting to local municipal sewer systems with appropriate pretreatment for co-treatment of leachate and wastewater in the WWTPs is a favored option for landfill leachate disposal.

However, the unique characteristics of landfill leachate create some challenges for co-treatment of leachate and wastewater. Even though landfill leachate composition is complex and highly variable, there are some common characteristics that challenge biological treatment in the waste water treatment plants (WWTPs), such as the high concentration of ammonia (He et al., 2006a)

and low biodegradability (Renou et al., 2008). In recent years, the presence of bio-refractory compounds in the landfill leachate has gained major attention (Vilar et al., 2011; He et al., 2009). Humic substances (humic acids and fulvic acids) are believed to be the main components that show recalcitrant properties (He et al., 2006b). Humic substances are heterogeneous mixtures of polydispersed substances formed by biological and chemical reactions during the decomposition and transformation of plant and microbial remains. Plant lignin and its derivatives, as well as polysaccharides, proteins, lipids, nucleic acids, etc., are important components taking part in this process (IHSS, 2007). Vegetation derivatives (paper and paperboard, yard trimmings and wood) based MSWs are believed to be the source of the lignin that forms humic substances. Food scraps in the MSW can provide proteins, polysaccharides, lipids and nucleic acids for humification. In 2010, vegetation and its derivatives in MSW accounted for 48.3% (28.5% from paper and paperboard, 13.4% from yard trimmings and 6.4% from wood) of total MSW generation by weight (US EPA, 2011). Hence, landfills can provide suitable conditions for the formation of humic substances.

Studies on the occurrence of humic substances in leachates have been reported in recent years (Šír et al., 2011; Bu et al., 2010; Zhang et al., 2009; Kang et al., 2002). Up to 60%-75% of the organic fraction in landfill leachates was reported to be contributed by humic substances (Zhang et al., 2009; Artiola-Fortuny and Fuller, 1982). Based on its large amount and high concentration, landfill leachate is a potential source of humic substance in the natural water environment. It is widely accepted that humic substances are not readily biodegradable (Poblete et al., 2011; Liang et al., 2009; He et al., 2006b), and thus can pass through biological treatment processes and enter the disinfection process (usually the last step in waste water treatment) and elevate the organic matter level in effluents.

For disinfection in WWTPs, chlorination has been employed for about a century (Tchobanoglous et al., 2004). Over the last four decades, disinfection by- products (DBPs) produced during chlorination have been of concern (Bellar et al., 1974; Wu et al., 2003; Nikolaou et al., 2004; Zhang et al., 2005; Kim and Yu, 2007) due to their carcinogenicity (Nikolaou et al., 2004; NCI, 1976). Trihalomethanes (THMs) and haloacetic acids (HAAs), which constitute a major class of DBPs, have been included in the discharge permits of WWTPs (Song et al., 2010). There has been a regulatory trend toward lower residual chlorine level, but with the same pathogen kill requirement, forcing WWTPs to turn to alternative disinfectants (NYSERDA, 1999). UV disinfection has become more popular for waste water treatment because it eliminates the formation of regulated DBPs, has small footprint and results in less risk for toxic/hazardous chemical leakage.

Recently, it was reported that humic substances can influence the UV disinfection in the surface water treatment plants by diminishing the effect of UV radiation on bacteria due to UV light absorption (Alkan et al., 2007). In practice, landfill leachates discharged to WWTPs are reported to interfere with their UV disinfection performance (personal communication) since landfill leachates from several landfills are found to strongly quench the UV light (Zhao et al., 2012). However, there have been limited investigations into the influence of bio-refractory organic matter, such as humic acids and fulvic acids on UV disinfection.

In this study, a variety of landfill leachates were collected from 3 landfills to examine their biodegradability, physic-chemical treatability and UV quenching characteristics. UV absorbance and organic matter level (TOC) were examined for bulk leachates. Then, the DOM in each leachate sample was fractionated into humic acids (HAs), fulvic acids (FAs) and hydrophilic (Hpi) fractions. UV quenching characteristics were examined for each fraction. Thereafter, the

size distribution of each fraction was characterized to provide information for membrane separation and filtration. This study provides insight into the short term biodegradation characteristics in the engineered biological treatment of different fractions of DOM in landfill leachate and their long term bio-decomposition characteristics in landfilling.

2. MATERIALS and METHODS

2.1 Leachate sample locations and processes

Leachates samples investigated in this research were collected from landfills located in Pennsylvania (PA), New Hampshire (NH) and Kentucky (KY), USA. Leachates before and after the on-site biological treatment were collected from PA and NH landfills, details about the on-site biological treatment facilities and the technical specifications of PA and NH landfills were described previously (Zhao et al., 2012).

The KY landfill is comprised of eight individual and separate units, designated Units 1 through 8. Leachate sample collected for this study were from Units 3, 5, 7 and 8 (KY-3, KY-5, KY-7 and KY-8). Unit 3 is an inactive landfill unit that is not receiving waste. Unit 5 has had no input for over a decade, but was operated as a bioreactor landfill for a period of time. Unit 7 was closed in 2005 and was operated as a bioreactor landfill. Unit 8 is an active permitted landfill unit. The landfill has been used for solid waste disposal for 35 years. The average ages of Units 3, 5, 7 and 8 are 30, 16, 9 and 2.5 years, respectively. The landfill has a total property of approximately 782 acres.

The leachate samples were shipped directly from the landfills in 20-liter polyethylene buckets and stored in a refrigerator at 4 ºC to reduce microbial activity. Leachate buckets were shaken well to resuspend settled particles before sampling.

Biological treatment of KY leachates in this study was conducted by continuous aeration in the lab. Since leachates contain microorganisms from the waste layer of the landfill, no external seed was added, biological flocs similar to activated sludge flocs were observed during the aeration process. Each leachate was aerated by using a porous ceramic air diffuser and distilled water was added to compensate the water lost by evaporation. KY-8 and KY-7 leachate samples were aerated for 53 days and aerated leachates were sampled on the 21st, 38th and 53rd days for fractionation and analysis. KY-5 and KY-3 leachate samples were aerated for 21 days, then sampled for fractionation and analysis.

2.2 Fractionation

Landfill leachate samples were fractionated into humic acids (HA), fulvic acids (FA) and hydrophilic (Hpi) fractions based on their hydrophobicity and solubility characteristics. Methods developed by Thurman and Malcolm (1981), Leenheer (1981) and Christensen et al. (1998) were used in this study since they have long been a standard method for the isolation and separation of humic substances from aquatic samples. This method uses chemical precipitation to remove humic acids and then an XAD resin to sorb fulvic acids. The remaining organic matter is considered to be the hydrophilic fraction.

To pack the XAD-8 resin (currently Supelite DAX-8 resin, Sigma-Aldrich, St. Louis, MO) column, the resin was cleaned following the method described by Leenheer (1981).

Approximately 3.5-4.5 mL bed volume of cleaned XAD-8 resin slurry was packed in a borosilicate glass column (1.0 cm×10 cm, Thomas Scientific, Swedesboro, NJ).

Leachate samples were firstly filtered with a 1.5 μm micro glass fiber filter and then acidified to pH 2 by concentrated HCl solution. The humic acids precipitated and were separated with 0.45 μm cellulose nitrate membrane (47 mm, Sartorius Stedim Biotech, France). The collected humic acids precipitates along with the glass fiber filter were put into a 0.1 M NaOH solution to re-dissolve the humic acids precipitate completely and at the same time minimize the loss of HA during transferring. The re-dissolved HA solution was used for analysis.

The supernatant containing fulvic acids and the hydrophilic organics was then passed through the XAD-8 resin column at a flow rate of 10-15 bed volumes/hour. Fulvic acids were sorbed and retained onto the resin column. Then 0.1 M NaOH was used to elute the fulvic acids. Thus the FA solution was prepared. The residual portion not sorbed by the resin is generally called hydrophilic fraction.

Ultrafiltration of leachate samples was conducted using a dead end batch ultrafiltration apparatus (Model 8200, Amicon, Belford, MA) and membrane discs with the molecular weight cut offs of 0.5 kDa, 1 kDa, 3 kDa and 100 kDa (YC05, YM1, PLBC, and PLHK, Millipore, Billerica, MA). Details can be found in Zhao et al. (2012).

2.3 Analysis

All the glassware used in this study were washed with soapy water, soaked in a 10% nitric acid solution, rinsed with deionized water then baked at 450ºC for four hours. All the chemicals used were analytical grade. Total organic carbon (TOC) was analyzed using high temperature combustion method with a TOC analyzer (TOC-5000A, Shimadzu, Japan). The Ultraviolet

absorbance at 254 nm (UV254 absorbance) was measured with a spectrophotometer (DU 640, Beckman Coulter, Brea, California). Specific ultraviolet absorbance ate 254 nm ($SUVA_{254}$) was calculated as UV_{254} divided by TOC. For FT/IR analysis, leachate samples were lyophilized under -75 ºC, 3 kPa, pressed with KBr pellets for the FT/IR spectroscopy (Equinox 55, Bruker, Billerica, MA) analysis. For details, please refer to Zhao et al. (2012).

2.4 Statistics

Data were graphed using Microsoft Office Excel 2010 (Microsoft Corporation, Redmond, WA). Linear regression, hypothesis testing and other statistical analysis were performed using R version 2.14.1.3.

3. RESULTS AND DISCUSION

3.1 Biodegradation of TOC and UV

In the first phase of this study, a comparison of biodegradability was made between the UV_{254} absorbing compounds and TOC. Leachate samples were examined for the treatment performance by various biological processes (Table 4-2). Figure 4-1 (A) shows the organic matter concentration (in terms of TOC) and Figure 4-1 (B) shows the UV_{254} absorbance data for various landfill leachates before and after biological treatment.

As shown in Figure 4-1, a significant removal of organic matter (in terms of TOC) was achieved in each biological treatment process, while UV_{254} absorbance removal by biological degradation was much less than TOC removal for all leachates. Almost no biological removal of UV_{254} absorbance was found for the KY-5, KY-3 and PA leachate samples. The data in Table 4-2

illustrates quantitatively the treatment efficiency of TOC and UV_{254} absorbance for various landfill leachates in the corresponding biological treatment processes. TOC removal efficiency ranged from 35% to 56%, while that of UV_{254} absorbance was no more than 29%. The data in Table 4-2 shows that more TOC than UV_{254} absorbance was always reduced in biological treatment, regardless of the type of treatment process and the leachate source (p=5.611e-05, refer to supplementary information 1 for details).

The KY leachate data provide insight into the biodegradability trends with landfill age. The amount of TOC removed from KY leachate samples was 656 mg/L (KY-8), 463 mg/L (KY-7), 104 mg/L (KY-5) and 87 mg/L (KY-3), indicating that the amount of biodegradable organic matter decreased as the landfill age increased. This decreasing trend of biodegradable organic matter with landfill age was expected and is the result of the biodegradation processes that occur during long term landfilling, which removes biodegradable organic matter during the earlier stage of landfilling, leaving the older leachates more stabilized.

The UV_{254} absorbance for untreated KY leachate samples was 37 cm^{-1}, 23 cm^{-1}, 6.3 cm^{-1} and 4.3 cm^{-1}, showing a decreasing trend with landfill age. This decreasing trend of UV_{254} absorbance indicates the effectiveness of the long term landfilling in degrading UV absorbing organics, while aerobic biological treatment showed limited effectiveness for the UV_{254} absorbance removal, especially for the oldest and most stabilized samples (KY-5 and KY-3). This phenomenon implies that the microorganisms with the capability to degrade the UV absorbing material need a long retention time and perhaps a different microbial environment that cannot be provided by short-term biological treatment processes. Long-term landfilling can provide a retention time long enough for the microorganisms to degrade much of the UV absorbing

organics, leaving the remaining UV absorbing organics in the stabilized leachate samples (such as KY- 5 and KY-3) non-degradable in short-term biological treatment processes.

FT/IR analysis was conducted for all KY leachate samples at various ages to provide insight into the change of organic matter chemical structure associated with long term landfilling. As shown in Figure 4-2, all 4 KY leachate samples show absorbance bands at the wavenumber of 1400-1310 cm^{-1}, which may be attributed to COO- groups in carboxylic organic matter (Calace et al., 2001). KY-8 and KY-7 spectra show absorbance bands around 1690-1630 cm^{-1} and 1570-1540 cm^{-1}, which may be attributed to the C=O stretching of amide groups (amide 1) and N-H bending of amide groups (amide 2) respectively (Bu et al., 2010; Huo et al., 2008; Barber et al., 2001). KY-5 and KY-3 did not show obvious absorbance around these ranges, this indicates decomposition of amide containing compounds, such as protein, peptide and combined amino acids during the long term landfilling process. In addition, both KY-8 and KY-7 samples have absorbance around 1120-1000 cm^{-1}, which may be assigned to the C-O stretching of aliphatic ethers. Both KY-5 and KY-3 samples show peaks at 1030-950 cm^{-1}, which may result from the carbon rings in cyclic compounds (Huo et al., 2008; Barber et al., 2001). The increasing trend of aromaticity with landfill age may result from the bio-refractory characteristics of the aromatic compounds during decomposition in landfills. Complex absorbance bands around 700-650 cm^{-1} are related to halogenated compounds (Zhang et al., 2009).

3.2 Hydrophobicity distribution of TOC and UV absorbance and their correlation

Previous studies (Chin et al., 1994; Dong et al., 2001; Weishaar et al., 2003) revealed a correlation between the UV absorbance of aqueous organic matter and the aromaticity. The study by Chin et al. (1994) showed that π-π* electron transitions occur in the wavelength of the UV

range for phenolic substances, lignin derivatives, benzoic acids, polyenes and polycyclic aromatic hydrocarbons, many of which are precursors or components of certain types of humic substances. Also, a strong correlation was indicated in Weishaar et al.'s study (2003) between the specific UV absorbance (SUVA) and the aromaticity extent determined by ^{13}C NMR for various aquatic environmental organic matter samples. Proportional correlation of the $SUVA_{254}$ and the aromatic content of organic matter were also reported by Dong et al. (2001). This correlation between the aromaticity and the UV spectroscopic properties of organic matter has been used to characterize and predict the removal of NOM by ozone (Westerhoff et al., 1999) and chlorine (Li et al., 2000).

In this study, based on the chemical structure and composition of their origin (lignin and its derivatives), the aromaticity of humic substances (humic acids and fulvic acids) is expected to be higher than other substances in landfill leachates. Therefore, humic substances are thought to be an important contributor of the UV quenching phenomenon in landfill leachates among all categories of organic matter. To verify this hypothesis, landfill leachate samples from several sources were separated into HA, FA and Hpi fractions, UV and TOC were measured for each fraction to provide a profile of the distribution of organic matter and the UV_{254} absorbance among these hydrophobicity fractions.

Figure 4-3 shows the hydrophobicity distribution of organic matter (in terms of TOC) for the various leachates. Figure 4-3 (A) shows the data for the PA leachate samples before and after on-site biological treatment (SBR). Figure 4-3 (B) shows the data for the NH leachate samples before and after the on-site biological treatment (PACT). Figure 4-3 (C) shows the data for the untreated KY leachate samples with different landfill ages. As shown in Figure 4-3, the TOC

concentration of the Hpi fraction was the highest among all three categories and even higher than the sum of HA and FA fractions in all leachates examined.

By investigating the PA and NH leachate before and after biological treatment, it can be seen that each fraction was partially removed by biological treatment. For the PA leachate, the HA, FA and Hpi fractions were removed 41%, 40 % and 27 % respectively in the on-site biological treatment process (SBR). For the NH leachate, the HA, FA and Hpi fractions were removed 59.8 %, 44.2 % and 53.1 % respectively in the on-site biological treatment (PACT). No significant change of the HA, FA and Hpi fractions distribution was observed for either the PA or the NH leachates after the biological treatment.

By comparing the KY samples with different landfill ages (Figure 3C), it can be seen that each fraction declined, as TOC, with increasing landfill age. The distribution of TOC also changed over time, with the HA fraction undergoing the greatest percentage decrease. The percentage of FA was greatest in the oldest leachate (KY-3), however, the major organic fraction for all the leachates was still the Hpi fraction.

Figure 4-4 shows the hydrophobicity distribution of UV_{254} absorbance among the HA, FA and Hpi fractions. Figure 4-4 A shows the UV_{254} absorbance data for the PA leachate samples and Figure 4-4 B shows the UV_{254} absorbance data for NH leachate samples, before and after on-site biological treatment. Figure 4-4 C shows the UV_{254} absorbance data for untreated KY leachate samples at different landfill ages. As shown in Figure 4-4, UV_{254} absorbance by the Hpi fractions was the highest among all three categories of fractions in all leachates studied. However, the UV absorbance by the combined HA and FA exceeded that of the Hpi fraction.

By comparing the untreated and biologically treated sample data for the PA and NH leachates, it can be seen that there was considerable difference between the impact of biological treatment between the PA and NH leachates. Almost no UV_{254} absorbance was removed by biological treatment for the PA leachate. For the NH leachate, the UV_{254} absorbance removal for the HA fraction was 27%, but the FA and Hpi fractions were degraded less than 10%. The removal of UV_{254} absorbing compounds is much lower than overall organic matter removal (in terms of TOC), indicating the bio-refractory characteristics of the UV absorbing material. The distribution of the Hpi, HA and FA fractions in terms of UV_{254} absorbance changed little for the PA leachate and NH leachates as a result of biological treatment.

By comparing the KY samples at different landfill ages (Figure 4-4), it can be seen that the UV_{254} absorbance of each fraction in the leachates decreased significantly with increasing landfill age. The percentages of Hpi fractions in terms of UV_{254} absorbance did not change much with landfill age, fluctuating from 39 % to 51 %. However, the distribution of HA and FA fractions changed with the landfill age. The HA fraction declined while the FA fraction increased in terms of percentage. The decreasing trend of the HA fractions and increasing trend of the FA fractions with the increasing of the landfill age might be due to the transformation of the HA fraction to the FA fraction during the long term landfilling process. Fulvic acids are generally lower molecular weight compounds derived from humic acids. The conversion from humic acids to fulvic acids may be caused by the partial degradation and decomposition during the years of landfilling. Based on the information in this study, this kind of conversion requires 10-20 years in a landfill.

To better understand the spectroscopic characteristics of the hydrophobic fractions of leachates, in a specific organic matter amount basis, UV_{254} absorbance and the corresponding TOC of all

leachates examined in this study were plotted in Figure 4-5. Regression plots were generated for HA, FA and Hpi fractions respectively. As shown in Figure 4-5, UV_{254} absorbance is directly proportional to the concentration of organic matter (in terms of TOC) in all three organic fractions (p values were 1.17e-06, 2.97e-05 and 2.38e-06 for the HA, FA and Hpi fractions respectively, refer to supplementary information 2 for details), R^2 values were 0.97, 0.93 and 0.97 for HA, FA and Hpi fractions respectively.

It should be noted in Figure 4-5 that, slopes of the three regression lines are clearly different from each other. The slope of HA regression curve (0.0334) is higher than that of FA (0.0234), while the slope of FA regression curve is higher than that of Hpi (0.0130). The differences between slopes indicate that, in a specific organic matter amount basis, the HA fraction in the landfill leachate is the strongest absorber of UV light, while the Hpi fraction is the weakest UV absorber.

Table 4-3 shows the $SUVA_{254}$ data of HA, FA and Hpi fractions for the leachates examined. Statistical analysis shows that the $SUVA_{254}$ for the leachate fractions follows: HA>FA>Hpi (refer to supplementary information 3 for details).

By comparing the $SUVA_{254}$ of untreated and treated leachate samples for the PA and NH landfills, it was found that the $SUVA_{254}$ of HA, FA and Hpi fractions in PA leachate increased from 2.77 L/mg·m, 1.92 L/mg·m and 1.55 L/mg·m to 4.70 L/mg·m, 3.25 L/mg·m and 2.05 L/mg·m respectively. The increasing trend of $SUVA_{254}$ indicates that, the organic matter that was biodegraded in the treatment facilities (SBR and PACT in PA and NH respectively) is not the same as the organic matter that absorbs UV light.

Different from the PA and NH leachate samples, the SUVA$_{254}$ of HA, FA and Hpi fractions in KY leachates at a variety of ages were comparable to each other, indicating that the organic matter that absorbs UV light was degraded along with the other organic matter during the long-term landfilling process.

3.3 Size distribution of HA/FA/Hpi fractions in terms of TOC and UV

The detailed size distribution data shown in Figure 4-6 is in the pore size range of microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF). This can be a useful reference when considering the selection of membrane technologies for treatment of landfill leachates and other wastewaters.

Figures 4-6 (A) and (B) show the size distribution (in terms of TOC) for the HA fraction of PA and NH leachates. It can be seen that the MWCO (in terms of TOC) for the HA fractions are mainly greater than 3 kDa. The > 3kDa material accounts for 78 % and 53 % TOC of the HA fractions of PA untreated and treated leachates respectively. For the NH leachates, the > 3 kDa part accounts for 50 % of the TOC of the HA fractions for both the treated and untreated leachate. It should be noted that, the > 100 kDa portion of the HA fractions of the PA and NH leachates were removed in the biological treatment processes. The removal of some of the HA fraction in the activated sludge processes might be caused by partial degradation or bio-flocculation.

Figures 4-6 (C) and (D) show the size distribution for the FA fraction of PA and NH leachates. Different from HA fractions, the size distribution of FA fractions is relatively evenly distributed among the size fractions. No single size fraction exceeded 50%. Except for the PA leachate, the largest fraction of FA was in the size fraction less than 500 Da.

Figures 4-6 (E) and (F) show the size distribution of Hpi fraction of PA and NH leachates. It can be seen that organic matter with MWCO < 1 kDa is the dominant in the Hpi fraction. For the Hpi fraction of PA untreated and treated leachates, the < 1 kDa part account for 68 % and 67 % of TOC respectively. For the Hpi fraction of NH untreated and treated leachates, the < 1 kDa part accounts for 73 % and 75 % of TOC respectively.

In addition, statistical analysis of the the percentage of < 1 kDa portion of HA, FA and Hpi fractions of leachatesis shown in Table 4-4, it can be seen that the percentage of < 1 kDa portion in HA fractions of all leachates is smaller than that of FA fractions, while, the percentage of < 1 kDa portion in FA fractions is smaller than that of Hpi fraction (refer to supplementary information 4 for details). Therefore, generally speaking, the size of HA fractions is bigger than FA fraction,while FA fraction is bigger than Hpi fraction. The order of size is HA > FA > Hpi. This result indicates that membrane separation with 1kDa MWCO can remove most of the HA and FA fractions leaving predominantly the Hpi fraction which is primarily < 1kDa size.

3.4 Performance of combined biological treatment and membrane separation

Because the SUVA is greatest for HA and least for Hpi, the removal of the HA and FA fractions will be important for the reduction of UV absorbance in landfill leachates. The mean size of the HA and FA fractions is bigger than the Hpi fraction so membrane separation with an approperiate pore size/MWCO is a practical technology that can remove much of the UV absorbing material by removing HA and FA fractions.

On the other hand, based on the abundance of organic matter in Hpi fractions, the total amount of UV absorbance of the Hpi fraction is always higher than either the HA or FA fractions in all leachates samples examined. A previous study showed that biological treatment can degrade

organic matter of low MW (Luo et al., 1998). However as shown in Figure 4-4 (A) and (B), biological removal of UV absorbing organics using conventional activated sludge technology is poor for some leachates.

In this study, the treatment performance for the removal of UV absorbing material was evaluated for the combination of biological treatment and membrane separation. As shown in Figure 4-7, biologically treated leachates samples (PA and NH leachates) were filtered by membranes with various MWCOs (500 Da, 1 kDa and 100 kDa). Then each filtrate was separated into HA, FA and Hpi fractions and the UV absorbance was measured for the fractions. Thus, the treatment efficiency and mechanism of UV absorbance in landfill leachates can be examined.

As shown in Figure 4-7 (A), the membrane with a MWCO of 100 kDa reduced the UV absorbance slightly (15%) for the PA treated leachate, while a significant removal was achived by the 1 kDa membrane, which reduced the UV_{254} absorbance by 65%. By comparing the UV absorbance of 1 kDa and 100 kDa filtrates, it can be seen that the overall UV absorbance decrease was contributed mostly by the removal of the HA and FA fractions. From 100 kDa to 1 kDa, HA, FA and Hpi fractions decreased by 3.5 cm^{-1}, 2.1 cm^{-1} and 1.3 cm^{-1} respectively. Eighty one percent of the UV absorbance reduction was contributed by removal of the HA and FA fractions.

By reducing the MWCO to 500 Da, the UV absorbance of the PA biologically treated leachate decreased from 4.88 cm^{-1} to 1.21 cm^{-1}. By comparing the UV absorbance of the 500 Da and 1 kDa filtrates, it can be seen that the overall UV absorbance decrease was mainly contributed by the Hpi fraction. From 1 kDa to 500 Da, the HA, FA and Hpi fractions decreased by 0.48 cm^{-1}, 0.85 cm^{-1} and 2.34 cm^{-1}, respectively. Sixty four percent of the UV absorbance reduction was

contributed by the Hpi fraction. This result shows that the 500 Da membrane can remove most of the UV absorbing Hpi fraction.

Figure 4-7 (B) shows the data for the NH leachate. Similar to the PA leachate, the 100 kDa membrane reduced the overall UV absorbance slightly (19%), while the 1 kDa membrane reduces the overall UV absorbance by 54%. Most of the reduction in UV absorbance by the 1 kDa membrane is contributed by the removal of the HA and FA fractions. The 500 Da membrane can further remove the Hpi fraction and reduce the overall UV absorbance to a lower level (2.13 cm^{-1}).

In practice, the POTWs require UV transmittance of mixed wastewater stream to exceed 60% to insure that the UV disinfection can work properly (personal communication). Moreover, the landfill leachate can make up to 5% of the mixed wastewater stream during dry weather conditions (personal communication). As shown in Figure 4-7 (A), the UV transmittance of the 1 kDa filtrate for the PA biologically treated leachate is 57 % when diluted to 5%, which is close to the 60% UV transmitance requirement. Similarly, the UV transmittance for the 1 kDa filtered NH biologically treated leachate sample (diluted to 5%) is 62 %, which meets the requirement. Hence, in this case, the combination of biological treatment and nanofiltration with a MWCO of 1 kDa or finer is a practical treatment option to make landfill leachates acceptable to the POTWs regarding the UV quenching problem.

4. SUMMARY AND CONCLUSION

Discharging to a POTW is a cost effective, practical and widely applied approach for the landfill leachate disposal. In a previous study, Zhao et al. (2012) reported that landfill leachates quench

the UV light strongly and interfere with the UV disinfection in POTWs, even when diluted. The aim of this study was to evaluate the biodegradability of UV absorbing material in landfill leachates, identify the source of the UV absorbing materials, and examine the treatability of the UV absorbing materials in landfill leachates.

Eight landfill leachates were collected from three municipal landfills, which covered a variety of landfilling conditions, namely age, treatment and waste acceptance, and therefore, have general applicability. This study evaluated the biodegradability of the UV absorbing substances in landfill leachates and its impact on POTWs, examined the source of UV absorbing substances and provided insight into their treatability before discharged into the POTWs. The main conclusions are as follows:

(1) Most of the UV absorbing substances are refractory in aerobic biological treatment processes. The microorganisms with the capability to degrade UV absorbing materials require very long retention times. Landfills under strict anaerobic conditions with a retention time greater than ten years are required to degrade UV absorbing substances.

(2) In all leachates examined, $SUVA_{254}$ follows: HA>FA>Hpi. The overall UV absorbance of the Hpi fraction is always higher than that of HA and FA fractions due to a higher amount of Hpi organic material.

(3) The organic matter size distribution study showed that in all leachates examined, the particle size distribution follows: HA>FA>Hpi. Nanofiltration can be used to selectively remove HA and FA.

(4) For the PA and NH leachates, on-site biological treatment followed by membrane separation with a 1 kDa NF was successful in meeting UV transmittance requirement (60% transmission at 5% dilution) for POTWs.

REFERENCES:

Ahn, W.Y., Kang, M.S., Yim, S.K., Choi, K.H., 2002. Advanced landfill leachate treatment using an integrated membrane process. Desalination 149, 109–114.

Alkan, U., Teksoy, A., Atesli, A., Baskaya, H.S., 2007. Influence of humic substances on the ultraviolet disinfection of surface waters. Water and Environment Journal 21 (1), 61–68.

Anglada, A., Urtiaga, A., Ortiz, I., 2009. Pilot scale performance of the electro-oxidation of landfill leachate at boron-doped diamond anodes. Environmental Science & Technology. 43(6), 2035-2040.

Artiola-Fortuny, J., Fuller, W.H., 1982. Humic substances in landfill leachates: I. Humic acid extraction and identification, Journal of Environmental Quality 11, 663–668.

Barber, L.B., Leenheer, J.A., Noyes, T.I., Stiles, E.A., 2001. Nature and Transformation of Dissolved Organic Matter in Treatment Wetlands. Environmental Science and Technology 35 (24), 4805-4816.

Batarseh, E.S., Reinhart, D.R., Daly, L., 2007. Liquid Sodium Ferrate and Fenton's Reagent for Treatment of Mature Landfill Leachate. Journal of Environmental Engineering 133(11), 1042-1050.

Bohdziewicz, J., Neczaj, E., Kwarciak. A., 2008. Landfill leachate treatment by means of anaerobic membrane bioreactor. Desalination 221, 559- 565.

Bu, L., Wang, K., Zhao, Q.L., Wei, L.L., Zhang, J., Yang, J.C., 2010. Characterization of dissolved organic matter during landfill leachate treatment by sequencing batch reactor, aeration corrosive cell-Fenton, and granular activated carbon in series. Journal of Hazardous Materials 179 (1-3), 1096-1105.

Calace, N., Liberatori, A., Pertonio, B.M., Pietroletti, M., 2001. Characteristics of different molecular weight fractions of organic matter in landfill leachate and their role in soil sorption of heavy metals. Environmental Pollution 113 (3), 331- 339.

Canellas, L.P., Piccolob, A., Dobbss, L.B., Spaccini, R., Olivares, F.L., Zandonadi, D.B., Façanha, A. R., 2010. Chemical composition and bioactivity properties of size-fractions separated from a vermicompost humic acid. Chemosphere 78 (4), 457- 466.

Chianese, A., Ranauro, R., Verdone, N., 1999. Treatment of landfill leachate by reverse osmosis. Water Research, 33(3), 647- 652.

Chin, Y.P, Alken, G., O'Loughlin, E., 1994. Molecular Weight, Polydispersity, and Spectroscopic of Aquatic Humic Substances. Environmental Science and Technology 28 (11), 1853-1858.

Christensen, J.B., Jensen, D.L., Grøn, C., Filip, Z., Christensen, T.H., 1998. Characterization of the dissolved organic carbon in landfill leachate-polluted groundwater. Water Research 32(1), 125-135.

Costa , A. R., de Pinho, M. N., 2005. Effect of membrane pore size and solution chemistry on the ultrafiltration of humic substances solutions. Journal of Membrane Science 255(1–2), 49–56.

Deng, Y., Ezyske, C.M., 2011. Sulfate radical-advanced oxidation process (SR-AOP) for simultaneous removal of refractory organic contaminants and ammonia in landfill leachate. Water Research 45(18), 6189–6194.

Edzwald, J.K., Tobiason, J.E., 1999. Enhanced coagulation: US requirements and a broader view. Water Science and Technology 40(9), 63-70.

EPD, 2005. Technical Memorandum Standards for Effluents Discharged into Drainage and Sewerage Systems, Inland and Coastal Water. Environmental Protection Department of Hong Kong Special Administrative Region, Hong Kong (Available from http://www.legislation.gov.hk/blisind.nsf/e1bf50c09a33d3dc482564840019d2f4/034c887c9e2774078825648a005d23b4?OpenDocument)

Fan, H.J., Chen, I.W., Lee, M.H., Chiu. T., 2007. Using FeGAC/H_2O_2 process for landfill leachate treatment. Chemosphere 67(8), 1647–1652.

He, P.J., Shao, L.M., Guo, H.D., Li, G.J., Lee, D.J., 2006a. Nitrogen removal from recycled landfill leachate by ex situ nitrification and in situ denitrification. Waste Management 26(8), 838-845.

He, P.J., Xue, J.F., Shao, L.M., Li, G.J., Lee, D.J., 2006b. Dissolved organic matter (DOM) in recycled leachate of bioreactor landfill. Water Research, 40 (7), 1465-1473.

He, P.J., Zheng, Z., Zhang, H., Shao, L.M., Tang, Q.Y., 2009. PAEs and BPA removal in landfill leachate with Fenton process and its relationship with leachate DOM composition. Science of the Total Environment 407, 4928-4933.

Huo, S.L., Xi, B.D., Yu, H.C., He, L.S., Fan, S.L., Liu, H.L., 2008. Characteristics of dissolved organic matter (DOM) in leachate with different landfill ages. Journal of Environmental Sciences 20 (4), 492–498.

International Humic Substances Society, 2007. http://www.humicsubstances.org/whatarehs.html.

Kang, K.H., Shin, H.S., Park, H., 2002. Characterization of humic substances present in landfill leachate with different landfill ages and its implications. Water Research 36, 4023-4032.

Kim, H.C., Yu, M.J., 2007, Characterization of aquatic humic substances to DBPs formation in advanced treatment processes for conventionally treated water. Journal of Hazardous Materials 143(1-2), 486-493.

Kurniawan, T.A., Lo, W.H., 2009. Removal of refractory compounds from stabilized landfill leachate using an integrated H_2O_2 oxidation and granular activated carbon (GAC) adsorption treatment. Water Research 43(16), 4079-4091.

Leenheer, J.A., 1981. Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters. Environmental Science and Technology 15(5), 578-587.

Li, C.W., Benjamin, M.M., Korshin, G.V., 2000. Use of UV Spectroscopy To Characterize the Reaction between NOM and Free Chlorine. Environmental Science and Technology 34 (12), 2570-2575.

Liang, Z., Liu, J.X., Li, J., 2009. Decomposition and mineralization of aquatic humic substances (AHS) in treating landfill leachate using the Anammox process. Chemosphere 74(10), 1315–1320.

Luo, X.H., Cao, L.L., Wang, Z.S., 1998. Study on the removal of different molecular weight organic by water purification process. China Environmental Science 18,341-344.

Meier, J., Melin, T., Eilers, L.H., 2002. Nanofiltration and adsorption on powdered adsorbents as process combination for the treatment of severely contaminated wastewater. Desalination 146, 361–366.

MEP and GAQSIQ, 2008. Standard for Pollution Control on the Landfill Site of Municipal Solid Waste (GB-16889-2008). Ministry of Environmental Protection, and General Administration of Quality Supervision, Inspection and Quarantine, People's Republic of China.

Nanny, M.A., Ratasuk, N., 2002. Characterization and comparison of hydrophobic neutral and hydrophobic acid dissolved organic carbon isolated from three municipal landfill leachates. Water Research 36 (6), 1572-1584.

NCI, 1976. Report on carcinogenesis bioassay of chloroform. National Technical Information Service, National Cancer Institute, Springfield, VA, USA. Report No. PB-264018.

Nikolaou, A.D., Golfinopoulos, S.K., Lekkas, T.D., Kostopoulou. M.N., 2004. DBP Levels in Chlorinated Drinking Water: Effect of Humic Substances. Environmental Monitoring and Assessment 93(1-3), 301- 319.

NYSERDA, 1999. Evaluation of Alternative Disinfection Technologies: Laboratory Studies of Reactivation and UV-Chlorination Synergism. National Technical Information Service,

New York State Energy Research and Development Authority, Albany, NY. USA. Report No. PB2000102547

Ozturk, I., Altinbas, M., Koyuncu, I., Arikan, O., Gomec-Yangin, C., 2003. Advanced physico-chemical treatment experiences on young municipal landfill leachates. Waste Management 23, 441–446.

Renou, S., Givaudan, J.G., Poulain, S., Dirassouyan, F., Moulin, P., 2008. Landfill leachate treatment: Review and opportunity. Journal of Hazardous Materials 150 (3), 468-493.

Pérez, G., Saiz, J., Ibañez, R., Urtiaga, A.M., Ortiz, I., 2012. Assessment of the formation of inorganic oxidation by-products during the electrocatalytic treatment of ammonium from landfill leachates. Water Research 46(8), 2579-2590.

Poblete, R., Otal, E., Vilches, L.F., Vale, J., Fernández-Pereira, C., 2011. Photocatalytic degradation of humic acids and landfill leachate using a solid industrial by-product containing TiO_2 and Fe. Applied Catalysis B: Environmental 102(1–2), 172–179.

Singh, S.K., Townsend, T.G., Mazyck, D., Boye, T.H., 2012. Equilibrium and intra-particle diffusion of stabilized landfill leachate onto micro- and meso-porous activated carbon. Water Research 46(2), 491–499.

Šír, M., Podhola, M., Patočka, T., Honzajková, Z., Kocurek, P., Kubal, M., Kuraš, M., 2012. The effect of humic acids on the reverse osmosis treatment of hazardous landfill leachate. Journal of Hazardous Materials 207–208, 86–90.

Siripinyanond, A., Worapanyanond, S., Shiowatana, J., 2005. Field-Flow Fractionation-Inductively Coupled Plasma Mass Spectrometry: An alternative approach to investigate metal-humic substances interaction. Environmental Science and Technology 39(9), 3295-3301.

Tchobanoglous, G., Burton, F.L., Stensel, H.D., 2004. Wastewater engineering, treatment and reuse (fourth edition), Metcalf and Eddy, Inc., McGraw-Hill, New York.

Thurman, E.M., Malcolm, R.L., 1981. Preparative isolation of aquatic humic substances. Environmental Science and Technology 15(4), 463-466.

Trebouet, D., Schlumpf, J.P., Jaouen, P., Quemeneur, F., 2005. Stabilized landfill leachate treatment by combined physicochemical–nanofiltration processes. Water Research 35, 2935–2942.

US EPA, 2011. Municipal Solid Waste Generation, Recycling, and Disposal in the United States: Facts and Figures for 2010. EPA-530-F-11-005, Washington, DC.

Uygur, A., Kargı, F., 2004. Biological nutrient removal from pre-treated landfill leachate in a sequencing batch reactor. Journal of Environmental Management 71(1), 9–14.

Vilar, V.J., Rocha, E.M., Mota, F.S., Fonseca, A., Saraiva, I., Boaventura R.A., 2011. Treatment of a sanitary landfill leachate using combined solar photo-Fenton and biological immobilized biomass reactor at a pilot scale. Water Research 45(8), 2647-2658.

Weishaar, J.L., Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fujii, R., Mopper, K., 2003. Evaluation of Specific Ultraviolet Absorbance as an Indicator of the Chemical Composition and Reactivity of Dissolved Organic Carbon. Environmental Science and Technology 37 (20), 4702-4708.

Westerhoff, P., Aiken, G., Amy, G., Debroux, J., 1999. Relationships Between the Structure of Natural Organic Matter and Its Reactivity towards Molecular Ozone and Hydroxyl Radicals. Water Research 33(10), 2265-2276.

Wu, W. W., Chadik, P.A., Delfino, J.J., 2003. The relationship between disinfection by-product formation and structural characteristics of humic substances in chloramination. Environmental Toxicology and Chemistry 22 (12), 2845-2852.

Zhang, L., Li, A., Lu, Y., Yan, L., Zhong, S., Deng, C., 2009. Characterization and removal of dissolved organic matter (DOM) from landfill leachate rejected by nanofiltration. Waste Management 29(3), 1035–1040.

Zhang, X., Minear, R.A., Barrett, S.E., 2005. Characterization of high molecular weight disinfection byproducts from chlorination of humic substances with/without coagulation pretreatment using UF-SEC-ESI-MS/MS. Environmental Science and Technology 39(4), 963-972,

Zhao, R.Z., Novak, J.T., Goldsmith, C.D., 2012. Evaluation of on-site biological treatment for landfill leachates and its impact: a size distribution study. Water Research 46(12), 3837-3848.

Table 4-1. Landfill leachate discharge limit of various countries and regions.

Country/Region	Landfill leachate quality parameter (mg/L)				Reference
	COD	BOD_5	Total Nitrogen	Ammonium	
China	100	30	40	25	(MEP of China, 2008)
France	120	30	30	5	(Trebouet et al., 2001)
Germany	200	20	70	--	(Meier et al., 2002)
Hong Kong	200	800	100	5	(EPD of HKSAR, 2005)
Poland	125	30	--	10	(Bohdziewicz et al., 2008)
South Korea	50	--	150	50	(Ahn et al., 2002)
Taiwan	200	--	--	--	(Fan et al., 2007)
Turkey	100	50	--	--	(Ozturk et al., 2003)

Table 4-2. Biological treatment efficiency of various landfill leachates in terms of TOC and UV absorbance.

Sample	TOC (%)	UV absorbance (%)	Condition
KY-8	37.40	17.85	53-day aeration; landfill closed for 3 years
KY-7	42.25	9.82	53-day aeration; landfill closed for 5-10 years
KY-5	36.49	2.70	21-day aeration; landfill closed for 20-30 years
KY-3	37.50	-2.30	21-day aeration; landfill closed for 36 years
PA	34.82	2.51	SBR treatment ; active landfill
NH	55.78	29.09	PACT treatment; active landfill

Table 4-3. SUVA$_{254}$ of hydrophobicity fractions of various landfill leachates.

Sample	SUVA$_{254}$ (L/mg·m)		
	HA	FA	Hpi
PA untreated	2.77	1.92	1.55
PA treated	4.70	3.25	2.05
NH untreated	2.65	2.31	1.30
NH treated	3.68	3.29	2.28
KY-8	3.37	2.57	1.45
KY-7	3.72	2.29	1.49
KY-5	3.79	2.64	1.87
KY-3	3.13	2.33	1.54

Table 4-4. TOC size distribution of hydrophobicity fractions in various landfill leachates.

Sample	HA %			FA %			Hpi %		
	< 1 kDa	1 kDa-100 kDa	> 100 kDa	< 1 kDa	1 kDa-100 kDa	> 100 kDa	< 1 kDa	1 kDa-100 kDa(10 kDa)	> 100 kDa (10 kDa)
PA untreated	17.78	39.59	42.63	29.54	33.29	37.17	67.93	10.16	21.91
PA treated	23.03	74.39	2.57	33.74	57.04	9.22	67.44	20.52	12.04
NH untreated	39.12	43.86	17.01	63.54	29.12	7.34	68.02	19.15[a]	12.83[b]
NH treated	37.43	48.55	14.02	48.28	34.51	17.21	73.66	16.91[a]	9.43[b]

[a] **1 kDa -10 kDa**

[b] **> 10 kDa**
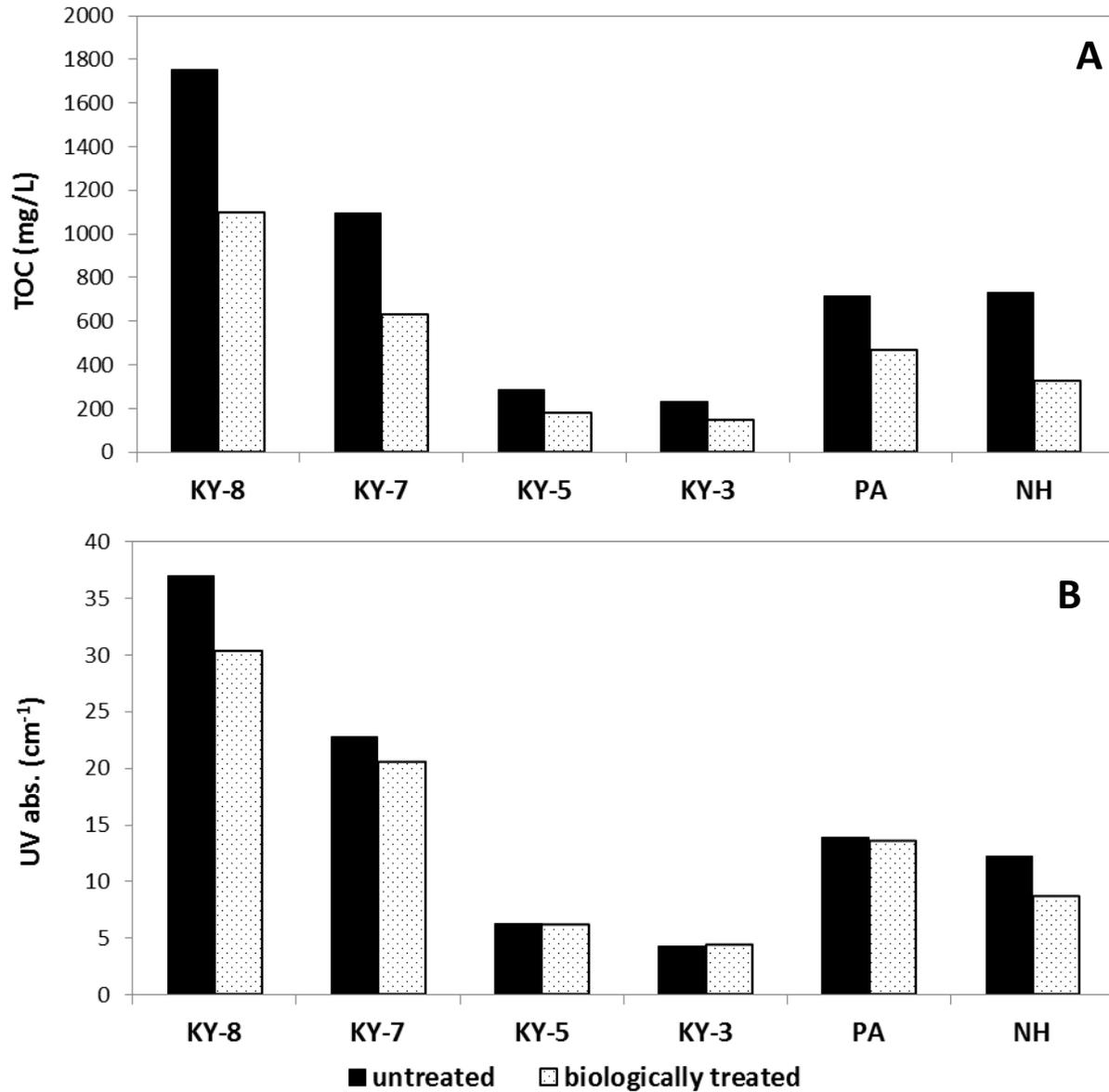
Figure 4-1. TOC (A) and UV254 absorbance (B) before and after biological treatment of various landfill leachates.
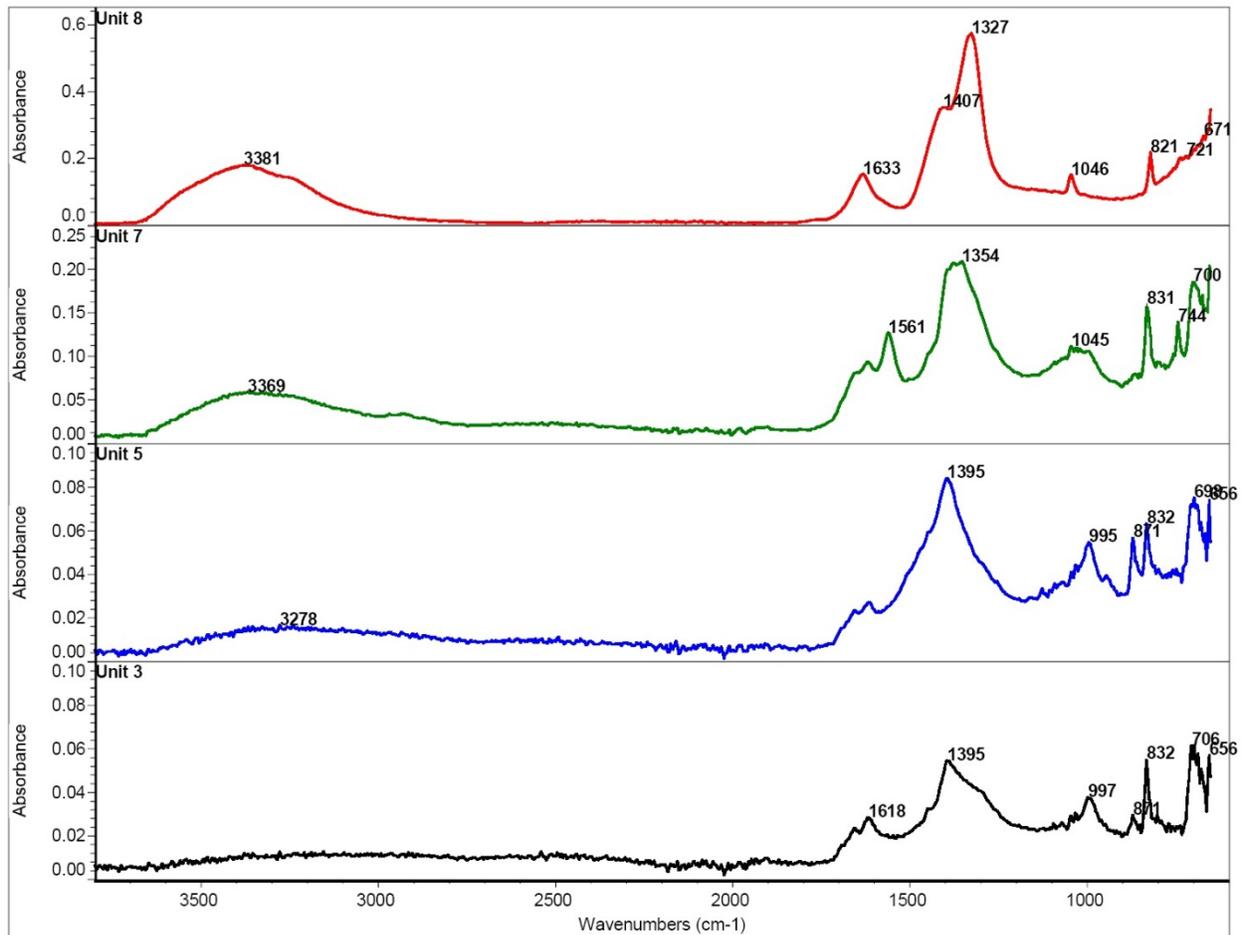
Figure 4-2. FTIR spectra of KY leachates.
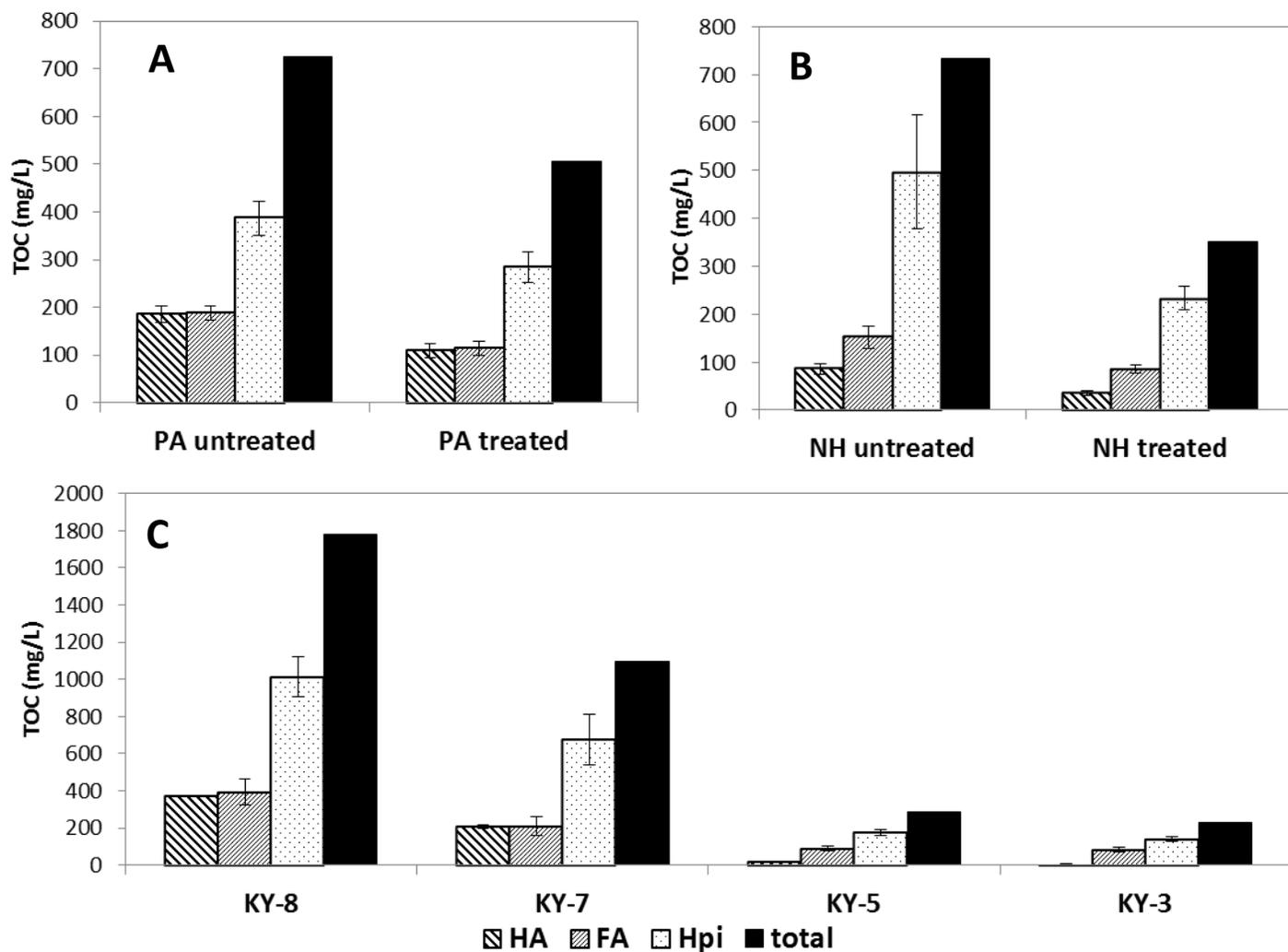
Figure 4-3. Hydrophobicity distribution of PA (A), NH (B) and KY (C) landfill leachates in terms of TOC.
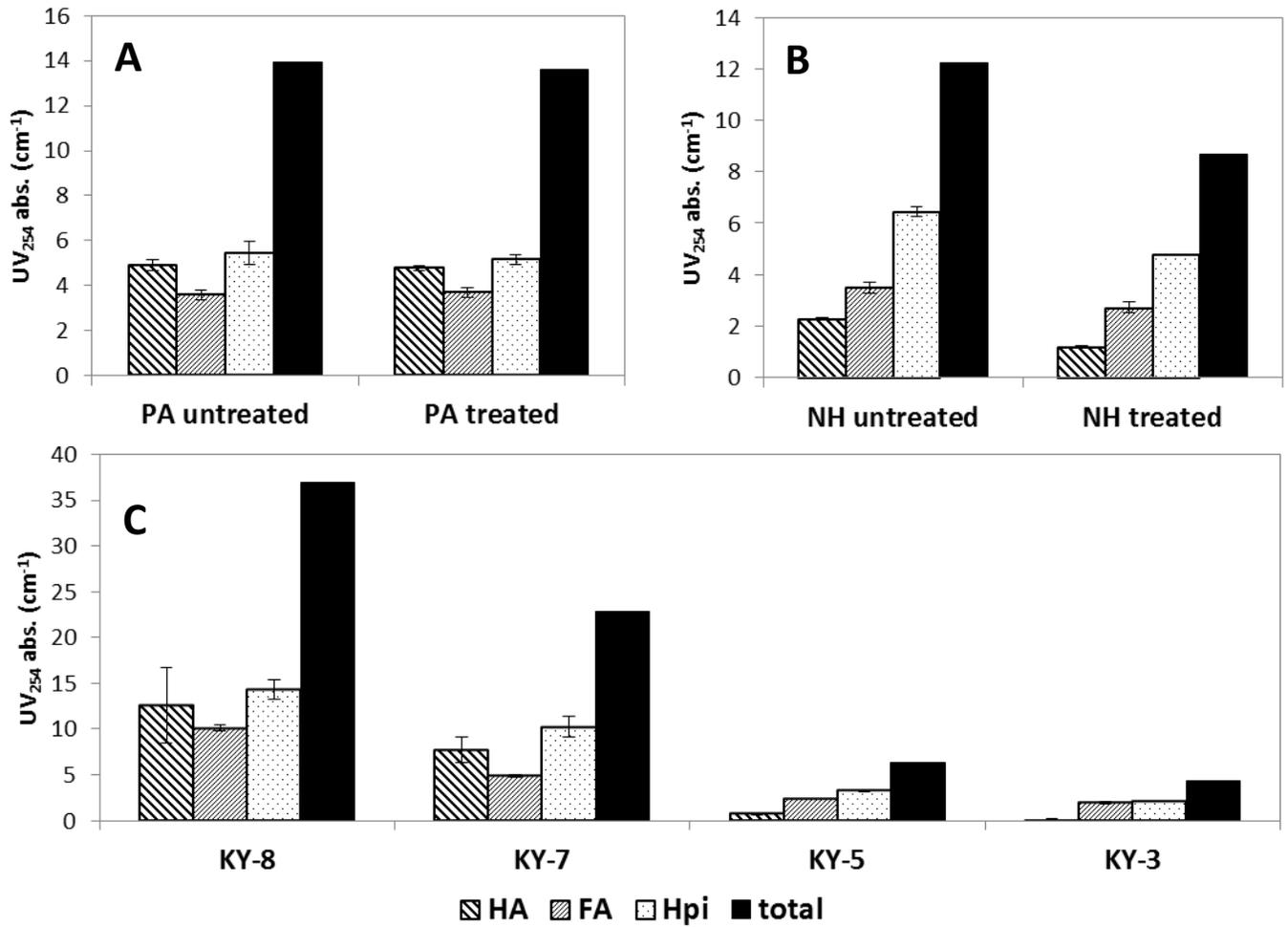
Figure 4-4. Hydrophobicity distribution of various landfill leachates in terms of UV$_{254}$ absorbance.
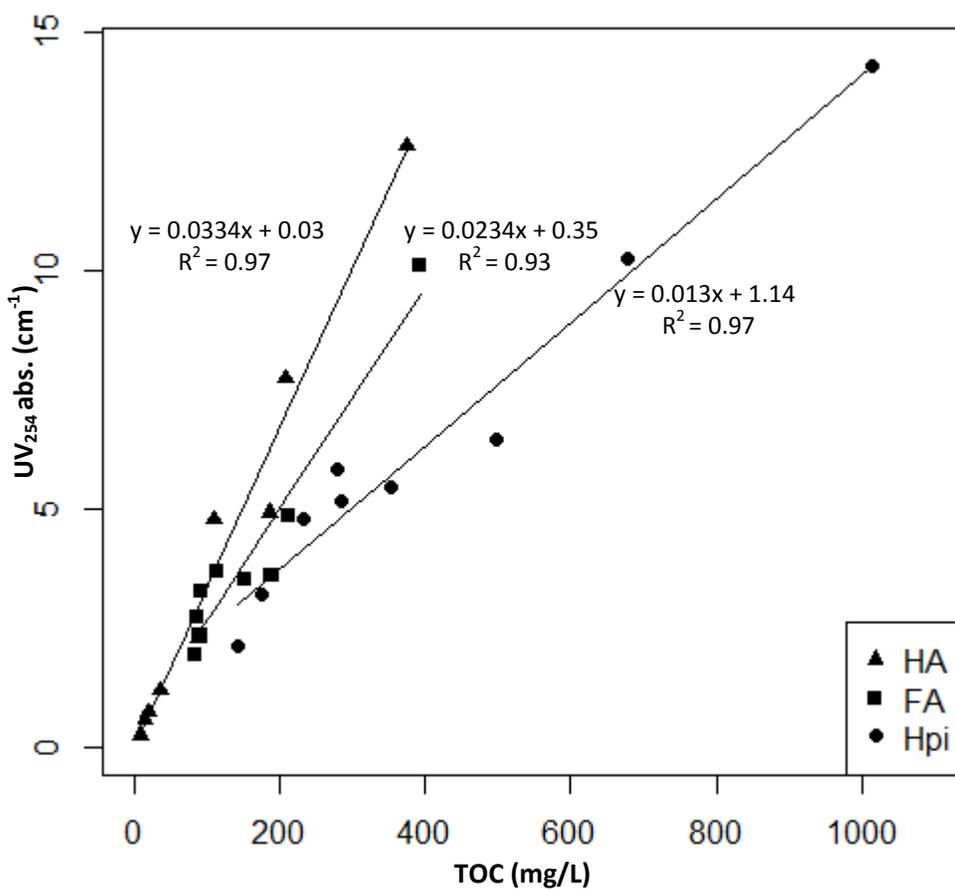
Figure 4-5. Linear Regression analysis of UV$_{254}$ absorbance and TOC for humic acids, fulvic acids and hydrophilic fraction in the landfill leachates.
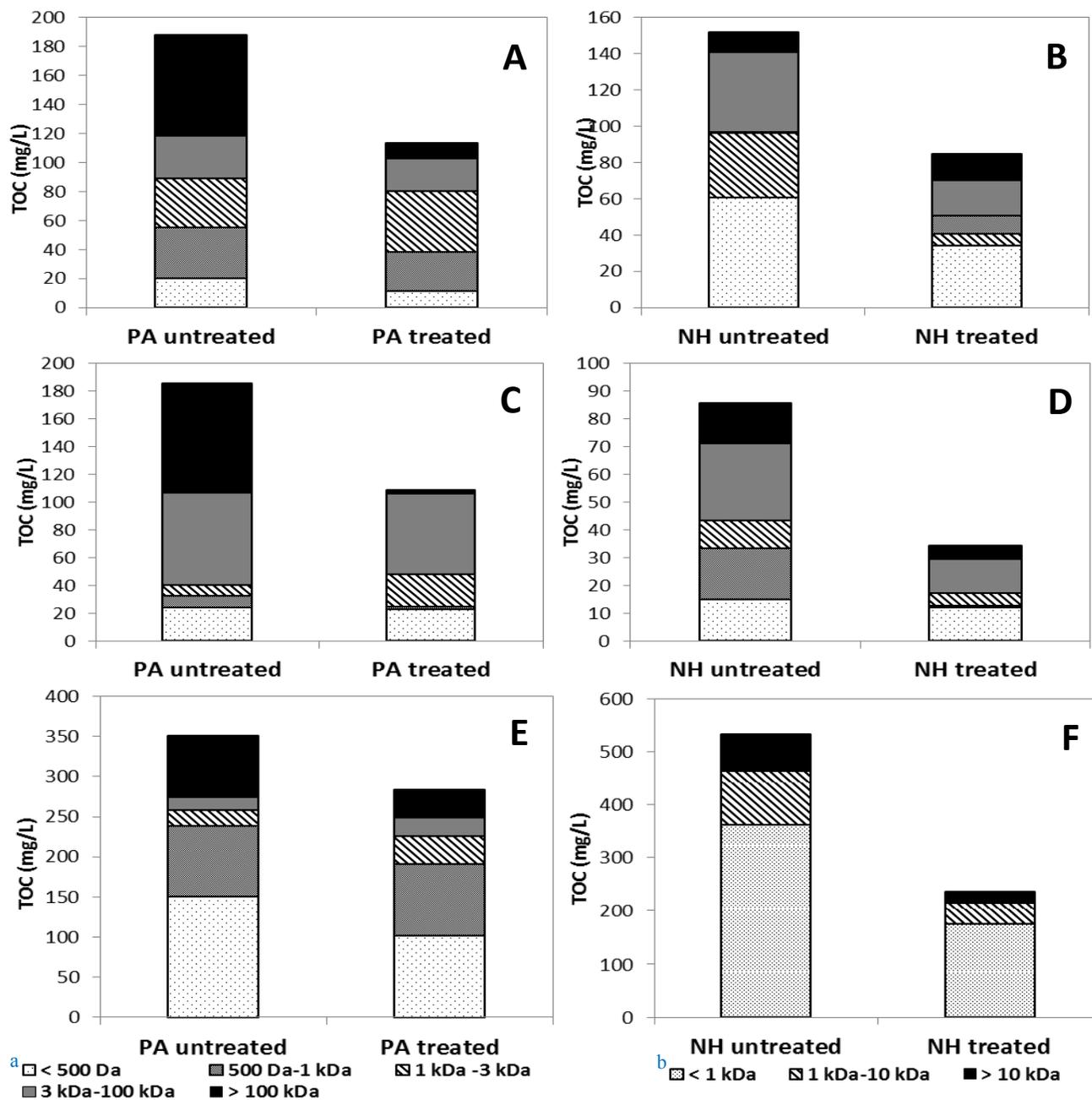
Figure 4-6 (A, B) Humic acids, (C, D) Fulvic acids and (E, F) Hydrophilic fraction

size distribution of various landfill leachates
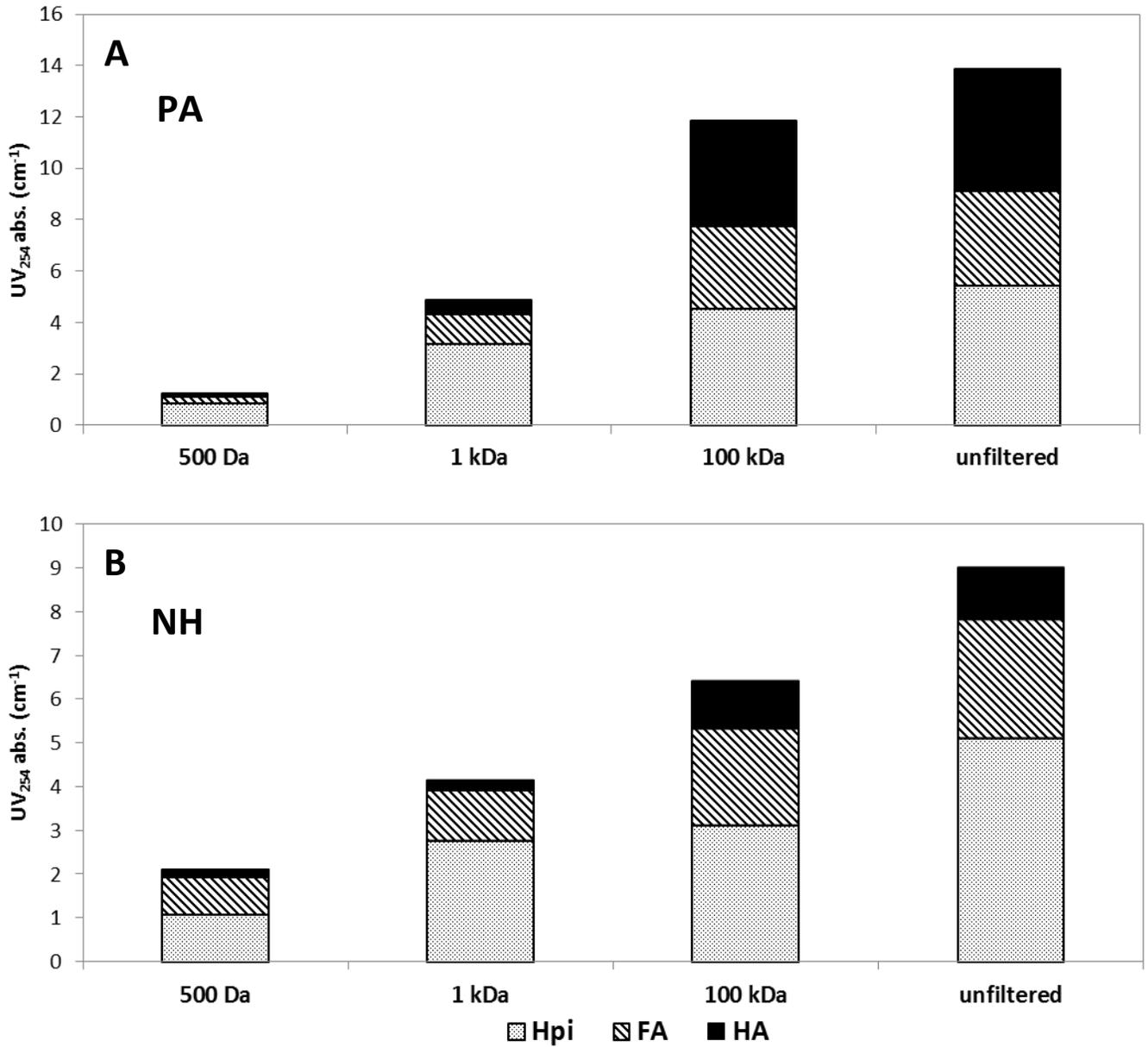
Figure 4-7. UV absorbance distribution of biologically treated PA leachate (A) and NH leachate (B).

Chapter 5. Nitrogen species in landfill leachates under various stabilization states

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Nitrogen species in landfill leachates under various stabilization states

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Abstract

Although the effect of landfill stabilization state on the characteristics of organic matter and ammonia is well documented, there are few investigations into the landfill leachate organic nitrogen under different stabilization stages. In this study, nitrogen species in landfill leachates under various stabilization states were investigated. Ammonia was found to leach slower than organic matter and can maintain a high level within the first a couple of years (< 10 years). Concentration and biodegradability of organic nitrogen were found to decrease with the landfill age. Size distribution study showed that most of organic nitrogen in landfill leachates is < 1 kDa. Protein concentration was analyzed and showed a strong correlation with the organic nitrogen. Different slopes of regression curves of untreated and treated leachates indicate that protein is more biodegradable than the other organic nitrogen species in landfill leachates. XAD-8 resin was employed to isolate the hydrophilic fraction of leachate samples, hydrophilic organic nitrogen was found to be more biodegradable/ bioavailable than the hydrophobic fractions.

1. Introduction

Landfilling as an ultimate disposal method for municipal solid waste is common and wildly applied (van Nooten el al., 2008). Extensive amounts of landfill leachate are generated by percolation and filtration of rainwater into the waste layer (Anglada et al., 2009). The potential environmental impacts of landfill leachate are mainly pollution of groundwater (Kjeldsen et al., 2002), interference with wastewater treatment when sewered (Zhao et al., 2012) and contamination of surface water (Kjeldsen et al., 2002). Historically, landfills were built without engineered liners and leachate collection systems. In recent years, to prevent the seepage of landfill leachate into aquifers, sanitary landfills with installed liners and leachate collection systems are encouraged or have been required. Consequently, a large volume of leachate needs to be discharged into the sewer systems with pretreatment (Primo et al., 2008) or discharged to surface water (Anglada et al., 2009) with complete treatment. Landfill leachate has the potential to impact sewage treatment facilities (Zhao et al., 2012) and water bodies directly or indirectly. Therefore, the component of landfill leachate maybe a critical factor influencing groundwater, publicly owned treatment works (POTWs) and surface waters.

Many factors can affect the composition of landfill leachate (Renou et al., 2008; Kurniawan et al., 2006; Åkesson and Nilsson, 1997), including stabilization stage, waste acceptance, precipitation and seasonal weather variation. The stabilization state is widely accepted as the major influencing factor for the landfill leachate composition (Kjeldsen et al., 2002; Baig et al., 1999; Bookter and Ham, 1982). Municipal solid waste (MSW) is decomposed in four major stages

(Kjeldsen et al., 2002), the aerobic phase, the anaerobic acid phase, the initial methanogenic phase and the stable methanogenic phase.

Leachate in the acidogenic phase contains a high concentration of volatile fatty acids (Ehrig, 1984), which account for the bulk of chemical oxygen demand (COD) and results in a low pH value (as low as 4). This acidic environment promotes an increasing concentration of metal species in the leachate (Erses et al., 2005). Acidic phase leachate is usually characterized by a high biological oxygen demand (BOD), high chemical oxygen demand (COD), a moderately high concentration of ammonia nitrogen and a high biodegradability (BOD/COD ratio ranges from 0.4-0.7) (Zouboulis et al., 2001; Morais and Zamora, 2005). By contrast, for most of the remaining organic materials are bio-refractory compounds with a high molecular weight, such as humic substances (Weis et al., 1989). This results in a moderately high level of COD and a low BOD/COD ratio of less than 0.1 and the pH rises to the alkaline range which drives the metal species to a low level.

Different from organic matter, many studies reported that there is no significant change in ammonia-N concentration from the acidic to the methanogenic phase. In a study of 50 German landfills, ammonia-N did not show a significant decrease 30 years after the landfill closure (Krumpelbeck and Ehrig, 1999). Similarly, in a study of 43 Finish landfills, ammonia-N concentrations tended to increase 30 years after landfill closure (Assmuth and Strandberg, 1993). The source of ammonia in landfill leachate is believed to be from the decomposition of proteinaceous substances (Kjeldsen et al., 2002). The primary mechanism for the decrease in the ammonia-N concentration is leaching or dilution (Burton and Watson-Craik, 1998). Ammonia concentrations in landfill leachates have been reported to be in the range of 500 – 2000 mg/L (Kjeldsen et al., 2002). When high concentrations of ammonia are discharged to waste water

treatment plants (WWTP), this can inhibit the biological process (Shiskowski and Mavinic, 1998). High amounts of ammonia can also be a challenge for the nitrification-denitrification process. When it is released to surface water bodies, there is a risk of eutrophication (Jokela et al., 2002).

In recent years, organic nitrogen has been recognized as a new emerging issue for the water environment. Stricter discharge limits for total nitrogen have increased the importance of and focus on organic nitrogen. With the wider use of nitrification/denitrification, organic nitrogen can account for up to 80% of dissolved nitrogen in the municipal WWTP nitrification-denitrification effluents (Qasim et al., 1999), impacting adversely many costal and estuarine ecosystems as well as certain freshwater ecosystems by eutrophication (Pehlivanoglu and Sedlak, 2004). Dissolved organic nitrogen (DON) can also be a potential source of nitrogenous disinfection by-products (NDBP) (Krasner at el. 2009; Mitch and Sedlak, 2004). Until now, there is no agreement on the compostion of organic nitrogen in WWTP effluents. As indicated by Pehlivanoglu-Mantas and Sedlak (2008), the sum of the specific compounds normally accounts for less than 10% of the organic nitrogen, leaving most of the organic nitrogen unidentified. Westgate and Park (2010)'s study showed that proteinaceous substances are significant correlated with organic nitrogen and could comprise up to 60% of the WWTP effluent organic nitrogen.

Even though the effect of stability states on the properties of landfill leachate is well documented, information of the amount and characteristics of organic nitrogen in landfill leachates under different stabilization stages is limited. Zhao et al. (2012) detected and characterized the organic nitrogen in a landfill leachate. The results show that organic nitrogen in landfill leachate is more bio-refractory than other organic matter, and that biologically treated landfill leachate contains

up to 60 mg/L organic nitrogen. The discharge of landfill leachate to WWTPs is economically effective so organic nitrogen in landfill leachate can contribute largely to the WWTP effluents. Hence, a better understanding of organic nitrogen in landfill leachates is beneficial for controlling the nitrogen loading to water bodies and the subsequent adverse effects.

In this study, four landfill leachates at various stabilization stages were collected from the same landfill to exclude the effect of other factors. Aeration was first conducted for each sample to remove readily biodegradable organic matter. Size fractionation was applied to untreated and aerated leachate samples in conjunction with analysis of various N species, including total N, ammonia, nitrate and nitrite, to give an estimate of organic N. Also, protein and amino acids were analyzed for each leachate sample and correlated with the amount of organic nitrogen. Finally, hydrophilic and hydrophobic fractions of leachate samples were separated with XAD-8 resin, followed with nitrogen species analysis to provide the information of hydrophobicity distribution of organic nitrogen in landfill leachates under various stabilization stages. The objective of this study is to:

(1) Evaluate the effect of stabilization stage on the concentration, biodegradability and size distribution of organic nitrogen in landfill leachates;

(2) Build the correlation of protein/amino acids and organic nitrogen in landfill leachates and evaluate the contribution of protein/amino acids degradation to the ammonia concentration;

(3) Investigate the hydrophobicity distribution of organic nitrogen in landfill leachates to give an implication of the bioavailability/biodegradability of landfill leachate based organic nitrogen and the eutrophication potential.

2. Material and Methods

2.1 Leachate and landfill

All leachates samples were collected from a landfill located in Kentucky (KY), USA. The landfill is comprised of eight individual and separate landfill units, designated Units 1 through 8. Leachate sample collected for this study were from Units 3, 5, 7 and 8, and designated KY-3, KY-5, KY-7 and KY-8 leachates, respectively. Unit 3 is an old inactive landfill unit that is not receiving waste. Unit 5, 7 and 8 are active permitted landfill units. The landfill has been used for solid waste disposal for 35 years. The ages of Unit 3, 5, 7 and 8 are 35, 14, 10 and 2 years, respectively. The landfill has a total property of approximately 782 acres. Average annual precipitation in the landfill region is 44.4 inches of rainfall, plus approximately 17.4 inches of snow. Due to the flat topography, the clayey nature of the soil and the relatively low elevation, the area is naturally poorly drained. It has been observed that seepage of groundwater into the landfill occurs.

The leachate samples were shipped directly from the landfills to our lab in 20-liter polyethylene buckets. The leachates were stored in a refrigerator at 4 ºC to reduce microbial activity. Leachate buckets were shaken well to resuspend settled particles before sampling.

2.2 Biological treatment

Biological treatment of landfill leachate in this study was conducted by continuous aeration. Since leachates contain microorganisms from the waste layer of the landfill, no external seed was added. Microbial flocs similar in appearance to activated sludge were observed during the

aeration process. Four liters of each leachate was aerated by using a porous ceramic diffuser. Distilled water was added to compensate the water lost by evaporation. The KY-8 and KY-7 leachate samples were aerated for 53 days and aerated leachates were sampled on the 21st, 38th and 53rd days for fractionation and analysis. The KY-5 and KY-3 leachate samples were aerated for 21 days, then sampled for fractionation and analysis.

2.3 Fractionation

Size fractionation

A Dead end batch ultrafiltration apparatus was employed for size fractionation in this study. The ultrafiltration apparatus consisted of a 200 mL stirred ultrafiltraion cell (model 8200, Amicon, Belford, MA), a nitrogen gas tank (pressure: 120 kPa) and membrane discs (Millipore, Billerica, MA) with a diameter of 63.5 mm. In each ultrafiltration process, about 180 mL of a leachate sample was pressed through the membrane disc driven by pressure from the nitrogen tank. The MWcutoffs of membrane discs used in this study were: 0.5 kDa, 1 kDa, 3 kDa, *5 kDa, 10 kDa, 30 kDa,* 100 kDa*, and 300 kDa* (YC05, YM1, PLBC, *PBCC, YM10, PLTK,* PLHK *and PBMK,* Millipore, Billerica, MA). *The microfiltration apparatus used in this study is a 300 mL filtration cell (GELMAN, Ann Arber, MI), a vacuum pump and membrane discs of 0.2 mm (47 mm, Millipore, Bedford, MA), 0.45 mm (47 mm, Sartorius Stedim Biotech, France) and 1.5 mm(55 mm, Florham park, NJ).* In each ultrafiltration*/microfiltration* process, about 180 mL of leachate sample without any pretreatment was filtered and collected in a glass bottle, then stored at 4 ºC for further analysis. Size fractionation was conducted in duplicate for one leachate and no significant variation was found *(see supplementary data part 1 for details)*, so all the other

leachate samples were fractionated once. Various analyses (ammonia, NO3, NO2, total nitrogen and protein) were applied to the filtrate.

2.4 Analysis

The glassware used in this study was washed with soapy water, soaked in 10% nitric acid solution, then rinsed with deionized water and baked for 4 hours at 450 ºC. All chemicals were analytical grade. Total organic carbon (TOC) was analyzed using a TOC analyzer (Shimadzu TOC-5000A, Japan). Organic nitrogen (ON) was estimated by subtracting nitrate, nitrite and ammonia nitrogen from total nitrogen (TN) (Pehlivanoglu and Sedlak, 2004; Westgate and Park, 2010). Total nitrogen concentrations of leachate samples and fractions were analyzed by the persulfate digestion method (Hach, Loverland, CO). Nitrate and nitrite concentrations of leachate samples and fractions were measured by an ion chromatograph (DX120, Dionex, Sunnyvale, CA) equipped with an AS9-HS column (Model No. 051786, Dionex, Sunnyvale, CA). Ammonia concentrations of leachate samples and fractions were analyzed with salicylate method (Hach, Loverland, CO). In most cases, organic nitrogen was measured at least three times for statistical purpose. Protein was determined by the modified Lowry method (Lowry et al., 1951) described by Frølund et al. (1996). Amino acids were determined at the Experimental Station Chemical labs at the University of Missouri-Columbia by using Association of Official Analytical Chemists Method 982.30E.

2.5 Statistics

Data graph and correlation analysis were created using Microsoft Office Excel 2010 (Microsoft Corporation, Redmond, CA).

3. Results and Discussion

3.1 Organic nitrogen, NH3 and TOC in association with landfill age.

Figure 5-1 shows the organic N concentration in landfill leachates at various landfill ages. It can be seen that, the organic N concentration decreases with the landfill age. KY-8 leachate sample (2 years old) contains the highest amount of organic N (219 mg/L), while the oldest leachate (KY-3) contains the lowest amount of organic N (18.93 mg/L). This decreasing trend of organic matter is similar to the results reported previously for landfill leachates, while different from the NH_3.

The organic N concentrations in biologically treated leachates at various ages is also shown in Figure 5-1. It can be seen that, the biodegradable organic nitrogen was 50mg/L in the KY-8 (2 years old) leachate and only 4mg/L in the KY-3 (35 years) leachate. So, the biodegradability of organic nitrogen in landfill leachates decreased with landfill age. This decreasing trend is also in consistent with the characteristics of organic matter in leachates as reported previously.

Figure 5-2 shows the NH_3-N concentration in landfill leachates with various landfill ages. It can be seen that, the NH_3-N concentration increased slightly from 1290 mg/L in the 2 years old sample (KY-8) to 1313 mg/L in the 10 years old sample (KY-7). The ammonia in the leachate is believed to be released from the decomposition of proteinaceous substances (Kjeldsen et al., 2002). However, in the 14 years old leachate (KY-5), the ammonia concentration dropped to 521 mg/L then was maintained at the level of 500 mg/L in the 35 year old leachate (KY-3). The decreasing trend of ammonia is different from the previously reported results. The lower concentration of ammonia concentration in the older leachates (KY-5 and KY-3) may be caused by leaching of ammonia. As leachate is removed, the ammonia concentration will drop as free

rainwater replaces ammonia rich leachate. The large drop from year 10 to year 14 is likely due to operational and rainfall condition.

The size distribution of organic nitrogen in biological treated leachates was investigated (Figure 5-6). As shown, generally, the size of organic nitrogen in biologically treated leachates is small. The majority of organic nitrogen lies in the < 500 Da size fractions: 45%, 66% and 64% of organic nitrogen is smaller than 500 Da in the KY-8, KY-7 and KY-5 leachates, respectively. A considerable amount of organic nitrogen was detected in the 500 Da - 1 kDa fractions, 25%, 19% and 11% of organic nitrogen in the size fraction for KY-5, KY-7 and KY-8 leachates, respectively. There was no significant amount of organic nitrogen detected in the 1 kDa -3 kDa size fractions. Hence, most of organic nitrogen in biologically treated landfill leachates is < 1 kDa. This result suggests the difficulties for the physic-chemical treatment of organic nitrogen in landfill leachates, such as membrane separation and coagulation-sedimentation.

Figure 5-3 shows the TOC concentration in raw and biologically treated leachates at various landfill ages. First, it shows the decreasing trend of organic matter concentration (TOC) with longer landfill age. KY-8 leachate (2 years old) contains the highest amount of organic matter (TOC=1834 mg/L) and the TOC concentration decreased with the landfill age increasing. The TOC concentration in the oldest leachate (KY-3) is the lowest (204 mg/L). Second, the biodegradability of leachates under various ages was also evaluated. KY-8 and KY-7 leachate samples were aerated for 53 days. TOC was measured on the 21st, 38th, and 53rd days. It was found that most TOC was removed in the first 21 days for the KY-8 and KY-7 leachates. By comparing the TOC concentration of raw and biologically treated samples, it was found that biodegradability of organic matter in landfill leachate decreased with landfill age. The removal

of TOC by 21days of aeration was 28% in the 2 years old leachate (KY-8) and decreased to 12% in the 35-year old leachate (KY-3).

3.2 protein and amino acids in association with landfill age

Protein concentrations were measured for the untreated and biologically treated leachates under various landfill ages. As shown in Figure 5-7, the concentration of protein in leachate samples decreased with the increasing landfill age. Protein concentration dropped significantly from 1958 mg/L as BSA in the KY-8 leachate (2 years old) to 276 mg/L as BSA in the KY-5 leachate sample (14 years old). The decreasing trend is slower from the KY-5 leachate (14 years old) to KY-3 leachate (35 years old). The protein concentration decreased from 376 mg/L as BSA to 193 mg/L as BSA even though there is a difference of 21 years. This result indicates that the degradation of protein in landfills is faster in the earlier stage, gradually the leachate gets stabilized and the degradation rate gets slower.

Also, the biodegradability of protein was evaluated by comparing the untreated and biologically treated leachates. Generally, the biodegradability decreased with the increasing of landfill age. The biological removal efficiency of protein in the 2 years old leachate (KY-8) is 44%. The removal efficiency of protein reduced to 38%, 32% and 15% sequentially for the 10 years (KY-7), 14 years (KY-5) and 35 years (KY-3) old leachates respectively. This result implies that most of the biodegradable protein was removed during the earlier stage of the landfilling process, leaving the old leachate protein recalcitrant.

Size distribution of protein in the untreated and biologically treated leachates is shown in Figure 5-8. Younger leachates (KY-8 and KY-7) and older leachates (KY-5 and KY-3) are showing different size distribution characteristics. By comparing the protein size distribution of untreated

and treated KY-8 leachates, it can be found that most of the protein removal was contributed by the reduction of the bigger and the smaller size fractions. After the biodegradation, > 100 kDa size fraction reduced significantly from 544.3 mg/L as BSA to 90.8 mg/L as BSA; < 500 Da fraction reduced largely from 668.9 mg/L as BSA to 104.5 mg/L as BSA; 500 Da -1 kDa size fraction decreased from 589.6 mg/L as BSA to 323.3 mg/L as BSA. While, the intermediate size fractions increased significantly or decreased slightly after the biological treatment. The 3 kDa-100 kDa size fraction increased largely from 19.3 mg/L as BSA to 469.3 mg/L as BSA. The 1 kDa-3 kDa size fraction decreased slightly from 135.5 mg/L as BSA to 103.8 mg/L as BSA. KY-7 leachate showed similar size distribution characteristics through the biological treatment. The increasing trend of the intermediate size fraction after the biological treatment can be explained by the partial degradation of bigger size fractions and bio-flocculation of the smaller size fractions. The size homogenization of biological treatment was reported previously for the organic matter in landfill leachate (Zhao et al., 2012). The result of this study proved that it is also the case for protein in landfill leachates.

Also in Figure 5-8, older leachates (KY-5 and KY-3) show different size distribution from younger leachates. Most of the removal through the biological treatment was contributed by the reduction of < 500 Da size fraction. Each of the other size fractions got removed moderately. This result implies that smaller size fraction is less recalcitrant than the bigger size fractions in the stabilized landfill leachates.

The correlation of organic nitrogen and protein in the untreated and biologically treated leachates is shown in Figure 5-10. There were significant linear-correlation between organic nitrogen and protein in both untreated and treated leachates (R^2= 0.96 and 0.97 respectively). It can be seen that, the slope of N-protein regression curve reduced from 9.3 to 7.2 after the biological

treatment, indicating that more protein was removed during the biological treatment comparing with the other species of organic nitrogen. Protein is less refractory than the other species of organic nitrogen.

3.3 hydrophobicity distribution of ON

Landfill leachate samples were separated into hydrophilic and hydrophobic fractions by using the XAD-8 resin. Nitrogen species were analyzed for the hydrophilic fractions to provide estimate of the organic nitrogen concentration, results are shown in Figure 5-9. It can be seen that hydrophilic organic nitrogen decreased significantly with the increasing landfill age. The decreasing rate of hydrophilic organic nitrogen was faster than that of the unfractionated leachate samples. Organic nitrogen in the hydrophilic fraction account for 68% of the total amount in the fresh leachate (KY-8), the proportion of hydrophilic organic nitrogen decreased to 16% and 5% for KY-7 leachate and KY-5 leachate respectively. These results indicate that the biodegradability/bioavailability of the hydrophilic organic nitrogen in higher than that of hydrophobic fractions of landfill leachates in the biological treatment system. This study coincides with a previous study on the waste water effluent (Liu et al., 2011), in which it was found that the hydrophilic DON in the WWTP effluent is more available for the algal uptake and growth.

4. Conclusion

(1) Organic nitrogen concentration in landfill leachates decrease with landfill age. Also, biodegradability of organic nitrogen in landfill leachates is lower in older landfills.

(2) Ammonia concentration in landfill leachates maintains a high level within the first 10 years of landfilling. After 10 years, ammonia concentration reduced to a lower level and keep at this level until 35 years.

(3) Size distribution study shows that most of organic nitrogen in landfill leachates is in the < 1 kDa fraction.

(4) Protein concentration also decreases with landfill age. Size distribution study showed that most of removal of protein in the biological treatment is contributed by the reduction of > 100 kDa and < 1 kDa size fractions, while, intermediate size fractions increased or decreased slightly. It can be explained by partial degradation and/or bio-flocculation in the biological treatment processes.

(5) Organic nitrogen and protein showed strong linear correlation. Different regression slopes indicates that more protein got removed than the other species of organic nitrogen in the biological treatment process.

(6) Hydrophilic organic nitrogen in leachates decreases faster with landfill age than hydrophobic fractions. Proportion of organic nitrogen in hydrophilic fraction reduces in older landfill leachate. Hydrophilic organic nitrogen is more prone to be biodegraded than hydrophobic fraction.

Reference:

van Nooten, T., Diels, L., Bastiaens, L., 2008. Design of a multifunctional permeable reactive barrier for the treatment of landfill leachate contamination: laboratory column evaluation. Environmental Science and Technology 42 (23), 8890-8895.

Anglada, A., Urtiaga, A., Ortiz, I., 2009. Pilot scale performance of the electro-oxidation of landfill leachate at boron-doped diamond anodes. Environmental Science & Technology. 43(6), 2035-2040.

Zhao, R.Z., Novak, J.T., Goldsmith, C.D., 2012. Evaluation of on-site biological treatment for landfill leachates and its impact: a size distribution study. Water Research 46(12), 3837-3848.

Primo, O., Rueda, A., Rivero, M.J., Ortiz, I., 2008. An Integrated Process, Fenton Reaction-Ultrafiltration, for the Treatment of Landfill Leachate: Pilot Plant Operation and Analysis. Industrial & Engineering Chemistry Research 47 (3), 946-952.

Renou, S., Givaudan, J.G., Poulain, S., Dirassouyan, F., Moulin, P., 2008. Landfill leachate treatment: Review and opportunity. Journal of Hazardous Materials 150 (3), 468-493.

Kurniawan, T.A., Lo, W., Chan, G.Y.S., 2006. Radicals-catalyzed oxidation reactions for degradation of recalcitrant compounds from landfill leachate. Chemical Engineering Journal 125 (1), 35-57.

Åkesson, M., Nilsson, P., 1997. Seasonal Changes of Leachate Production and Quality from Test Cells. Journal of Environmental Engineering 123(9), 892-900.

Baig, S., Coulomb, I., Courant, P., Liechti, P., 1999. Treatment of landfill leachates: Lapeyrouse and Satrod case studies. Ozone: Science & Engineering 21(1), 1-22.

Bookter, T.J., Ham, R.K., 1982. Stabilization of solid waste in landfills. Journal of Environmental Engineering 108(6), 1089-1100.

H.J. Ehrig, Treatment of sanitary landfill leachate: biological treatment, Waste Manage. Res. 2 (1984) 131–152.

A.S. Erses, M.A. Fazal, T.T. Onay, W.H. Craig, Determinatio,n of solid waste sorption capacity for selected heavy metals in landfills, J. Hazard. Mater. 121 (1–3) (2005) 223–232.

A.I. Zouboulis, M.X. Loukidou, K. Christodoulou, Enzymatic treatment of sanitary landfill leachate, Chemosphere 44 (2001) 1103–1108.

J.L. Morais, P.P. Zamora, Use of advanced oxidation process to improve the biodegradability of mature landfill leachate, J. Hazard. Mater. B123 (2005) 181–186.

P.H. Chen, Assessment of leachates from sanitary landfills: impact of age, rainfall, and treatmen,t, Environ. Int. 22 (2) (1996) 225–237.

M. Weis, G. Abbt-Barun, F.H. Frimmel, Humic-like substances from landfill leachates—characterization and comparison with terrestrial and aquatic humic substances, Sci. Total Environ. 81/82 (1989) 343–352.

Kruempelbeck, I, Ehrig, H.J., 1999. Long-term behavior of municipal solid waste landfills in Germany, in Cardinia 99, Seventh International Waste Management and Landfill Symposium, 4-8 October, S. Margherita di Pula, Cagliari, Proceedings vol. I, Christensen, T.H., Cossu, R., and Stegmann, R. Eds., CISA—Environmental Sanitary Engineering Centre, Cagliari, Italy, 1999, 27.

Assmuth, T., Strandberg, T., 1993. Groundwater contamination at Finnish landfills, Water Air Soil Pollution 69(1-2), 179-199.

Burton, S.Q., Watson-Craik, I.A., Ammonia and nitrogen fluxes in landfill sites: applicability to sustainable landfilling, Waste Management and Research 16(1), 41-53.

Shiskowski, D.M., Mavinic, D.S., 1998. Biological treatment of a high ammonia leachate: influence of external carbon during initial startup. Water Research 32(8), 2533–2541.

Jokela, J.P.Y., Kettunen, R.H., Sormunen, K.M., Rintala, J.A., 2002. Biological nitrogen removal from municipal landfillleachate: low-cost nitrification in biofilters and laboratory scale in-situ denitrification. Water Research 36(16), 4079–4087.

Mitch, W.A., Sedlak, D.L., 2004. Characterization and fate of N-nitrosodimethylamine precursors in municipal wastewater treatment plants. Environmental Science and Technology 38(5), 1445-1454.

Pehlivanoglu, E., Sedlak, D.L., 2004. Bioavailability of wastewater-derived organic nitrogen to the alga *Selenastrum Capricornutum*. Water Research 38(14-15), 3189-3196.

Qasim, S.R., 1999. Wastewater treatment plants: Planning, design, and operation. Technomic, Pennsylvania.

Krasner, S.W., Westerhoff, P., Chen, B., Rittmann, B., Nam, S., Amy, G., 2009. Impact of Wastewater Treatment Processes on Organic Carbon, Organic Nitrogen, and DBP Precursors in Effluent Organic Matter. Environmental Science and Technology 43 (8), 2911-2918.

Pehlivanoglu-Mantas, E., Sedlak, D.L., 2008. Measurement of dissolved organic nitrogen forms in wastewater effluents: Concentrations, size distribution and NDMA formation potential. Water Research, 42(14), 3890-3898.

Westgate, P.J., Park, C., 2010. Evaluation of proteins and organic nitrogen in wastewater treatment effluents. Environmental Science and Technology 44(14),5352-5357.

Liu, H.Z., Jeong, J., Gray, H., Smith, S., Sedlak, D.L., 2011. Algal uptake of hydrophobic and hydrophilic dissolved organic nitrogen in effluent from biological nutrient removal municipal wastewater treatment systems. Environmental Science & technology 46(2), 713-721.

Frølund, B., Palmgren, R., Keiding, K., Nielsen, P.H., 1996. Extraction of extracellular polymers from activated sludge using a cation exchange resin. Applied Microbiology and Biotechnology 30(8), 1749-1758.

Lowry, O.H., Rosebrough, N.J., Farr, A.L., Randall, R.J., 1951. Protein measurement with the folin phenol reagent. Journal of Biological Chemistry 193(1), 265-275.
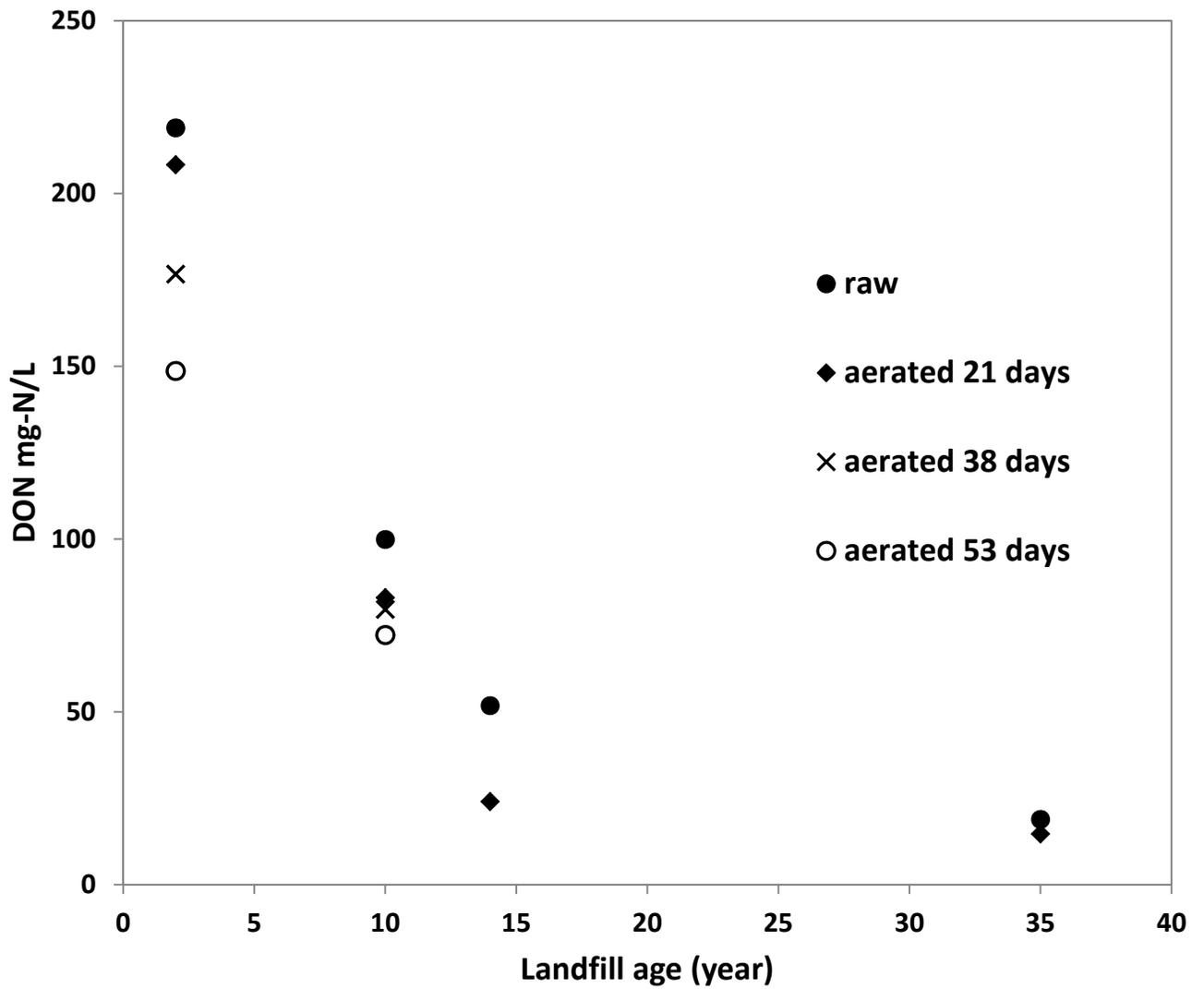
Figure 5-1. Organic nitrogen concentration in associate with landfill age.
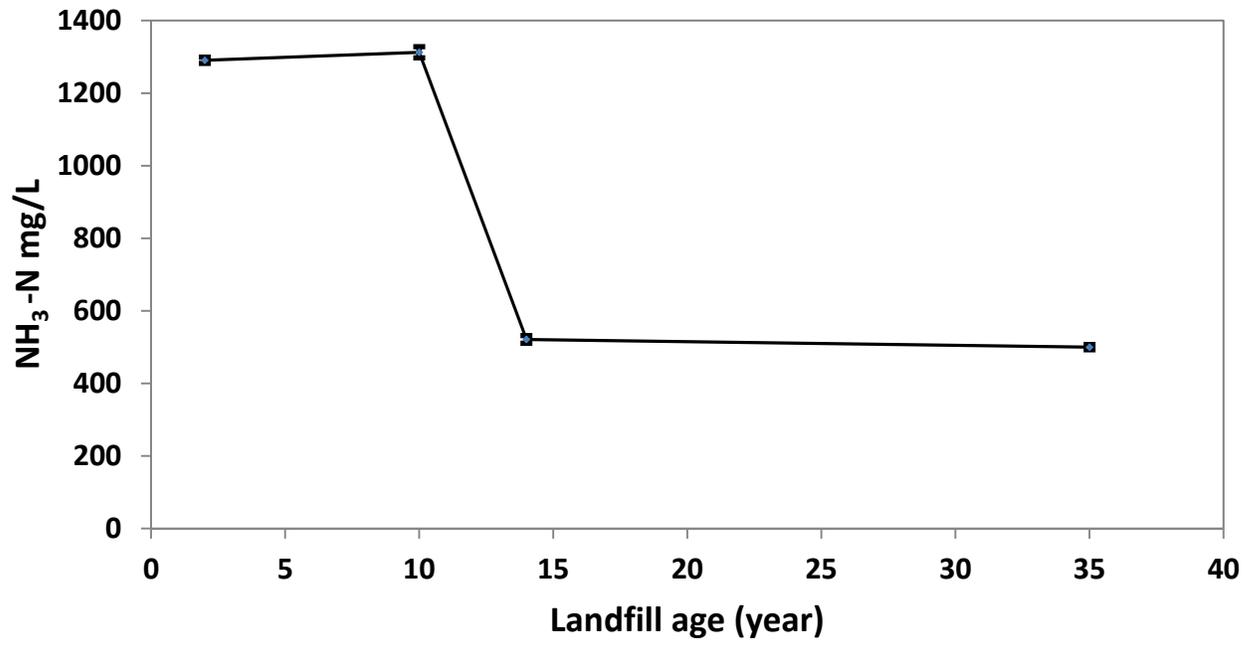
Figure 5-2. Ammonia concentration in association with landfill age.
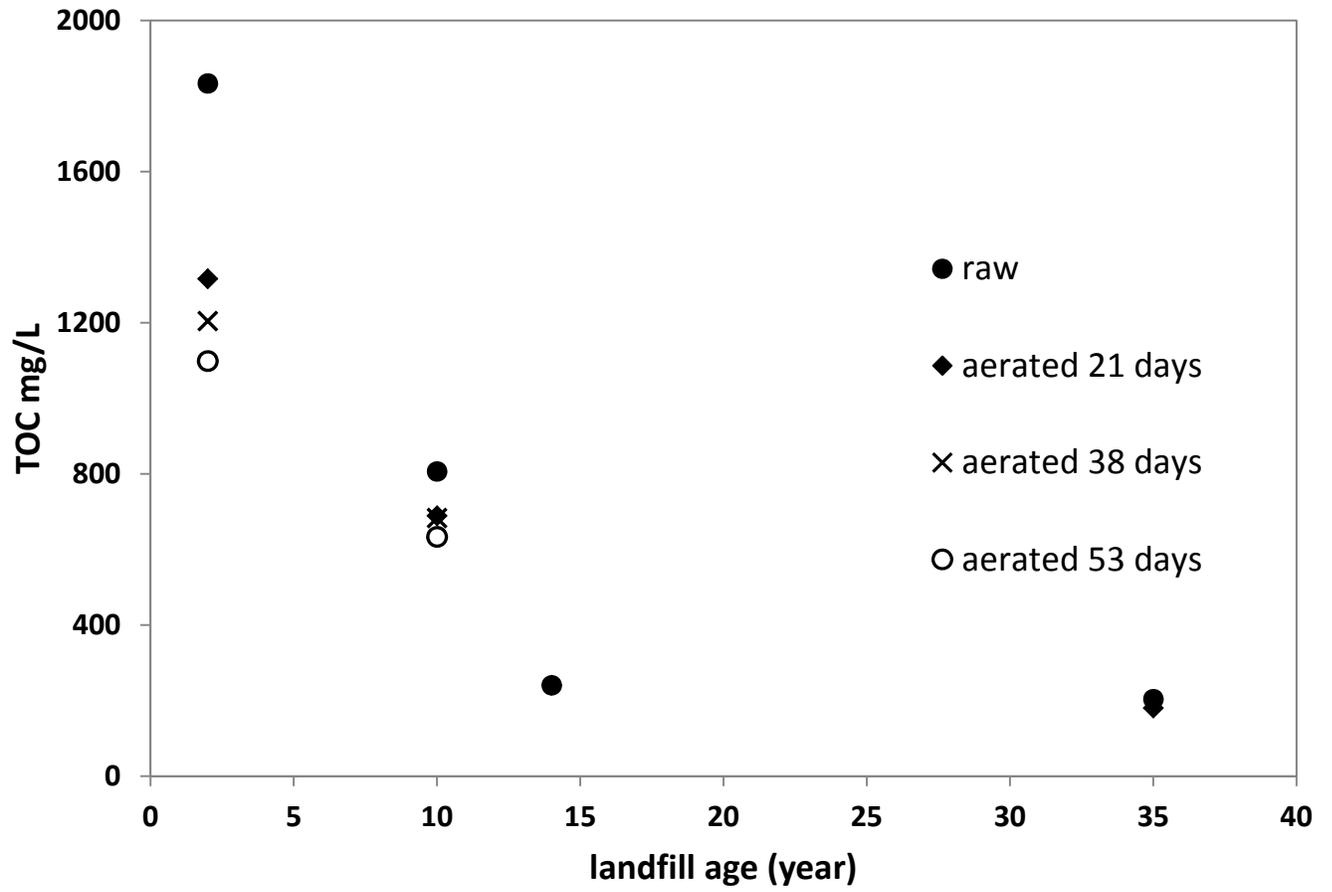
Figure 5-3. TOC concentration in association with landfill age.
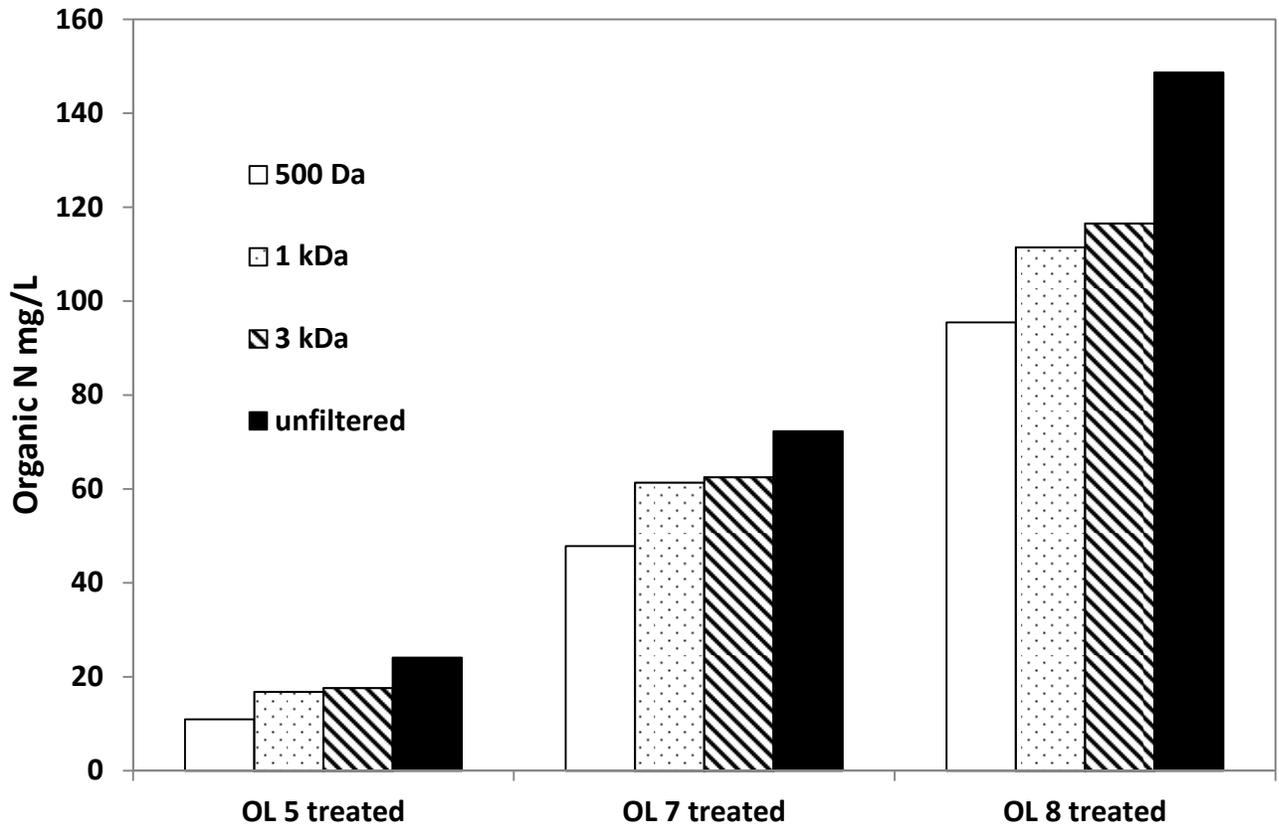
Figure 5-4. Organic Nitrogen size distribution of biologically treated leachates.
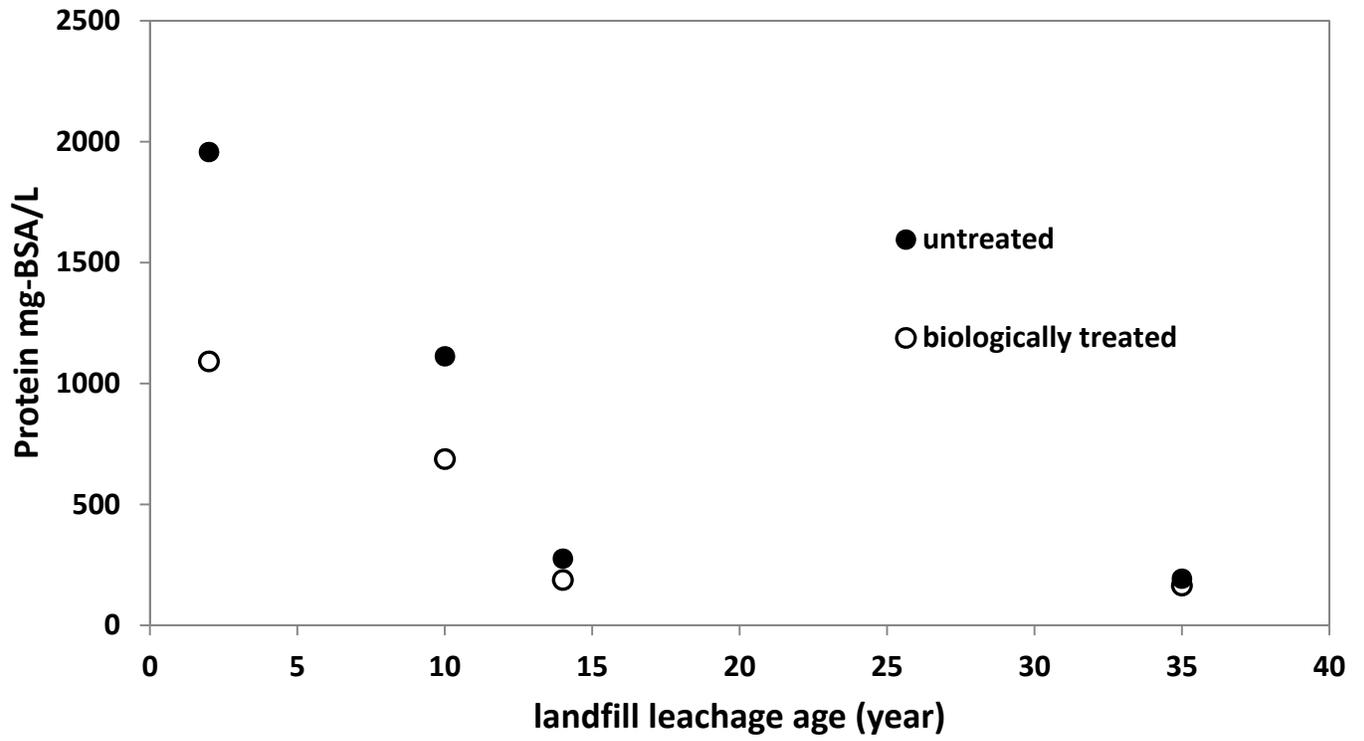
Figure 5-5. Protein concentration in associate with landfill age.
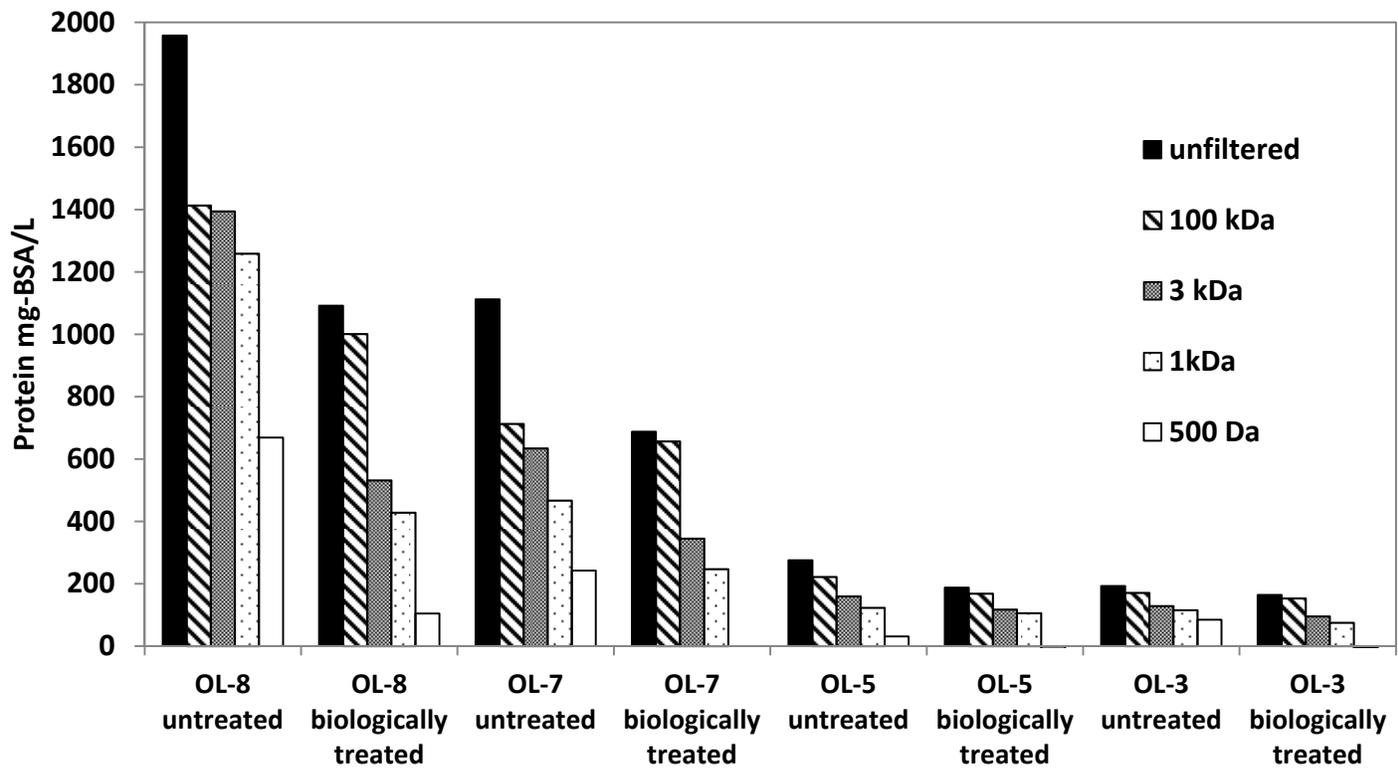
Figure 5-6. Protein size distribution in the landfill leachates with various landfill ages.
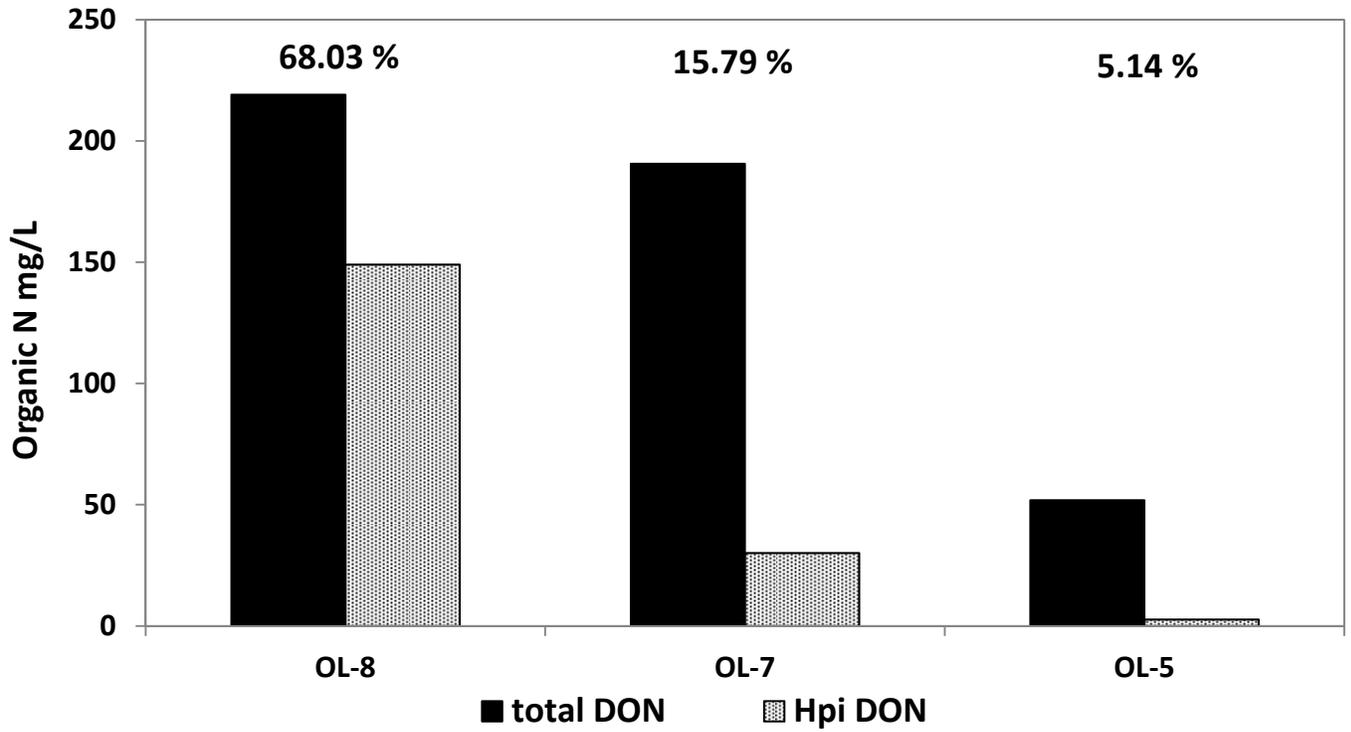
Figure 5-7. Total and hydrophilic organic nitrogen in leachates with various landfill ages.
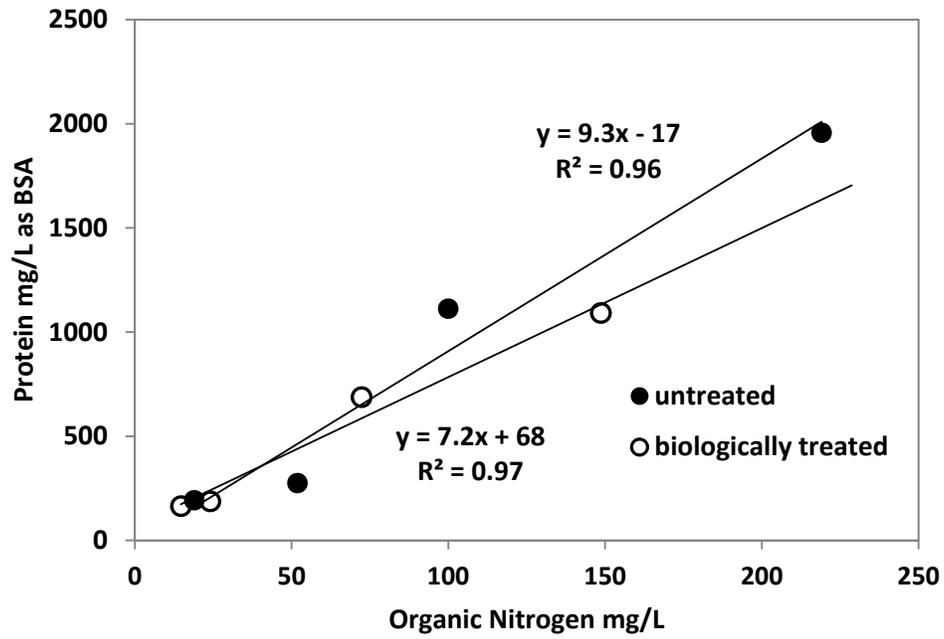
Figure 5-8. Correlation of organic nitrogen and protein in the untreated and biologically treated

landfill leachates.

Chapter 6. Treatment of Organic Matter and Methylated Arsenic in Landfill Biogas Condensate

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Abstract

Biological and physical-chemical treatment methods were used to treat a landfill biogas (LFG) condensate to explore the feasible treatment alternatives for organic contaminant and arsenic removal efficiency. The treatment using a sequencing batch reactor (SBR) showed that biological treatment was effective for the degradation of organic matter, even in an environment containing high levels of arsenic. This indicated a relatively low toxicity of organic arsenic as compared to inorganic arsenic. However, for arsenic removal, oxidation-coagulation, including biological oxidation, conventional oxidation and advanced oxidation followed by ferric salt coagulation, and carbon adsorption were not effective for what is believed to be tri-methyl arsenic. Among these, advanced oxidation-coagulation showed the best treatment efficiency (15.1% removal). Only reverse osmosis (RO) could reduce the arsenic concentration to an acceptable level to meet discharge limits. These results implied high stability and low toxicity of organic arsenic.

Keywords: sequencing batch reactor, coagulation-flocculation, Fenton's reagent, granular activated carbon, reverse osmosis, cost analysis.

1. Introduction

Biogas (methane) generation, collection and utilization could have an important impact on future energy and global warming scenarios. Biogas is a renewable biofuel and there is interest in using this to replace fossil fuel. Also, since the global warming potential (GWP) of methane is 25 times of carbon dioxide (Forster et al., 2007), the oxidation of biogas methane to carbon dioxide and water can reduce the GWP of these gases. Biogas originates either from landfills or anaerobic digesters, produced mainly from organic fractions of municipal solid waste (Barlaz et al., 2004; Levis and Barlaz, 2011; Amini and Reinhart, 2011) and sewage sludge (Tchobanoglous et al., 2004). LFG is collected from landfill gas extraction wells, transported via under and above ground piping systems,,and properly treated to be suitable for turbine, engine and combustion systems. Through natural or artificial cooling or through physical processes such as volume expansion, water and other vapors are removed from landfill gas. The collected liquid is referred to as condensate or gas derived liquids and requires treatment before discharge to a POTW or the environment.

LFG condensate is composed principally of an aqueous phase and a floating hydrocarbon phase. Pollutant compounds found in most condensate samples in either the aqueous or organic phase are benzene, toluene, 2-butanone (MEK), phenol, ethyl benzene, benzyl alcohol, bis (2-chloroisophropyl) ether, bis (2-ethylhexyl) phthalate, naphthalene, n-nitrosodimethylamine, 2, 4-dimethylphenol, and 4-methylphenol (Briggs, 1988). The organics partition between the aqueous phase and organic phase depending on the temperature and the organic phase/water partition coefficients (Briggs, 1988). LFG condensate production can amount to 5000 liter/day in a

municipal landfill (Briggs, 1988). The management of LFG condensate is problematic since there is little information available concerning condensate treatment and therefore, disposal options are not clear.

In this study, a LFG condensate sample was collected from a landfill located in Pennsylvania, USA. In a preliminary test, BOD (18000 mg/L) and arsenic (7-40mg/L) concentrations were found to be unacceptable for discharging this waste stream to the existing landfill waste water treatment plant. In particular, attention was paid to the high level arsenic because of its well-known toxicity and strict regulation. The arsenic was reported to be in the form of organic arsenic.

The natural input of arsenic in the environment may be due to weathering processes of As-bearing minerals in soils and sediments. Anthropogenic activities include mining and smelting, and commercial use of wood preservatives, biocides and alloying agents (Huang et al., 2009; Lafferty and Loeppert, 2005).

Arsenic has been a human health concern since it is carcinogenic to several organs in the human body (Parks et al., 2003; Smith et al., 1992). The drinking water standard of arsenic in the US was reduced from 50µg/L to 10µg/L in 2001 (USEPA, 2001). Up to 250 mg/L of As was found in landfill leachate samples (unpublished data). In environmental systems, inorganic arsenic exists in two oxidation states: iAs^{III} and iAs^{V}; organic arsenic occurs as methylated and more complex compounds: $MMAs^{III}$, $MMAs^{V}$, $DMAs^{III}$, $DMAs^{V}$,$TMAsO^{V}$, $TMAs^{V}$. (Lafferty and Loeppert, 2005) as listed in Table 6-1.

In landfills, anaerobic bio-decomposition combines with complex chemical-physical processes, providing a condition for inorganic arsenic transformation through bio-alkylation and hydride

generation (Pinel-Raffaitin et al., 2007; Michalke et al., 2000). Extensive mechanistic studies have been conducted to explore the organic transformations of arsenic. Bio-methylation leads to the formation of methylated arsenic by combining reduction and methylation (Challenger, 1945; Cullen and Reimer, 1989). Volatile methyl derivatives of arsenic can potentially be transported from waste to biogases and ultimately reside in the landfill biogas condensate.

Inorganic arsenic treatment has been extensively studied to meet the stricter regulation. Coagulation and Fe-Mn treatment showed some success to immobilize soluble inorganic arsenic (Edwards, 1994), for removal from aqueous solution by sedimentation, filtration and membrane separation. Enhanced coagulation can be employed either to meet stricter regulations for arsenic in treated water (Boccelli et al., 2005) or to treat the water with high arsenic concentration (Song et al., 2006). Polymeric coagulants also showed better performance than conventional coagulants for arsenate (Fan et al., 2003). However, there is limited information for organic arsenic treatment, although some research is reported for organic arsenic removal for drinking water treatment (Thirunavukkarasu et al., 2002).

2. Material and Methods

2.1 Sample collection

The landfill gas condensate sample was collected from a pilot scale chiller system which removed liquids from the gas stream in a landfill located at Pennsylvania (PA), USA. The gas condensate sample was shipped in polyethylene containers directly from the landfills to our lab, and stored at 4°C in the dark immediately after being received to reduce microbial activity. Before sampling for treatment and analysis, containers were shaken well to resuspend settled particles.

2.2 Treatment methods

Sequencing Batch Reactor (SBR)

Biological treatment of landfill biogas condensate was operated in a lab-scale SBR system using a 10 liter reactor. The initial biomass was taken from an operating biological reactor treating condensate at a landfill. The solids retention time and hydraulic retention time were 25 days and 10 days, respectively. To simulate the dilution achieved by the treated effluent from the biological leachate treatment plant, the gas condensate was diluted to 15% with water containing the sufficient nutrients (180 mg/l of nitrogen as urea and 38 mg/L of phosphorus as K_2HPO_4). The feed TOC and arsenic concentrations were 930mg/L and 10.6mg/L respectively. The MLSS of the reactor averaged 3300mg/L ± 400mg/L at steady state and the pH value was maintained at 8.2-8.3.

Coagulation

Coagulation was conducted with a six paddle stirrer (Model 300, Phipps & Bird, Inc., Richmond, VA). Ferric chloride ($FeCl_3$) was used as coagulant with various concentrations (25, 50, 100, 200, 500 and 1000 mg/L). 600 mL beakers were used to fit paddles of the stirrer. The sample size was limited to 200 mL in each beaker because of the limited amount of condensate available for testing. The coagulation procedure was as follows: Flash stirring for 1 min at 150 rpm; slow stirring for 25min at 35 rpm; Settling for 25 min.

Permanganate Oxidation

Potassium permanganate ($KMnO_4$) was used as a conventional oxidant with various concentrations (100, 500, 1000 and 1500 mg/L). Sample size was 100 mL each. Samples were stirred for 15 min with $KMnO_4$ then settled overnight in a 250 mL beaker.

Fenton's reagent oxidation

Advanced oxidation processes generate and use hydroxyl radical (•OH) which can breakdown compounds that cannot be destroyed by conventional oxidation methods. The electrochemical oxidizing potential of hydroxyl radical is 2.8 V, which is much higher than other conventional oxidants, such as ozone, hydrogen peroxide and chlorine and only second to fluorine (Al-Kdasi. 2004). Fenton's reagent was used in this study as an advanced oxidation technology because of its operational simplicity and effectiveness (Lopez et al. 2004). The reaction for Fenton's reagent is shown as follows:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + •OH + OH^- \qquad (1)$$
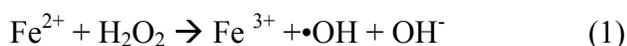
As shown in equation (1), the hydroxyl radical (•OH) is generated as the oxidant and Fe^{3+} can be used as the coagulant, because OH^- generated in the Fenton's reaction at a low pH value is preferred thermodynamically.

In this study, the Fenton's reaction was conducted in an acid environment. Before the reaction, pH was adjusted to 3.49 to make the reaction thermodynamically favorable. The Fenton's reaction took place in a 250 mL beaker with magnetic stirrer and the sample size was 100 mL. The dosage of Fe^{2+} (in $FeSO_4$) was set at 1000 mg/L with a varied H_2O_2 dose (50, 500, 1000, 2000, 3000 and 5000mg/L).

Carbon absorption

In the granular activated carbon (GAC) absorption test, 500 mL of SBR effluent was mixed with various amounts of GAC (0, 4, 10 and 20g/L). Then the mixture of sample and GAC was shaken for 4 hours in a 1-liter capped plastic bottle to achieve saturated absorption.You need some data for the carbon brand and mesh size. Do you know where the carbon came from?

Membrane separation

Reverse osmosis (RO) was used as a membrane separation method in this study. The RO system (Model WHER25, Whirlpool, Ecodyne Water Systems Inc., Woodbury, MN) was driven by a peristaltic pump with pressure measured as 14.5 psig. The recovery ratio was 9.83%.

2.3 Analyses

All chemicals used in this study were analytical grade. All the glassware was washed with soapy water, water rinsed, soaked in 10% nitric acid, rinsed with deionized water and baked for 4 h at 450ºC. Total organic carbon (TOC) was analyzed using high temperature combustion with a TOC analyzer (Shimadzu TOC-5000A, Japan). Arsenic analysis was conducted by using a Thermo Electron X-Series inductively coupled plasma with mass spectrometer (ICP-MS) per Standard Method 3125-B (APHA, 1998). ICP-MS Samples and calibration standards were prepared in a matrix of 2% nitric acid by volume. Mixed liquid suspended solid (MLSS) was measured as per standard method (APHA, 1998).

Arsenic speciation was done at Exova (Santa Fe spring, CA). Different species of arsenic was differentiated into As^{III}, As^{V}, DMA and MMA by with liquid chromatography (LC), arsenic species was quantified by inductively coupled plasma-mass spectroscopy (ICPMS). 1.0 mL of sample was diluted to 5mL before analysis for arsenic species.

2.4 Cost evaluation

Cost analysis of chemicals used in this study was based on the optimum dosage and the unit price in the U.S. market. Activated carbon may be used for four times before reaching saturation. No other factors, such as chemical sludge disposal, reject solution treatment were included in cost consideration. Price of chemicals may vary for different time and locations. The cost evaluation was used to provide a reference for price comparison of different technologies.

3. Results and Discussion

3.1 Biological treatment

Biological treatment was conducted in a SBR system to treat the diluted landfill gas condensate, since this process is widely used at landfills for leachate treatment. The performance of the SBR system on TOC and total arsenic removal are shown in Figures 6-1 and 6-2, respectively. As shown in figure1, there were three phases regarding the organic matter removal in the SBR system. In phase I, from day 1 to day 9, the TOC concentration in the SBR effluent dropped sharply from 143 mg/L (day 1) to 64 mg/L (day 9). Over this same time period, the biomass concentration in the biological reactor (Figure 6-3) was reduced from 8728 mg/L (day 2) to 3590 mg/L (day 9) in terms of MLSS. The biomass in the SBR system was taken from another activated sludge system treating undiluted landfill gas condensate, which resulted in the high initial MLSS.

In Phase II, from day 10 to day 25, the MLSS did not changed little, but the effluent organic matter continued to decline from 57mg/L (day 10) to 22 mg/L (day 25). In Phase III, the effluent

organic matter remained relatively constant and averaged 25 mg/L effluent TOC from day 26 to the end of operation. The biomass concentration also remained constant. The overall TOC removal in the SBR was around 85%.

Concerning the toxicity of arsenic, the biological system performed well under the high arsenic environment. This result indicated that arsenic in organic form did not hinder the biological activity in the biological system. The low toxicity of organic arsenic has reported from toxicology studies of arsenic species (Hughes, 2002; Cullen and Bentley, 2005); the toxicity of inorganic As was reported to be hundreds to thousands higher than organic species of arsenic in terms of the lethal dose that can cause 50% death for mice.

The arsenic removal performance of the SBR system is shown in figure 6-2. There were two phases regarding the As treatment. During phase I, the effluent total arsenic concentration was reduced from 17 mg/L to 9 mg/L. As mentioned above, the biomass of the SBR system was taken from anther activated sludge system treating undiluted landfill gas condensate, which resulted in the As concentration in the reactor being higher than in the feed. From day 10 to the end of the operation, which corresponds to phases II and III of the TOC treatment, the effluent total arsenic concentration fluctuated around 7.8 mg/L. The total arsenic removal efficiency from day 10 day 37 was 26%.

A comparison of the removals in these phases provided insight into the mechanisms for reduction in arsenic and TOC. During phase I the biomass concentration in the reactor rapidly declined and most of the TOC and As removal was thought to be caused by biomass wastage. After day 9, biomass and arsenic concentrations remained steady but the TOC continued to decline, which is believed to be caused by bio-degradation. The organic compounds found in

most landfill gas condensates have been reported to be volatile and readily degradable (Briggs, 1988). It is thought that a small fraction of the organic arsenic is immobilized by biomass absorption then removed from the biological system by sludge wastage. Biosorption of different species of metal (loid)s was reported previously (Çeçen and Gürsoy, 2001), however, arsenic absorption by biomass has not been investigated.

$FeCl_3$ is known to be an effective coagulant for inorganic arsenic so was used as a coagulant for the SBR daily effluent. Each day, the effluent from the bioreactor was dosed with 400 mg/L of $FeCl_3$. The results are shown in figure 6-2. By comparing the effluent arsenic following coagulation over days 9, 10 and 11 with the uncoagulated effluent, it can be seen that the addition of ferric chloride removed approximately and additional 1 mg/L of arsenic.

Additional coagulation studies were conducted with a wider range of doses using the SBR effluent collected over day 12 to day 20. As shown in Figure 6-4, the maximum removal efficiency of arsenic in the SBR effluent was 8.0% at a dose of 500 mg/L of $FeCl_3$, leaving 6.7 mg/L of arsenic in the treated solution. While organic matter was removed up to 65% in terms of TOC with 200 mg/L of $FeCl_3$ (Figure 6-5), resulting in an effluent TOC of 11 mg/L, the effect on arsenic, shown in Figure 6-4, was minimal. Since inorganic arsenic was reported to be successfully removed by coagulation-flocculation (Edwards, 1994; Boccelli et al., 2005; Song et al., 2006; Fan et al., 2003), these results indicate that most of arsenic in the SBR effluent was in organic form and bio-oxidation did not mineralize the organic arsenic in the SBR system.

Hence, regarding the landfill gas condensate treatment, biological system (SBR) showed success for organic matter removal. For arsenic removal, biosorption by biomass followed by wastage

removed approximately 25% of the arsenic, but the concentration in the effluent was not low enough to be discharged directly to receiving waters.

3.2 Oxidation followed by coagulation

The failure of biooxidation/coagulation to remove arsenic from the condensate led to an attempt to oxidize the organic arsenic using chemical oxidation. Potassium permanganate ($KMnO_4$) was used as an oxidant to treat the SBR effluent using doses of 100, 500, 1000, 1500 mg/L. As shown in figure 6-6, up to 62% of the residual organic matter was removed in terms of TOC with a $KMnO_4$ dose of 1000 mg/l, leaving the effluent TOC at 12mg/L. The removal efficiency increased with higher amounts of $KMnO_4$ up to 500 mg/L. Additional $KMnO_4$ above 500 mg/L did not improve the treatment performance.

$FeCl_3$ coagulation was applied on the $KMnO_4$ treated SBR effluent to determine if the arsenic had been oxidized. As shown in figure 6-7, no more than 6% of arsenic could be removed by the combination of chemical oxidation and $FeCl_3$ coagulation with FeCl3 dose of 600 mg/L. Even though a slight increase in removal efficiency was observed with more coagulant, no significant removal was found within a practical dose range.

As reported by a previous study (Torrens and Salerno, 1995), $KMnO_4$ was superior to peroxide and ozone for ground water arsenic treatment as an oxidant the results from this study, combined with the study of Torrens and Salerno indicate that, $KMnO_4$, an chemical oxidants in general, do not break down the organic structure of organic arsenic, although it could remove other organic matter contained in biologically treated condensate.

Some advanced oxidation processes are believed to be capable of breaking down the compounds that cannot be destroyed by conventional oxidation methods. Fenton's reagent is widely used as

an advanced oxidation process since it's simple and effective. Fenton's treatment is believed to be a combination of oxidation and coagulation since both radical hydroxide ($\cdot OH$) and ferric cation exist in the system. So in this study, no additional coagulant was added to the Fenton's effluent.

Fenton's reagent with various concentrations of H_2O_2 (2.9, 14.7, 29.4, 58.8, 88.2 and 147.1 mg/L) and a constant amount of Ferrous sulfate (17.9 mg/L) was applied to the SBR effluent. The treated arsenic concentration was plotted with H_2O_2 concentration and is shown in figure 6-8. It can be seen that, arsenic removal efficiency increased with the H_2O_2 dose up to 15mg/L. The maximum removal efficiency achieved by Fenton's reagent was 18%, leaving the effluent arsenic as low as 5.9 mg/L. The results showed that, Fenton's reagent as an advanced oxidation process, performed much better than coagulation alone (8.0 % removal) or $KMnO_4$ followed by coagulation (5.6 % removal) for the SBR effluent. However, the Fenton's treatment effluent arsenic concentration (5.9 mg/L) was still far higher than the acceptable level for discharge.

3.3 Carbon adsorption

Activated carbon has been widely used as an adsorbent on inorganic and organic environmental contaminants removal, such as Cd (Liu et al, 2010), Hg (Kim et al, 2010), bromate in raw water (Liu et al, 2011), dissolved organic carbon in surface water (Yapsakli and Çeçen, 2010), and surfactants (Rosu et al, 2007).Activated carbon adsorption is also used for landfill gas treatment (Gaur et al. 2010) aromatics and chlorinated compounds removal. However, it was seldom reported for arsenic removal in landfill gas/ landfill gas condensate.

In this study, granular activated carbon was applied for to the SBR effluent for arsenic removal. As shown in figure 6-9, more arsenic was removed by higher dose of activated carbon. The

highest removal efficiency (6.5%) was achieved with 20 g/L of activated carbon, leaving 6.6mg/L arsenic in the carbon treated liquid. A higher dose of activated carbon was not tried since no obvious improvement could be expected over a practical dose range. Activated carbon showed limited treatment capacity for arsenic in LFG condensate. The treated liquid was not acceptable for discharge.

3.4 Membrane separation

Reverse osmosis (RO) is widely used to separate a variety of contaminants from aqueous solution. Arsenic treatment by RO was reported for drinking water (Walker et al, 2008; Kang et al, 2000; Ning, 2002) and ground water (Schneiter and Middlebrooks, 1983; Akin et al, 2011). Most of these studies focused on inorganic species of arsenic. It was reported (Clifford et al, 1986) that RO systems are typically capable of removing arsenate with high efficiency (98%-99% removal), but can be significantly less efficient in treating arsenite (46-75% removal). Organic arsenic species treatment by RO has not been reported.

In this study, RO was applied to SBR treated LFG condensate. The results are shown in figure 6-10 and figure 6-11. As shown in figure 6-10, 95.8 % of the arsenic was removed by the RO systems, leaving 311.4 µg/L of arsenic in the RO permeate. When the RO feed was diluted to 3:1, the arsenic concentration in RO permeate was reduced to 135µg/L and the removal efficiency was 93.1%, which can meet the discharge limit of 200µg/L.

An arsenic speciation study showed (table 6-2) that 108 µg/L out of 135 µg/L of arsenic in the RO permeate was arsenite (As^{III}). This result coincides with previous study that RO is not highly effective for arsenite removal (Clifford et al, 1986) and also it verifies the feasibility of organic arsenic treatment by RO system.

3.5 Cost analysis and treatment comparison

The treatment methods for arsenic removal tested in this study for SBR effluent are listed in table 6-3. Reverse osmosis showed outstanding performance on organic arsenic removal in the LFG condensate SBR effluent, making it a feasible method for the direct discharge of treated LFG condensate in terms of arsenic concentration. None of the other methods listed in table 6-3 were effectivefor organic arsenic treatment. Among those methods, Fenton's reagent performed best with 15.1 % removal efficiency, however the arsenic concentration in the treatment sample (5.9 mg/L) was much higher than the discharge limit for arsenic (200 µg/L), indicating it's not an effective alternative.

4. Conclusions

1. Biological treatment is effective for removal of TOC in landfill gas condensate. The high removal efficiency (more than 95%) and low effluent TOC concentration (25 mg/L) in the SBR system in this study verified the biodegradability of organic matter in the landfill gas condensate.

Biological treatment is not effective for organic arsenic in the landfill gas condensate. A maximum of 26 % of total arsenic was removed from the SBR system at steady state. Arsenic removal in the biological system was believed to be through adsorption to biomass and removal with waste activated slduge.

2. Physico-chemical treatment methods, such as $FeCl_3$ coagulation, $KMnO_4$ followed by coagulation, Fenton's reagent and activated carbon, were tested and proved ineffective for organic arsenic treatment. Among those, Fenton's reagent performed best with 15.1 % removal efficiency and 5.9 mg/L arsenic in the treated sample.

3. Though reported not highly effective for As^{III}, RO system showed success on organic arsenic treatment in this study with up to 95.8% arsenic removed. A speciation analysis indicated that, most arsenic in the RO permeate was As^{III}.

Reference

Akin, I., Arslan, G., Tor, A., Cengeloglu, Y., Ersoz, M., 2011. Removal of arsenate [As (V)] and arsenite [As (III)] from water by SWHR and BW-30 reverse osmosis. Desalination 281, 88-92.

Al-Kdasi, A., Idris, A., Saed, K., Guan, C.T., 2004. Treatment of textile wastewater by advanced oxidation processes—a review. Global Nest Int. J. 6 (3), 226–234.

Amini, H.R., Reinhart, D.R., 2011. Regional prediction of long-term landfill gas to energy potential. Waste Management 31(9-10), 2020-2026.

APHA, 1998. Standard Methods for Examination of Water and Wastewater. In: Clesceri, L.S., Greenburg, A.E., Eaton, A.D. (Eds.), 20th Ed. American Public Health Association, Washington, D.C.

Barlaz, M.A., Green, R.B., Chanton, J.P., Goldsmith, C.D., Hater, G.R. 2004. Evaluation of a Biologically Active Cover for Mitigation of Landfill Gas Emissions. Environmental Science & Technology 38(18), 4891-4899.

Boccelli, D.L., Small, M.J., Dzombak, D.A., 2005. Enhanced Coagulation for satisfying the Arsenic Maximum Contaminant Level under Variable and Uncertain Conditions. Environmental Science and Technology 39(17), 6501-6507.

Briggs, J., 1988. Municipal landfill gas condensate. EPA report No. 600/2-87-090, Cincinnati, OH.

Çeçen, F., Gürsoy, G., 2001. Biosorption of Heavy metals from landfill leachate onto activated sludge. Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering. 36(6), 987-998.

Challenger, F., 1945. Biological Methylation. Chemical Reviews 36(3), 315-361.

Clifford, D., Subramonian, S., Sorg, T.J. 1986. Water treatment processes.III. Removing dissolved inorganic contaminants from water. Environment Science and Technology 20 (11), 1072-1080.

Cullen, W.R., Reimer, K.J. 1989. Arsenic Speciation in the Environment. Chemical Reviews 89(4), 713-764.

Cullen, W.R., Bentley, R., 2005. The toxicity of trimethylasine: an urban myth. Journal of Environmental Monitoring 7(1), 11-15.

Edwards, M., 1994. Chemistry of arsenic removal during coagulation and Fe-Mn oxidation. Journal of AWWA 86(9), 64-78.

Fan, M., Brown, R.C., Sung, S.W., Huang, C.P., Ong, S.K., van Leeuwen, J., 2003.Comparisons of Polymeric and Conventional Coagulants in Arsenic(V) Removal. Water Environment Research 75(4), 308-313.

Forster, P., Ramaswamy, V., Artaxo, P., Berntsen, T., Betts, R., Fahey, D.W., Haywood, J., Lean, J., Lowe, D.C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M., Van Dorland, R., 2007. Climate Change 2007: The Physical Science Basis. Changes in Atmospheric Constituents and in Radiative Forcing. Cambridge University Press, Cambridge.

Gaur, A., Park, J.W., Maken, S., Song, H.J., Park, J.J., 2010. Landfill gas (LFG) processing via adsorption and alkanolamine absorption. Fuel Processing Technology 91(6), 635-640.

Huang, J.H., Ilgen, G., Vogel, D., Michalzik, B., Hantsch, S., Tennhardt, L., Bilitewski, B., 2009. Emissions of Inorganic and Organic Arsenic Compounds via the Leachate Pathway from Pretreated municipal Waste Materials: A Landfill Reactor Study. Environmental Science and Technology 43(18), 7092-7097.

Hughes, M.F., 2002. Arsenic toxicity and potential mechanisms of action. Toxicology Letters. 133(1). 1-16.

Kang, M., Kawasaki, M., Tamada, S., Kamei, T., Magara, Y., 2000. Effect of pH on the removal of arsenic and antimony using reverse osmosis membranes. Desalination 131 (1-3), 293-298.

Kim, E.A., Seyfferth, A.L., Fendorf, S., Luthy, R.G., 2011. Immobilization of Hg (II) in water with polysulfide-rubber (PSR) polymer-coated activated carbon. Water Research 45(2), 453-460.

Lafferty, B.J., Loeppert, R.H., 2005. Methyl Arsenic Adsorption and Desorption Behavior on Iron Oxides. Environmental Science and Technology 39 (7), 2120-2127.

Levis, J.W., Barlaz, M.A., 2011. Is Biodegradability a Desirable Attribute for Discarded Solid Waste? Perspectives from a National Landfill Greenhouse Gas Inventory Model. Environmental Science & Technology 45(13), 5470-5476.

Liu, T.M., Zhao, Z.W., Cui, F.Y., Liu, D.M., Wang, H., Zhu, Q., 2011. Bromate removal by activated carbon adsorption: Material selection and impact factors study. Journal of Harbin Institute of Technology (New Series) 18 (5), 81-85.

Liu, X., Chen, Z., Ye, M., Xu, J., 2010. The enhancement of Cd (II) adsorption by immobilsation of tannic acid onto powdered activated carbon. 4th International Conference on Bioinformatics and Biomedical Engineering, iCBBE 2010, June 18, 2010 - June 20, 2010.

Lopez, A., Pagano, M., Volpe, A., Di Pinto, A., 2004. Fenton's pre-treatment of mature landfill leachate, Chemosphere 54, 1005-1010.

Michalke, K., Wickenheiser, E.B., Mehering, M., Hirner, A.V., Hensel, R. 2000. Production of Volatile Derivatives of Metal(loid)s by Microflora Involved in Anaerobic Digestion of Sewage Sludge. Applied and Environmental Microbiology. 66(7), 2791–2796.

Ning, R.Y., 2002. Arsenic removal by reverse osmosis. Desalination 143 (3), 237-241.

Parks, J.L., Novak, J., MacPhee, M., Itle, C., Edwards, M., 2003. Effect of Ca on As release from ferric and alum residuals. Journal of American Water Works Association 95(6), 108-118.

Pinel-Raffaitin, P., Le Hencho, I., Amouroux, D., Potin-Gautier, M., 2007. Distribution and Fate of Inorganic and Organic Arsenic Species in Landfill Leachates and Biogases. Environmental Science and Technology 41(13), 4536-4541.

Rosu,M., Marlina, A., Kaya, A., Schumpe, A., 2007. Surfactant adsorption onto activated carbon and its effect on absorption with chemical reaction. Chemical Engineering Science 62(24), 7336-7343.

Schneiter, R.W., Middlebrooks, E.J., 1983. Arsenic and Fluoride Removal from Ground Water by Reverse Osmosis. Environment International, 9 (4), 289-292.

Smith, A.H., Hopenhayn-Rich, C., Bates, M. N., Goeden, H. M., Hertz-Picciotto, I., Duggan, H.M., Wood, R., Kosnett, M. J., Smith, M. T., 1992. Cancer risks from arsenic in drinking water. Environmental Health Perspectives 97, 259–267.

Song, S., Lopez-Valdivieso, A., Hernandez-Campos, D.J., Peng, C., Monroy-Fernandez, M.G., Razo-Soto, I., 2006. Arsenic removal from high-arsenic water by enhanced coagulation with ferric ions and coarse calcite. Water Research 40(2), 364-372.

Tchobanoglous, G., Burton, F.L., Stensel, H.D., 2004. Wastewater engineering, treatment and

reuse (fourth edition), Metcalf and Eddy, Inc., McGraw-Hill, New York.

Thirunavukkarasu, O.S., Viraraghavan, T., Subramanian, K.S., Tanjore, S., 2002. Organic arsenic removal from drinking water. Urban Water 4(4), 415-421.

Torrens, K.D., Salerno, L.P. 1995. Experience with removal of arsenic from groundwater to ultra-low levels. 68th Annual Water Environment Federation Conference, October, Miami Beach, Florida.

US EPA. 2001. Drinking water standard for arsenic. EPA 815-F-00-015. Washington, DC.

Yapsakli, K., Çeçen, F., 2010. Effect of type of granular activated carbon on DOC biodegradation in biological activated carbon filters. Process Biochemistry 45(3), 355-362.

Walker, M., Seiler, R.L, Meinert, M., 2008. Effectiveness of household reverse-osmosis systems in a Western U.S. region with high arsenic in groundwater. Science of Total Environment 389 (2-3), 245-252.

Table 6-1. As species in environment (Edwards, 1994; Lafferty and Loeppert, 2005)

	As species			
	Oxidation State III		**Oxidation State V**	
		Abbreviation		Abbreviation
Inorganic	Arsenite	iAs^{III}	Arsenate	iAs^{V}
	Methylarsonous acid	MMAs^{III}	Methylarsonic acid	MMAs^{V}
Organic	Dimethylarsinous acid	DMAs^{III}	Dimethylasinic acid	DMAs^{V}
	Trimethylasine	TMAs^{III}	Trimethylasine oxide	TMAsO^{V}

Table 6-2. As species of RO permeate with diluted LFG condensate SBR effluent.

As species	As^{III}	As^{V}	MMA	DMA	other	Total
Concentration (µ/L)	108	ND^a	ND	ND	27	135

^{a} not detected.

Table 6-3. Treatment efficiency and cost comparison of different physical/chemical technologies for arsenic in SBR effluent.

Treatment method	Maximum removal %	Effluent As concentration	Condition	Cost level*
Coagulation/Flocculation ($FeCl_3$)	8.0	6.7 mg/L	500 mg/L $FeCl_3$	1
Oxidation+ Coagulation ($KMnO_4+FeCl_3$)	5.6	6.8 mg/L	500mg/L $KMnO_4$ + 600mg/L $FeCl_3$	4.7
Advanced Oxidation (Fenton's reagent)	15.1	5.9 mg/L	1000mg/L Fe^{2+} +500mg/L H_2O_2 pH = 3.49	9.4
Carbon Absorption	6.5	6.6 mg/L	20g/L granular activated carbon Contact time = 4Hours	43.2
Membrane separation (Reverse Osmosis)	95.8	311 µg/L	Pressure = 14.5psig Recovery = 9.83%	43.6

* Cost of coagulation-flocculation by $FeCl_3$ was taken as a cost equivalent.
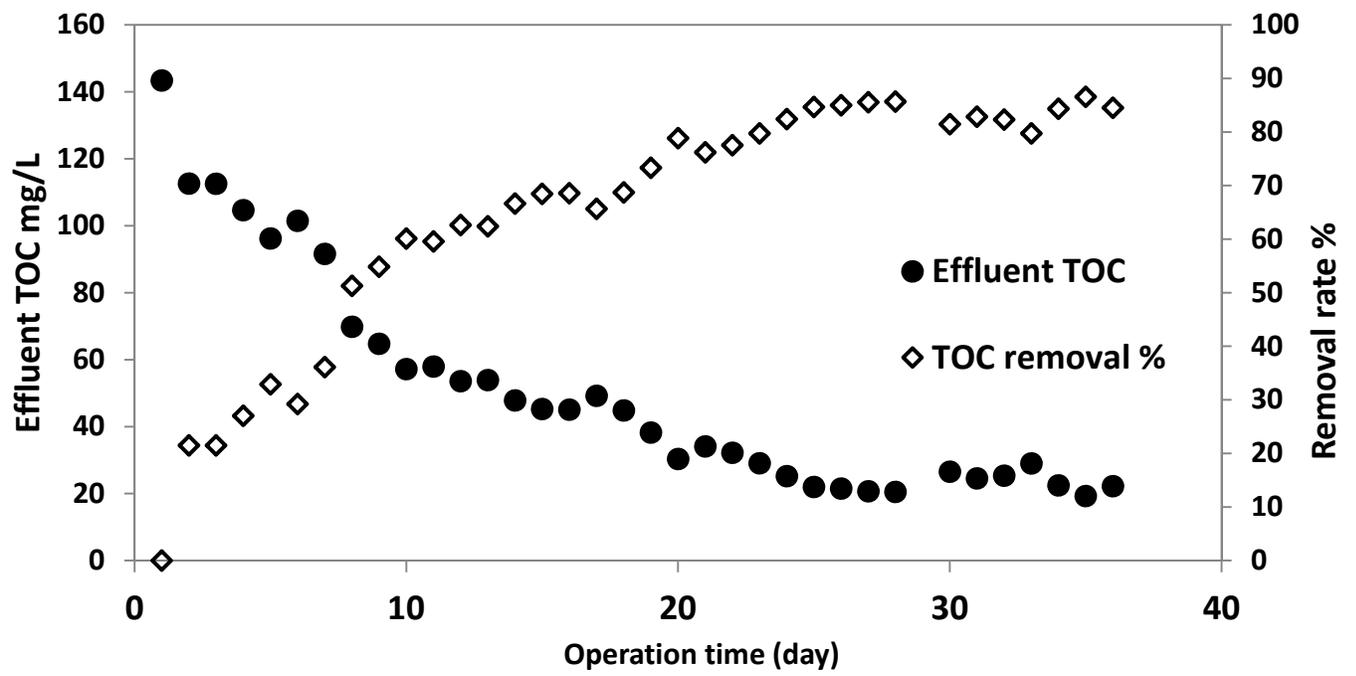
Fig. 6-1. Daily effluent TOC in the SBR system.
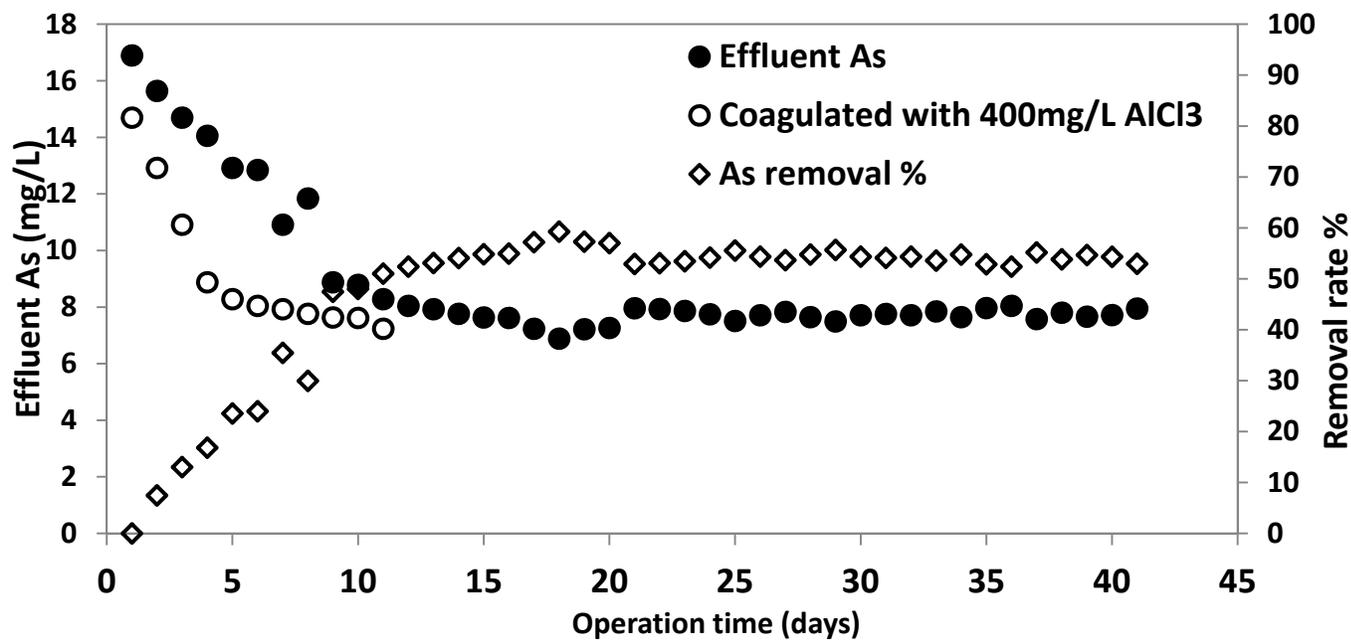
Fig. 6-2. Daily effluent As concentration in the SBR system.
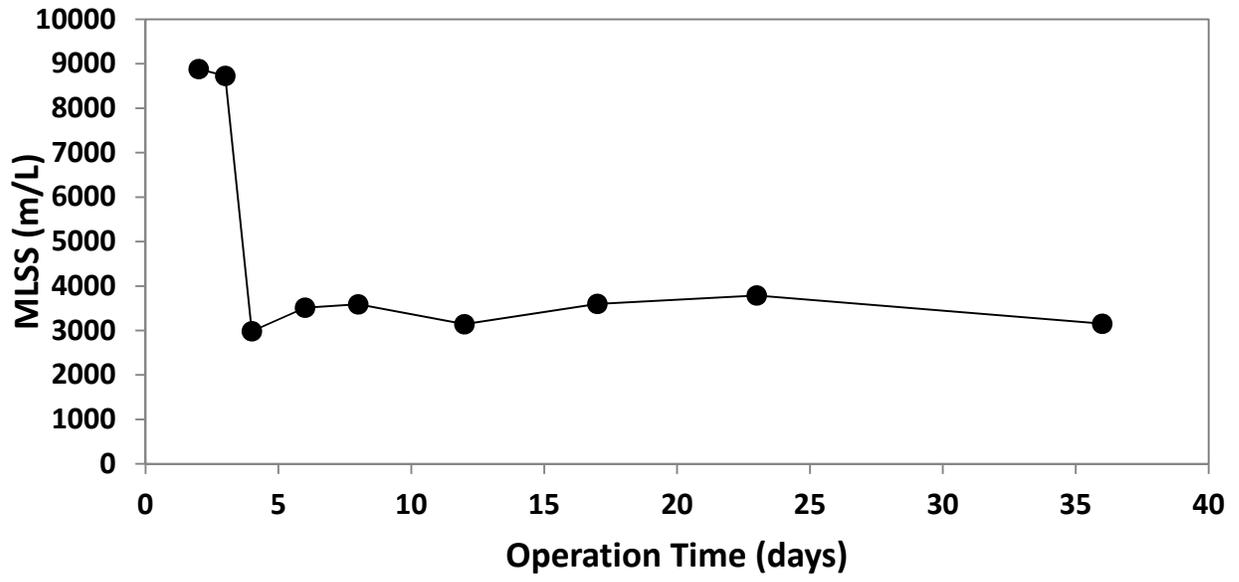
Fig. 6-3 Daily MLSS of SBR system
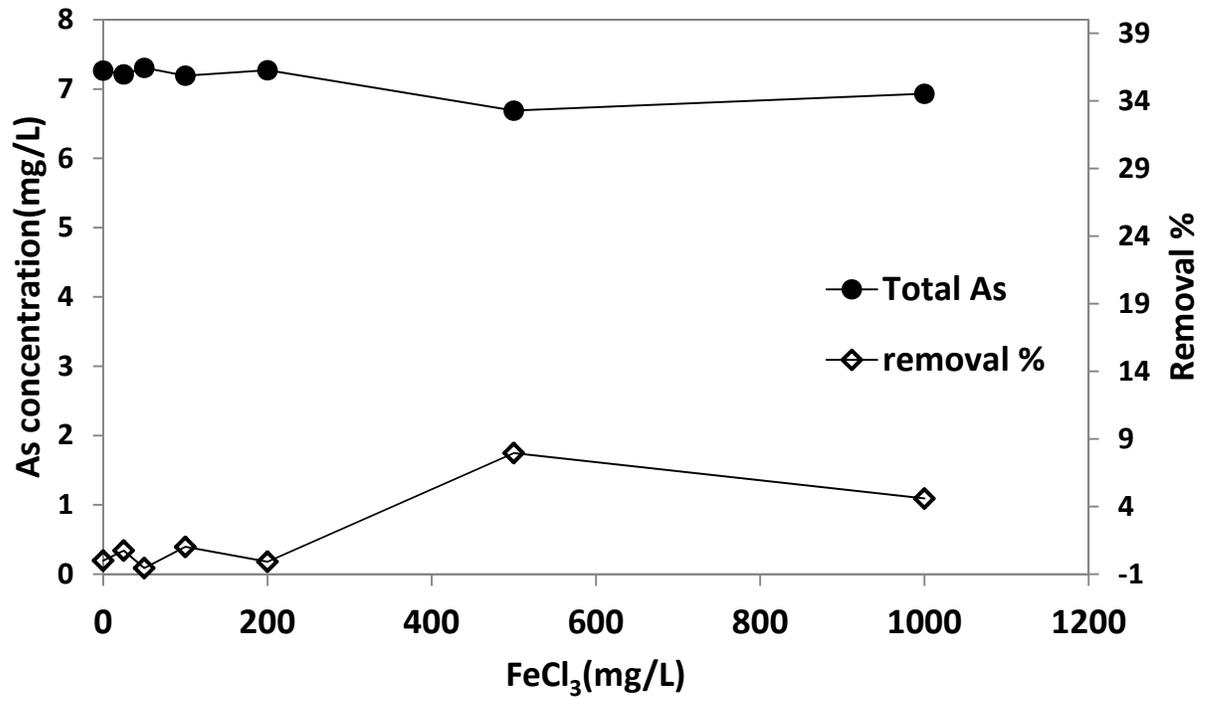
Fig. 6-4. As concentration of coagulated SBR effluent.
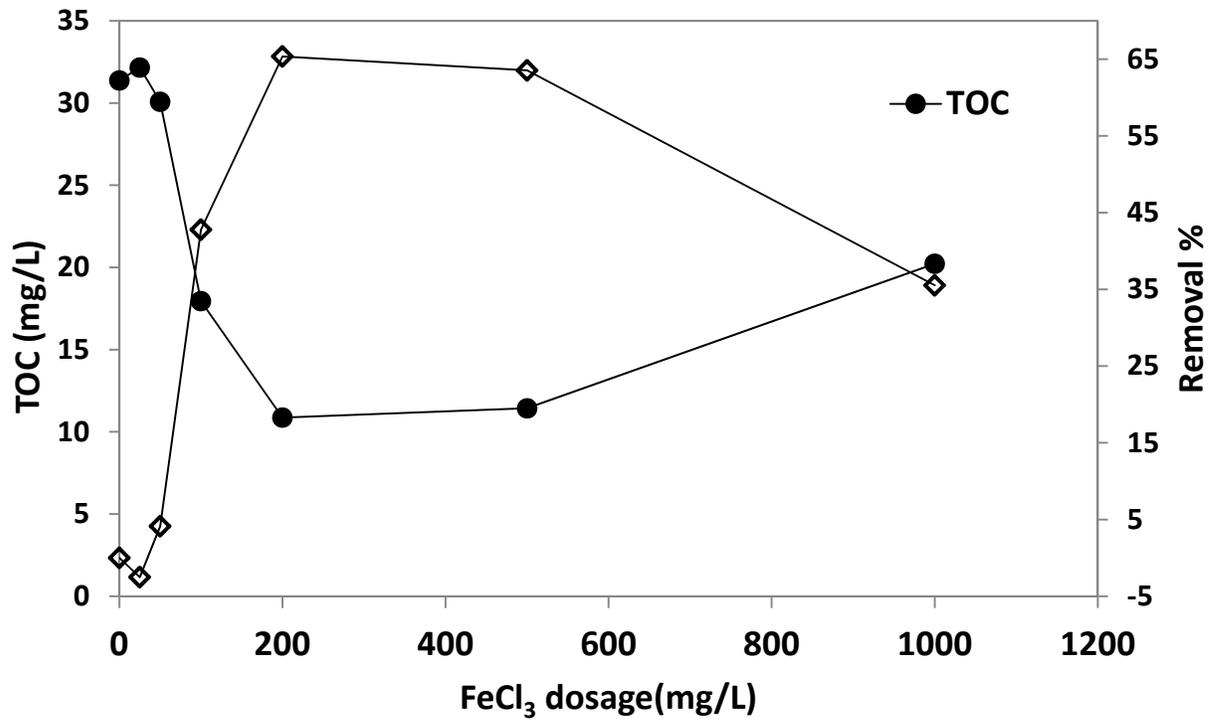
Fig. 6-5. TOC of coagulated SBR effluent.
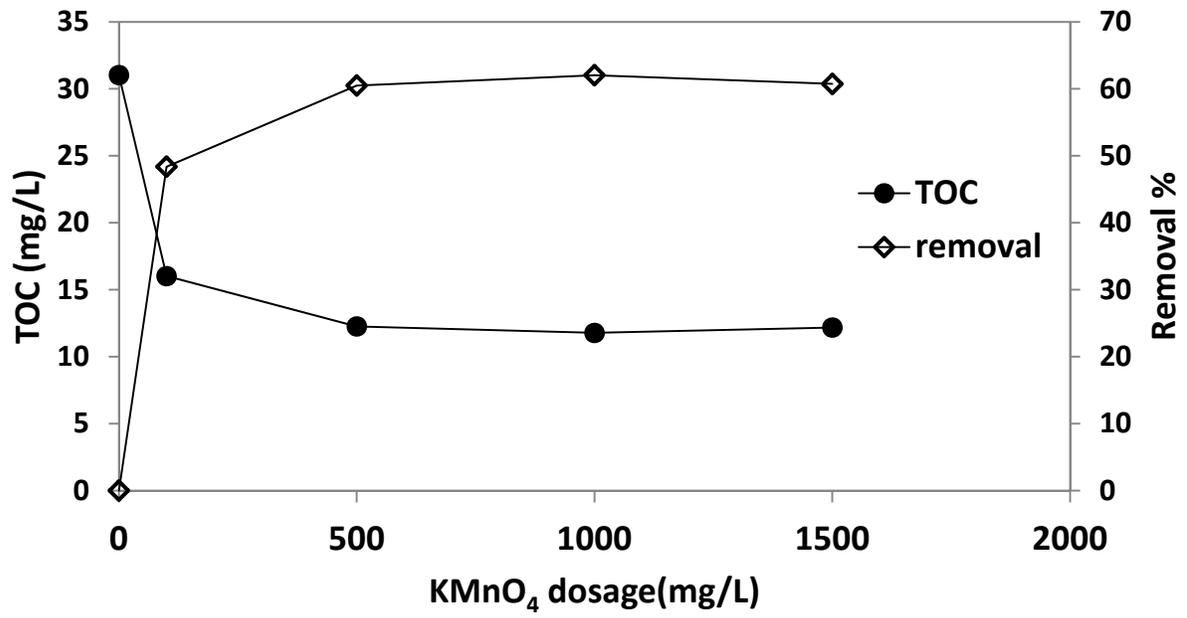
Fig. 6-6. TOC of permanganate oxidized SBR effluent.
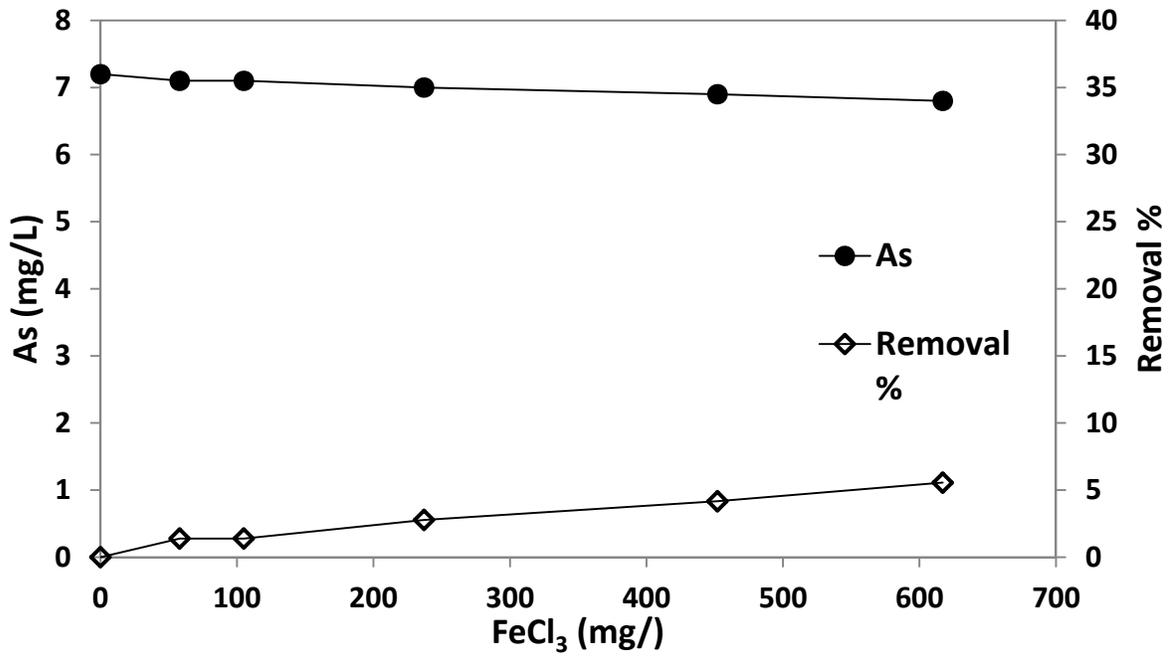
Fig. 6-7. As in SBR effluent treated with permanganate oxidation followed by coagulation.
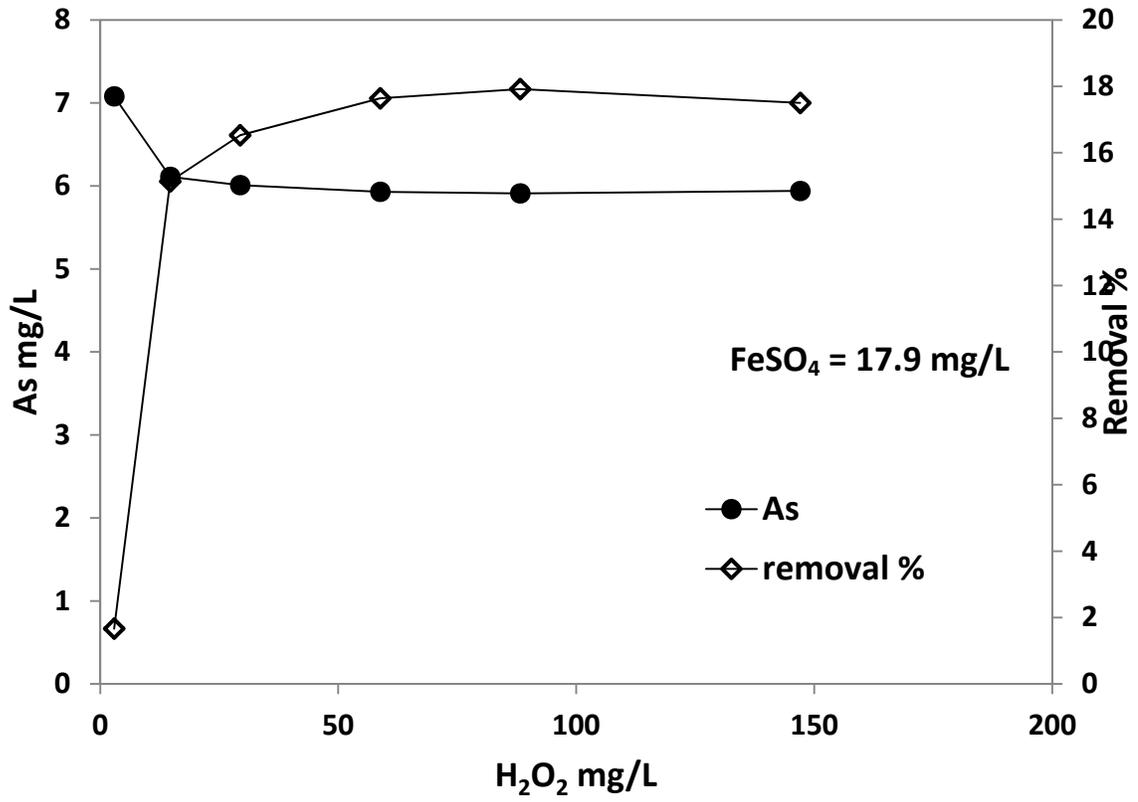
Fig. 6-8. Fenton's treatment results for As in SBR effluent.
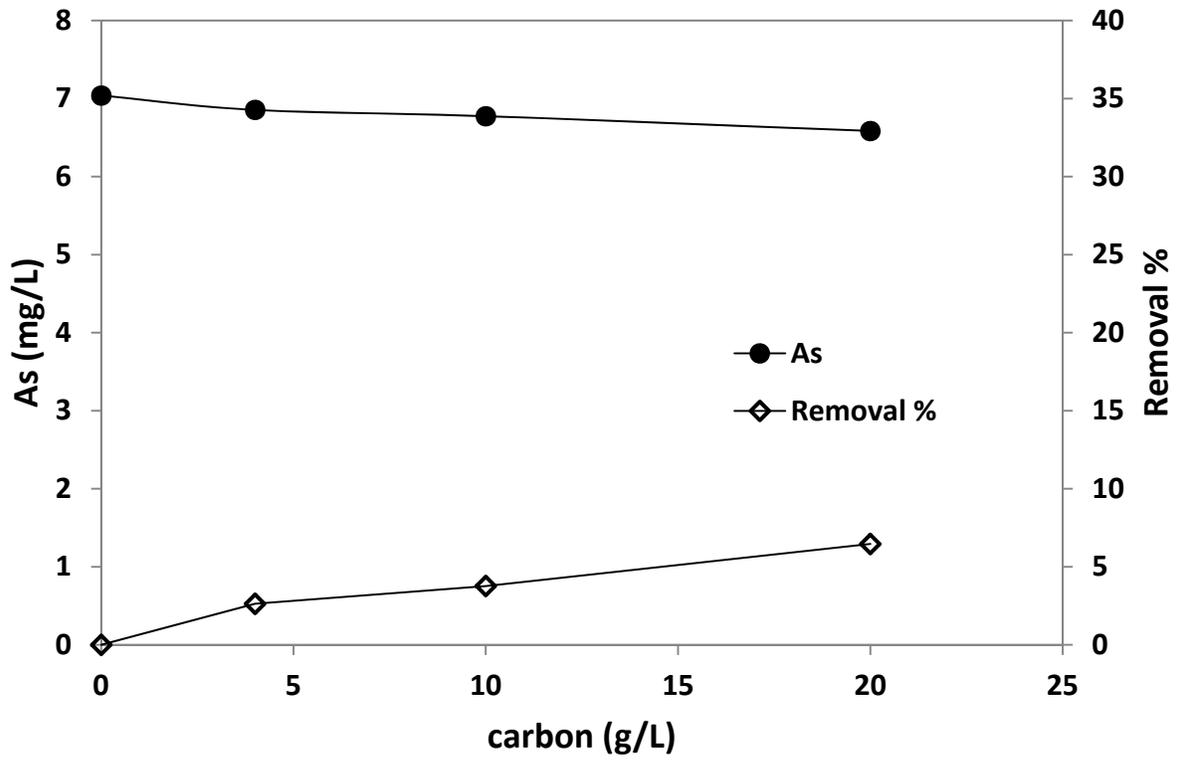
Fig. 6-9. Carbon Absorption results for As in SBR effluent.
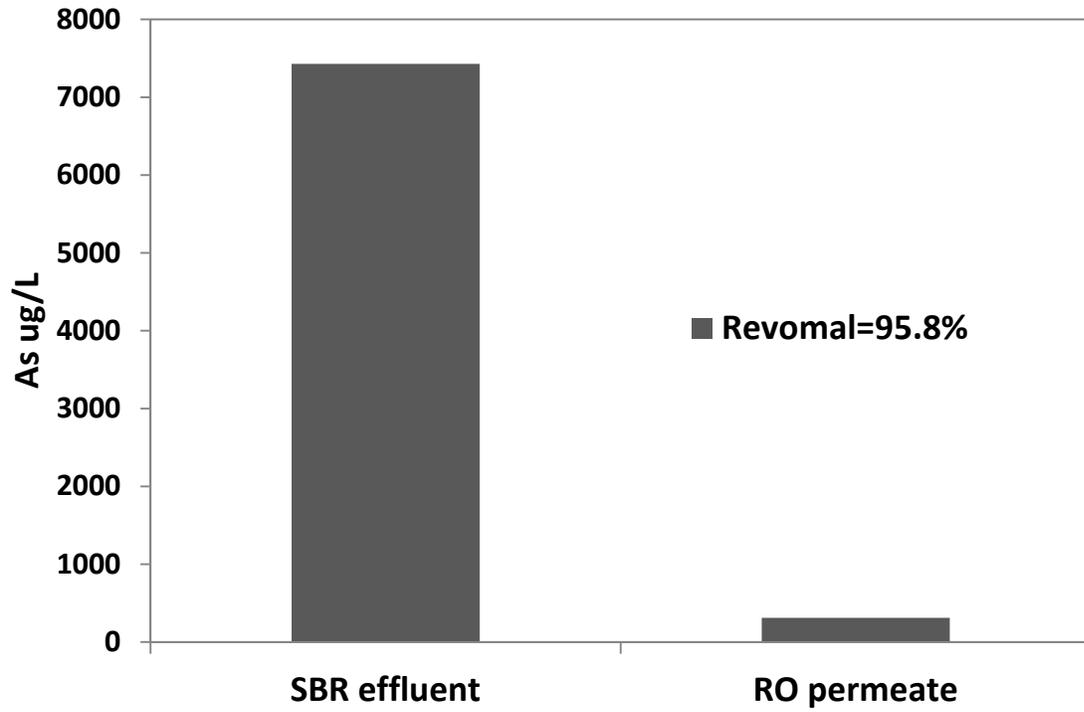
Fig. 6-10. Reverse osmosis arsenic removal for SBR effluent.
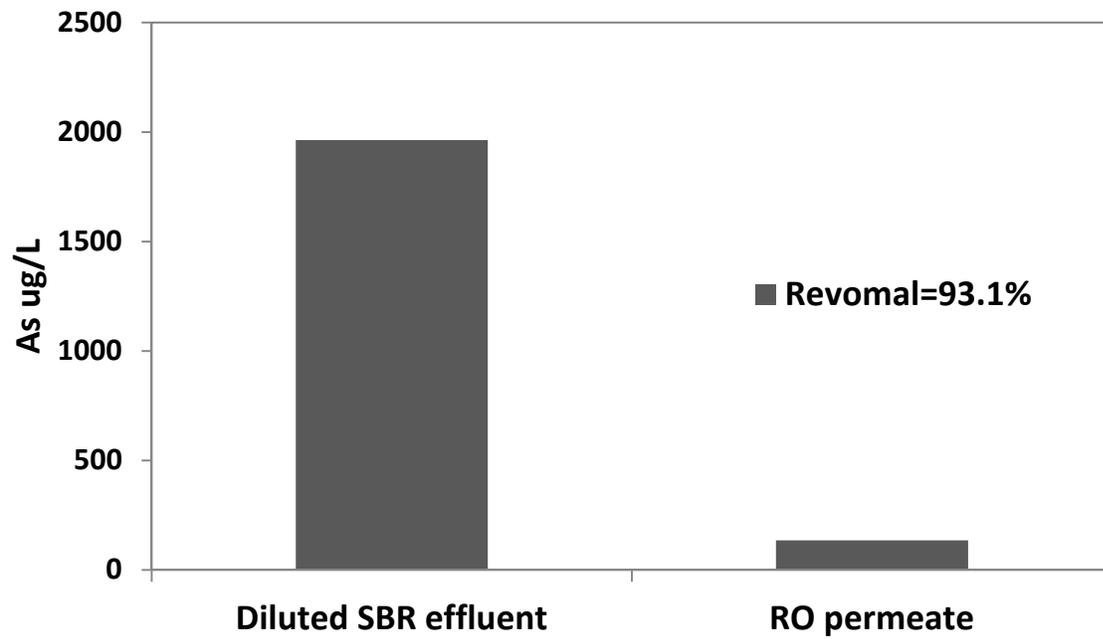
Fig. 6-11. Reverse osmosis arsenic removal for diluted SBR effluent.

APPENDIX A (CHAPTER 3)

1. TOC concentration of NH treated leachate sample size fractions from duplicated ultrafiltration.

Sample	Test 1	Test 2	SD mg/L
	TOC mg/L		
NH treated 500 Da	73.72	63.94	6.915504
NH treated 1k Da	158.2	163.5	3.747666
NH treated 3k Da	304	286.5	12.37437
NH treated 5k Da	293.4	292.8	0.424264
NH treated 10k Da	295.5	310.3	10.46518
NH treated 30k Da	342.3	343.4	0.777817
NH treated 100k Da	313.9	321.1	5.091169
NH treated 0.2 um	343.4	352.7	6.576093
NH treated 0.45 um	338.9	346.1	5.091169
NH treated 1.5 um	337.6	318.3	13.64716

Note: 1. Data shown are analysed several months later than those shown in figure 3-3, slight but not significant difference from those shown in figure 3-3 can be observed;

2. Data shown are used to give a reference of the variation extent between different batches of ultrafiltration.

2. pH/Eh evolution during the filtration/ultrafiltration of NH treated leachate.

Sample	pH value
NH treated unfiltered	6.98
NH treated 1.5 um filtered	7.02
NH treated 0.45 um filtered	7.70
NH treated 0.2 um filtered	7.32
NH treated 100 kDa filtered	7.56
NH treated 30 kDa filtered	7.46
NH treated 10 kDa filtered	7.69
NH treated 5 kDa filtered	7.19
NH treated 3 kDa filtered	7.26
NH treated 1 kDa filtered	7.56
NH treated 500 Da filtered	7.45

3. Statistical analysis of regression in figure 3-4 part A and part B.

p values (probability level) for correlation curve slopes of NH untreated TOC and ON, NH treated TOC and ON, NH untreated COD and ON, NH treated COD and ON are 6.66e-07, 3.01e-04, 2.57e-05 and

2.05e-05. Under the level of $\alpha = 0.05$, all the correlations are significant in terms of slope. Statistics analysis was conducted with R language.

R code attached, where a1 is NH untreated TOC, a2 is NH untreated ON, b1 is NH treated TOC, b2 is NH treated ON, c1 is NH untreated COD, c2 is NH untreated ON, d1 is NH treated COD, d2 is NH treated ON.

R code:

```
> a1=c(33.12722222,
+ 41.67416667,
+ 51.45625,
+ 51.6,
+ 51.04444444,
+ 52.63425926,
+ 54.65833333,
+ 60.04833333,
+ 55.18819444,
+ 65.48263889,
+ 61.18796296)
>
> a2=c(2.28,
+ 2.99,
+ 3.86,
+ 3.76,
+ 4.23,
+ 4.25,
+ 4.51,
+ 5.31,
+ 5.01,
+ 5.57,
+ 5.50)
>
> lm1=lm(a1~a2)
> summary(lm1)

Call:
```

lm(formula = a1 ~ a2)

Residuals:

  Min   1Q Median   3Q   Max

-3.3280 -1.2019 0.0539 1.3787 3.5392

Coefficients:

      Estimate Std. Error t value Pr(>|t|)

(Intercept) 16.6111   3.0227 5.495 0.000382 ***

a2   8.3643   0.6852 12.206 6.66e-07 ***

Residual standard error: 2.263 on 9 degrees of freedom

Multiple R-squared: 0.943,   Adjusted R-squared: 0.9367

F-statistic: 149 on 1 and 9 DF, p-value: 6.658e-07

>

>

> b1=c(15.15097222,

+ 21.41875,

+ 30.8474537,

+ 27.3249537,

+ 28.63611111,

+ 29.94375,

+ 33.89981481,

+ 32.6412963,

+ 33.53944444)

>

> b2=c(0.718415937,

+ 1.735633273,

+ 2.536210512,

+ 2.21014343,

+ 2.407778995,

+ 3.46083237,

+ 3.64916706,

+ 3.958102843,

+ 4.121243128)

>

> lm2=lm(b1~b2)

> summary(lm2)

Call:

lm(formula = b1 ~ b2)

Residuals:

  Min   1Q Median   3Q   Max

-2.646 -1.632 -1.551 1.942 3.806

Coefficients:

      Estimate Std. Error t value Pr(>|t|)

(Intercept) 14.1431   2.2726 6.223 0.000435 ***

b2   5.0858   0.7691 6.613 0.000301 ***

Residual standard error: 2.464 on 7 degrees of freedom

Multiple R-squared: 0.862,   Adjusted R-squared: 0.8423

F-statistic: 43.73 on 1 and 7 DF, p-value: 0.0003007

>

> c1=c(51.5,

+ 92,

+ 100,

+ 97,

+ 114,

+ 114,

+ 117,

+ 117,

+ 121,

+ 128,

+ 140)

>

> c2=c(2.278571429,

+ 2.992857143,

+ 3.857142857,

+ 3.757142857,

+ 4.228571429,

+ 4.253571429,

+ 4.514285714,

+ 5.307142857,

+ 5.014285714,

+ 5.567857143,

+ 5.5)

>

>

```
> lm3=lm(c1~c2)

> summary(lm3)

Call:

lm(formula = c1 ~ c2)

Residuals:

    Min     1Q  Median     3Q     Max
-14.6352  -4.5807  0.8809  6.5757  10.9400


Coefficients:

            Estimate Std. Error t value Pr(>|t|)

(Intercept)  18.525    11.741   1.578   0.149

c2           20.895     2.662   7.851 2.57e-05 ***

---

Residual standard error: 8.791 on 9 degrees of freedom

Multiple R-squared: 0.8726,    Adjusted R-squared: 0.8584

F-statistic: 61.63 on 1 and 9 DF,  p-value: 2.572e-05


>
```

```
>

> d1=c(16.5625,

+ 43.6875,

+ 67.8125,

+ 59.25,

+ 67.25,

+ 80.0625,

+ 92.8125,

+ 93)

>

> d2=c(0.718415937,

+ 1.735633273,

+ 2.536210512,

+ 2.21014343,

+ 2.407778995,

+ 3.46083237,

+ 3.64916706,

+ 4.121243128)

>

> lm4=lm(d1~d2)

> summary(lm4)
```

Call:

lm(formula = d1 ~ d2)

Residuals:

   Min   1Q Median   3Q   Max

-6.4551 -4.7308 0.7531 4.1297 6.6680

Coefficients:

        Estimate Std. Error t value Pr(>|t|)

(Intercept)   5.957   5.311   1.122   0.305

d2   22.687   1.894 11.981 2.05e-05 ***

Residual standard error: 5.565 on 6 degrees of freedom

Multiple R-squared: 0.9599,   Adjusted R-squared: 0.9532

F-statistic: 143.5 on 1 and 6 DF, p-value: 2.05e-05

APPENDIX B (CHAPTER 4)

1. Statistical analysis of hypothesis from Table 4-2

p value (probability level) for the alternate hypothesis that the TOC removal percent > UV_{254} removal percent is 5.611e-05. Under the confidence level of $\alpha = 0.05$, the null hypothesis was rejected and the alternate hypothesis was accepted. Statistics analysis was conducted with R language.

R code:-

> TOCremovalpercent <- c(37.4,42.25,36.49,37.5,34.82,55.78)

> UVremovalpercent <- c(17.85,9.82,2.7,-2.3,2.51,29.09)

> t.test(TOCremovalpercent,UVremovalpercent,alt="greater",var.equal=T,paired=T)

    Paired t-test

data: TOCremovalpercent and UVremovalpercent

t = 10.9141, df = 5, p-value = 5.611e-05

alternative hypothesis: true difference in means is greater than 0

95 percent confidence interval:

 25.0822   Inf

sample estimates:

mean of the differences

30.76167

2. Statistical analysis of regression in Figure 4-5

p values (probability level) for correlation curve slopes of HA, FA and Hpi fractions for their UV abs. (cm^{-1}) and TOC (mg/L) were 1.17e-06, 2.97e-05 and 2.38e-06 respectively. Under the confidence level of $\alpha = 0.05$, all the correlations were significant in terms of slope. Statistics analysis was conducted with R language.

R code:-

```
> HAUV <- c(12.6,7.73,4.91,4.76,2.28,1.19,0.24,0.71,0.55)

> HATOC <- c(373.82,207.75,186.05,109.28,85.91,34.56,7.73,18.78,13.91)

> lmHA <- lm(HAUV~HATOC)

> summary(lmHA,corr=T)

Call:

lm(formula = HAUV ~ HATOC)

Residuals:

    Min      1Q   Median      3Q      Max

-1.34037 -0.04920  0.05140  0.07256  1.07602
```

Coefficients:

Estimate Std. Error t value Pr(>|t|)

(Intercept) 0.030789   0.353477   0.087   0.933

HATOC   0.033430   0.002171   15.400 1.17e-06 ***

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.7487 on 7 degrees of freedom

Multiple R-squared: 0.9713,   Adjusted R-squared: 0.9672

F-statistic: 237.2 on 1 and 7 DF, p-value: 1.174e-06

Correlation of Coefficients:

    (Intercept)

HATOC -0.71

> FAUV <- c(10.1,4.84,3.59,3.5,3.68,3.25,2.73,2.36,1.94)

> FATOC <- c(392.24,211,188.35,152.07,113.65,90.36,84.93,89.68, 83.18)

> lmFA <- lm(FAUV~FATOC)

> summary(lmFA,corr=T)

Call:

```
lm(formula = FAUV ~ FATOC)
```

Residuals:

```
   Min      1Q   Median     3Q     Max
-1.16138 -0.40322 -0.08467  0.58208  0.78944
```

Coefficients:

```
            Estimate Std. Error t value Pr(>|t|)
(Intercept) 0.348123   0.448738   0.776    0.463
FATOC       0.023378   0.002457   9.515 2.97e-05 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.6982 on 7 degrees of freedom
Multiple R-squared: 0.9282,    Adjusted R-squared: 0.918
F-statistic: 90.54 on 1 and 7 DF,  p-value: 2.966e-05
```

Correlation of Coefficients:

```
      (Intercept)
FATOC -0.86
```

```
> HpiUV <- c(14.3,10.25,6.46,5.44,5.15,5.84, 4.77, 3.21, 2.11)
```

> HpiTOC <- c(1014.5,678.04, 496.07, 351.6,283.98,277.23, 232.78, 175.53, 141.65)

> lmHpi <- lm(HpiUV ~ HpiTOC)

> summary(lmHpi, corr=T)

Call:

lm(formula = HpiUV ~ HpiTOC)

Residuals:

   Min   1Q Median   3Q   Max

-1.1028 -0.2513 0.0214 0.3347 1.1121

Coefficients:

          Estimate Std. Error t value Pr(>|t|)

(Intercept) 1.1366064 0.4531262   2.508   0.0405 *

HpiTOC   0.0129542 0.0009334 13.879 2.38e-06 ***

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.7466 on 7 degrees of freedom

Multiple R-squared: 0.9649,   Adjusted R-squared: 0.9599

F-statistic: 192.6 on 1 and 7 DF, p-value: 2.382e-06

Correlation of Coefficients:

(Intercept)

HpiTOC -0.84

The R code for the figure 4-5 illustrating the linear regression of HA, FA and Hpi fractions for UV_{254} abs (cm^{-1}) and TOC (mg/L) :-

>plot(HpiTOC,HpiUV, xlab="", ylab="", pch=19, xlim=c(0,1100), ylim=c(0,14.5))

>lines(HpiTOC, fitted(lmHpi))

>points(FATOC,FAUV, pch=15)

>lines(FATOC, fitted(lmFA))

>points(HATOC,HAUV, pch=17)

>lines(HATOC, fitted(lmHA))

>legend("bottomright", c("HA", "FA", "Hpi"), pch=c(17,15,19))

3. Statistical analysis of the $SUVA_{254}$ for the leachate fractions (Table 4-4)

p value (probability level) for the repeated measure multivariate ANOVA test with null hypothesis that the mean $SUVA_{254}$ values for the HA, FA and Hpi fractions were equal is 2.42e-08. Under the confidence level of $\alpha = 0.05$, the null hypothesis was rejected and the alternate hypothesis that the mean $SUVA_{254}$ for

atleast one of the fractions was different was accepted. Then a general linear hypothesis testing model was used to perform multiple comparisons between the $SUVA_{254}$ values of the leachate fractions using the Tukey's all pair comparison. From Figure 4-1, the order of the $SUVA_{254}$ for the leachate fractions followed: HA>FA>Hpi. Statistics analysis was conducted with R language.

R code:-

> SUVA <-

c(2.77,1.92,1.55,4.7,3.25,2.05,2.65,2.31,1.3,3.68,3.29,2.28,3.37,2.57,1.45,3.72,2.29,1.49,3.79,2.64,1.87,3.13,2.33,1.54)

> Leachate <-

c("PAr","PAr","PAr","PAt","PAt","PAt","NHr","NHr","NHr","NHt","NHt","NHt","OL8","OL8","OL8","OL7","OL7","OL7","OL5","OL5","OL5","OL3","OL3","OL3")

> Fraction <-

c("HA","FA","Hpi","HA","FA","Hpi","HA","FA","Hpi","HA","FA","Hpi","HA","FA","Hpi","HA","FA","Hpi","HA","FA","Hpi","HA","FA","Hpi")

> means.Fraction <- tapply(SUVA,Fraction, mean, na.rm = TRUE)

> residuals <- SUVA-means.Fraction[Fraction]

> shapiro.test(residuals)

    Shapiro-Wilk normality test

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data: residuals

W = 0.9661, p-value = 0.5714

> mydata <- data.frame(SUVA,Leachate,Fraction)

> y <- aov(SUVA ~ Fraction + Error(Leachate/Fraction), data=mydata)

> summary(y)

Error: Leachate

        Df Sum Sq Mean Sq F value Pr(>F)

Residuals 7   4.29 0.6128

Error: Leachate:Fraction

        Df Sum Sq Mean Sq F value   Pr(>F)

Fraction   2 12.745   6.373   78.72 2.42e-08 ***

Residuals 14 1.133   0.081

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

> am2 <- lme(SUVA ~ Fraction, random = ~1|Leachate/Fraction, data=mydata)

```
> x <- glht(am2,linfct=mcp(Fraction="Tukey"))
```

```
> plot(x)
```

95% family-wise confidence level
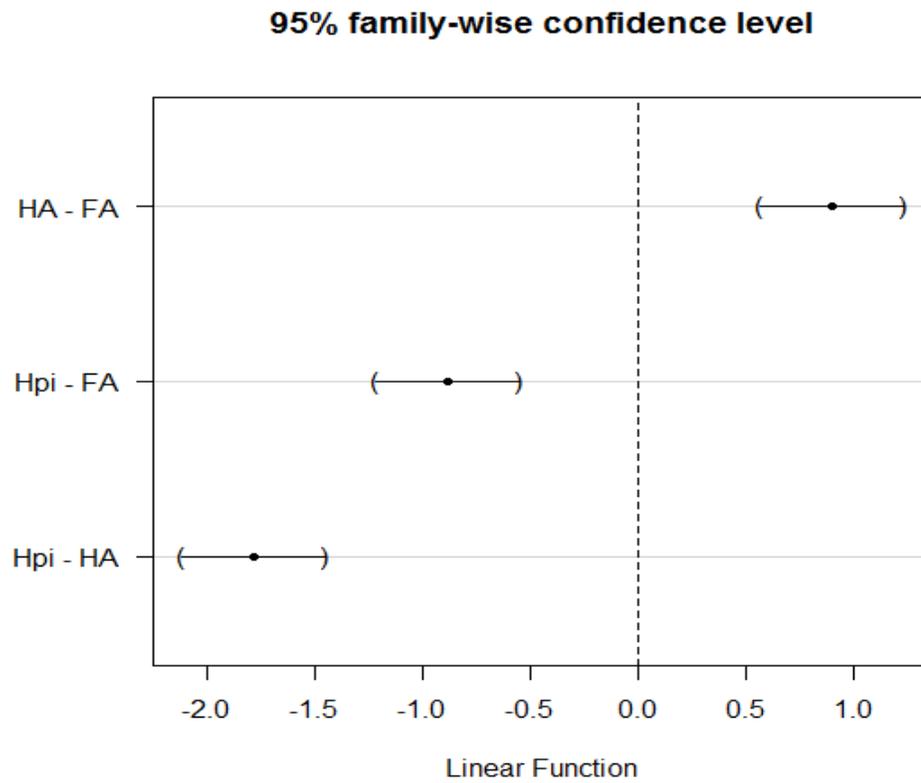
SF 1: Multiple comparisons of SUVA$_{254}$ values among the leachate fractions

4. Statistical analysis of the TOC percent < 1 kDa for the leachate fractions (Table 4-5)

p value (probability level) for the repeated measure multivariate ANOVA test with null hypothesis that the mean TOC percent < 1kDa values for the HA, FA and Hpi fractions were equal is 0.000949. Under the confidence level of $\alpha = 0.05$, the null hypothesis was rejected and the alternate hypothesis that the mean TOC percent < 1 kDa for atleast one of the fractions was different was accepted. Then a general linear hypothesis testing model was used to perform multiple comparisons between the TOC percent < 1 kDa values of the leachate fractions using the Tukey's all pair comparison. From Figure 4-2, the order of the TOC percent < 1 kDa for the leachate fractions followed: Hpi>FA>HA. Statistics analysis was conducted with R language.

R code:-

```
> TOCpercent <- c(17.78,29.54,67.93,23.03,33.74,67.44,39.12,63.54,68.02,37.43,48.28,73.66)

> Leachate <- c("PAr","PAr","PAr","PAt","PAt","PAt","NHr","NHr","NHr","NHt","NHt","NHt")

> Fraction <- c("HA","FA","Hpi","HA","FA","Hpi","HA","FA","Hpi","HA","FA","Hpi")

> means.Fraction <- tapply(TOCpercent, Fraction, mean, na.rm = TRUE)

> residuals <- TOCpercent-means.Fraction[Fraction]

> shapiro.test(residuals)
```

Shapiro-Wilk normality test

data: residuals

W = 0.9681, p-value = 0.8895

```
> mydata <- data.frame(TOCpercent,Leachate,Fraction)

> y <- aov(TOCpercent ~ Fraction + Error(Leachate/Fraction), data=mydata)

> summary(y)
```

Error: Leachate

```
      Df Sum Sq Mean Sq F value Pr(>F)
```

Residuals 3 718.6   239.5

Error: Leachate:Fraction

```
         Df Sum Sq Mean Sq F value   Pr(>F)
```

Fraction   2   3269 1634.5   27.53 0.000949 ***

Residuals 6   356   59.4

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

> am2 <- lme(TOCpercent ~ Fraction, random = ~1|Leachate/Fraction, data=mydata)

> x <- glht(am2,linfct=mcp(Fraction="Tukey"))

> plot(x)
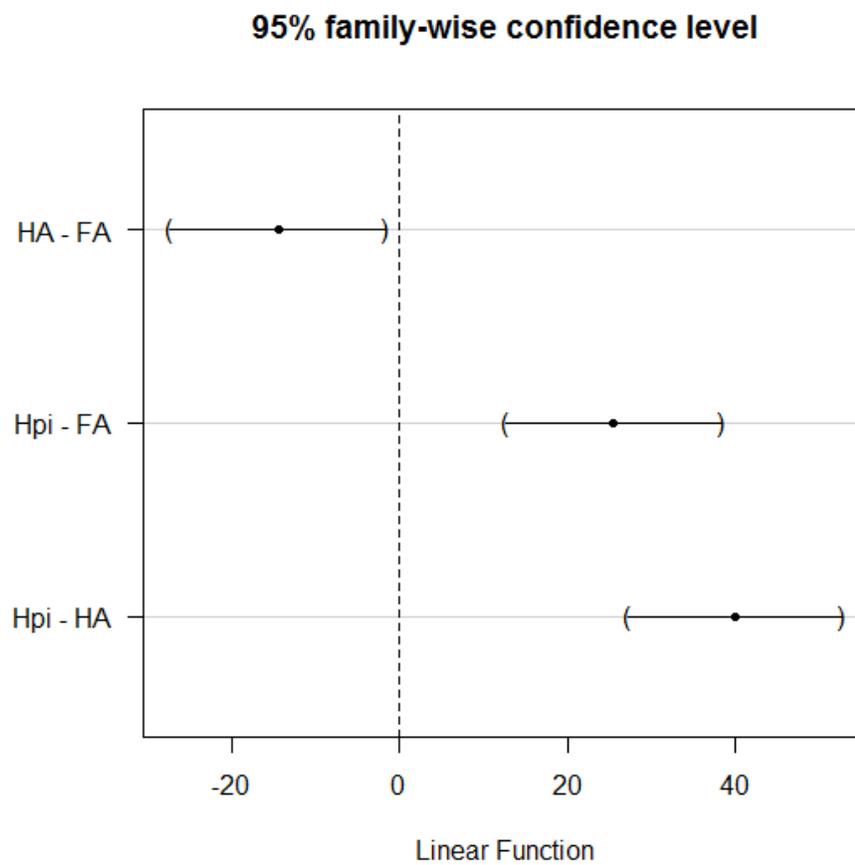
SF 2: Multiple comparisons of TOC percent < 1 kDa values among the leachate fractions