

# Chlorophenols in leachates originating from different landfills and aerobic composting plants

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## Abstract

Both type and concentration of organic contaminants in landfill leachates show great variation depending on many factors, such as type of wastes, rate of water application, moisture content, landfill design and operation age. In this paper, highly toxic chlorophenol derivatives, poorly biodegradable, carcinogenic existence and recalcitrant properties are determined by solid phase microextraction (SPME)-GC/FID in different leachates from landfill and composting plant in Istanbul. Leachates originated from acidogenic, methanogenic phases of Odayeri sanitary landfill (OSL) and from an aerobic composting plant are considered for different chlorophenol types. It is observed that acidogenic leachate from Odayeri landfill includes 2,4-dichlorophenol, 2,6-dichlorophenol, 2,3,4-trichlorophenol, 2,3,4,5-tetrachlorophenol and 2,3,4,6-tetrachlorophenol at concentration ranges, 15–130, 18–65, 8–40, 5–20 and 10–25  $\mu\text{g/l}$ , respectively. Whereas, only 2,4-dichlorophenol at a concentration range 8–40  $\mu\text{g/l}$  is determined in the methanogenic leachate of the landfill, which can be considered as an indication of reductive dechlorination. There is no chlorophenol derivative in aerobic composting leachate. It is determined that acidogenic leachate from Odayeri landfill includes more species of chlorinated phenols at higher concentration.

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**Keywords:** Chlorophenols; Composting; Landfill; Leachate

## 1. Introduction

Daily 10,000 tonnes of municipal solid waste (MSW) are generated in Istanbul. The quantity of MSW gradually increases depending on the population growth. The problems such as leachate, landfill gas and landfill area occur during the landfilling of wastes. Hence, disposal of MSW constitutes one of the most environmentally important problems in Istanbul [1]. MSW landfills in Istanbul may receive large quantity of materials generated by industrial facilities that are potential sources of hazardous contaminants in MSW landfills. Moreover, hazardous contaminants may originate from small capacity generators of hazardous wastes, household hazardous wastes and biological and/or chemical transformation products of placed wastes. Hence, landfill leachates represent a serious environmental concern with regard to trace priority

pollutants introduced into the aquatic environment. Furthermore, landfills constitute a continuous source of atmospheric and groundwater pollution because of uncontrolled degradation of organic matter.

Leachate is produced as water percolates through the solid waste, leaching soluble components and degradation products from the refuse. As water passes through a landfill, contaminants are leached from the solid waste. Mechanisms of contaminant removal include leaching of inherently soluble materials, leaching of soluble chemical products or biological reactions and fine washout and colloids [2]. Phenolic compounds found in the leachate include phenol, cresols in addition to substituted and chlorinated phenols [3]. Chlorophenols are widely used as wood preservatives, in paper, herbicide and pesticide industries [4]. Especially, penta-chlorophenol is widely used as preservatives. It is possible that tri- and tetra-chlorophenols are derived from deposited penta-chlorophenol via a dechlorination reaction in an anaerobic environment [3]. Previously reported phe-

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nol, cresols, short-chain phenols in leachates of municipal and industrial landfills may originate from different types of wastes [5,6]. Also, MSW landfill leachate or contaminated groundwater plumes include organic acids, ketones, aromatic compounds, chlorinated aromatic compounds, ethers, phthalates, halogenated aliphatic compounds, alcohols, aminoaromatic compounds, nitroaromatic compounds, phenols, heterocyclic compounds, pesticides, sulfur substituted aromatic compounds, polyaromatic hydrocarbons, polychlorinated biphenyls and organophosphates [2,7–9]. Therefore, the characteristics of the leachate are highly variable depending on the composition of the solid waste, rate of water application, refuse moisture content, as well as landfill design, operation and age [8]. Because chlorophenols are among the most widely industrial compounds and listed as priority pollutants by the U.S. Environmental Protection Agency (U.S. EPA), toxicity of those compounds are of great importance both in natural environment and bioremediation technologies [10]. Although toxicity of chlorophenols may show variation depending on both the number and the location of chlorine atoms, it may be generalized that the toxicity of chlorophenols increases with increasing the number of chlorine atom in aerobic environment. In this context, Valecillo et al. reported that although 25 mg/l 2,4-dichlorophenol (2,4DCP) caused around 50% inhibition (IC<sub>50</sub>), 300 mg/l of 4CP caused the same degree of inhibition. Unlike to aerobic environment, under anaerobic conditions, the rate of reductive dechlorination increases with increasing the number of chlorine atom [11].

Leachates are complex aqueous matrices with high organic content, which requires a specific extraction procedure in order to avoid analysis interferences. Because the chlorophenols exhibit different behavior in terms of acidity and polarity, different interactions occur between matrix and analytes. The experimental conditions may not be adequate to analyse a restricted set of chlorophenols and other molecules of the same group. Several studies have already described solid phase microextraction (SPME) technique to extract chlorophenols in aqueous samples instead of liquid–liquid extraction. Consideration of the matrix that constitutes landfill leachates, SPME is a fast, solvent-free methodology and it is the only sample preparation procedure before analysis [4]. Some researchers have studied phenols by SPME under low pH levels and saturated salt conditions in wastewater [12], water samples [13], standard mixture [14] and aqueous samples [15]. Chlorophenols in complex matrix like leachates, are determined by some researchers [4,16]. On the other hand, Lee et al. [17] evaluated SPME coupled to GC–MS to determine five chlorophenols in landfill leachates. SPME experimental procedure is optimized with a polyacrylate coated fiber at pH 1 during 40 min extraction time. Ribeiro et al. [4] tested a great number of chlorophenol derivatives successively by recent analytical techniques such as SPME and GC–MS with different physicochemical properties in landfill leachates. Several studies have shown that phenols can be extracted by SPME with good recoveries and detection limits at

the sub- $\mu\text{g/l}$  level [4,13]. Ribeiro et al. [4] investigated SPME for determination of 13 chlorophenol and phenol contained in landfill leachate. The good results are obtained with SPME by a polyacrylate (PA) fiber and detection limits that range from 0.005 to 2.5  $\mu\text{g/l}$  and reproducibility is on the average inferior to 10%.

So far, most of the literature studies have focused on the total organic content, nitrogen and heavy metals concentrations to characterize leachate originating from landfills. However, although concentrations of priority pollutants are lower compared to other pollutants, they may have much important health impact due to exerted much higher toxicity. Hence, knowledge on the fate of such pollutants may help to improve integrated solid waste management, especially, in metropolises, such as Istanbul with a population close to 10 million. Therefore, in this study, 13 chlorophenol derivatives concentrations in acidogenic, methanogenic and aerobic leachate are determined by SPME and GC–FID. Analyses are carried out at five different times with acidogenic, methanogenic and aerobic leachate samples from active landfilling and landfilled area of Odayeri landfill and aerobic composting plant.

### 1.1. Study areas and leachate characteristics

MSWs of the Istanbul European side are disposed to Odayeri sanitary landfill (OSL) and recycling and composting plant. OSL is in operation since 1995. Approximately, 6000 tonnes/day of municipal solid wastes are being disposed to this landfill and 1000–1500 m<sup>3</sup> leachate/day is being produced. MSWs are disposed at a part of 20 ha (average waste height: 40 m) of 125 ha landfill area in the last 5 years and the landfill site is projected for 25 years usage [18]. So, methanogenic conditions are dominant in this part of the landfill as the age of waste is close to 10 years (Table 1). A part of the landfill is currently active and leachate of active site is collected by a separate drainage pipe line. Acidogenic conditions prevail in this active site, which was also supported by the leachate characterization studies (Table 1). Recycling and composting plant has a capacity of 1000 tonnes/day. This plant has been operated since 2001. The recycled materials, such as paper, glass, plastic and non-iron metals are

Table 1  
Concentration ranges of landfill and composting leachates

Parameter	Odayeri leachate		Composting plant leachate
	Acidogenic	Methanogenic	Aerobic
pH	5.3–5.8	7.0–7.4	6.8–7.2
COD (mg/l)	32500–35600	21000–24000	8500–9000
NH <sub>4</sub> -N (mg/l)	1200–1400	1500–1600	250–300
TKN (mg/l)	1600–1700	1800–1900	350–400
PO <sub>4</sub> -P (mg/l)	50–60	45–65	30–50
Alkalinity (mg/l)	3300–3700	2800–3750	3000–3500
Suspended solid (mg/l)	720–750	600–650	350–400

sorted with handle in this plant. The organic material of MSWs is processed in aerobic fermentation line [19]. Furthermore, chlorophenols are determined in leachates including acidogenic and methanogenic characteristic of Odayeri landfill and leachate from aerobic composting plant. Acidogenic leachates are produced from active Odayeri landfill area and methanogenic leachate originates from not active area landfilled between 1995 and 2000. In order to determine the characteristic of different leachates all analyses, except chlorophenols, are performed according to standard methods of APHA [20]. Concentration ranges of leachate samples are presented in Table 1.

## 2. Material and methods

### 2.1. Extraction procedure

The same SPME experimental conditions to Ribeiro et al. [4] are followed in this study. For this purpose an 85  $\mu\text{m}$  polyacrylate fiber (from SUPELCO) and a SPME fiber holder (from SUPELCO) are used. The fiber is conditioned in the GC injector for 1 h at 250 °C. Whenever needed, this procedure is repeated for fiber cleanup. The vial capacity is 4 ml, handling 2 ml of sample. The temperature and stirring velocity (750 rpm) are controlled during extraction. In this study, optimum extraction conditions are immersion sampling at 40 °C for 60 min, with an 85  $\mu\text{m}$  PA coated fiber, saturated salt conditions and sample pH < 2. pH is adjusted with H<sub>2</sub>SO<sub>4</sub> and to saturate the samples Na<sub>2</sub>SO<sub>4</sub> are used.

### 2.2. Phenol calibration mixture

EPA 8040A phenol calibration mixture (from SUPELCO) containing 24 phenols with an individual concentration of 500  $\mu\text{g}/\text{ml}$  in isopropyl alcohol was used to obtain 13 chlorophenol derivatives which were 2-chlorophenol (2CP); 2,4-dichlorophenol (24DCP); 2,6-dichlorophenol (26DCP); 2,3,5-trichlorophenol (235TCP); 2,4,6-trichlorophenol (246TCP), 2,4,5-trichlorophenol (245TCP); 2,3,6-trichlorophenol (236TCP); 2,3,4-trichlorophenol (234TCP); 2,3,4,5-tetrachlorophenol (2345TeCP); 2,3,5,6-tetrachlorophenol (2356TeCP); 2,3,4,6-tetrachlorophenol (2346TeCP); penta-chlorophenol (PCP). A working standard containing the 13 chlorophenols at a concentration of 500  $\mu\text{g}/\text{l}$  was prepared in isopropyl alcohol. Before extraction, sample pH was adjusted with H<sub>2</sub>SO<sub>4</sub> and salt (Na<sub>2</sub>SO<sub>4</sub>) were added until saturation.

### 2.3. Chromatographic analysis

GC/FID analyses are carried out using a GC–FID FISIONS (GC 8000) with SPME with the helium carrier gas at 1 ml/min. Injector and detector temperatures are 250 and 320 °C, respectively. The temperature program is 40 °C (held for 5 min), increasing to 280 °C (held for 5 min), at a heat-

ing rate of 6 °C/min. The column is 30 m  $\times$  0.32 mm with a film thickness of 0.25  $\mu\text{m}$ . Chlorophenols are quantified by peak area using external standard method. Quantification is achieved using peak area calculations, and compound identification is partly carried out using correlations between retention times [21]. Working standard at a concentration of 500  $\mu\text{g}/\text{l}$  is extracted in the same conditions as samples.

## 3. Results and discussion

Organic contaminants of leachate and decomposition products of biodegradable fractions of municipal refuse are primarily soluble components. In a review of risk associated with landfill leachate, Brown and Donnelly [7] reported that hazardous organic compounds are found in leachate from all 58 landfills investigated, regardless of the waste type. The origin of these chemicals is thought to be illegally dumped hazardous waste, hazardous household waste, such as paints, solvents, oils, cleaning compounds, pesticides and degreasing compounds as well as plasticizers and pharmaceutical materials routinely placed in landfill.

The leachate used in the study has different compositions depending on the sources (Table 1). As it can be clearly seen from the table aerobic composting plant has higher degradation capacity compared to anaerobic landfills. Additionally, leachate compositions of acidogenic and methanogenic phases have different characteristics. Although there may be possible reasons of these observations, the most important ones are different age of landfills and degree of waste stabilization. In support, numerous landfill investigation studies [22] have suggested that the stabilization of waste proceeds in five sequential and distinct phases. The rate and characteristics of waste from a landfill vary from one phase to another. The rate of progress through these stages is dependent upon the physical, chemical and microbiological conditions developed within the landfill with time [23].

In this study, 13 chlorophenol derivatives are determined by SPME-GC/FID techniques in acidogenic and methanogenic leachates from landfills in Istanbul. Also these compounds are determined in leachate from aerobic composting plant. Fig. 1 shows chromatogram of standard mixture extracted according to SPME experimental procedure under same conditions with leachate samples containing 13 chlorophenols with an individual concentration of 500  $\mu\text{g}/\text{l}$ .

Table 2 lists the number of detections, the means and standard deviations for each parameter for acidogenic, methanogenic and aerobic leachates. These concentrations are obtained from ratio between peak area of standard mixture and leachate samples. The results obtained with SPME (pH < 2, saturated Na<sub>2</sub>SO<sub>4</sub> conditions and with PA coated fiber) and GC/FID show that acidogenic leachate from Odayeri landfill includes 24DCP, 26DCP, 234TCP, 2345TeCP and 2346TeCP at concentration ranges of 15–130, 18–65, 8–40, 5–20 and 10–25  $\mu\text{g}/\text{l}$ , respectively. Similarly, in a review of organic contaminants identified in

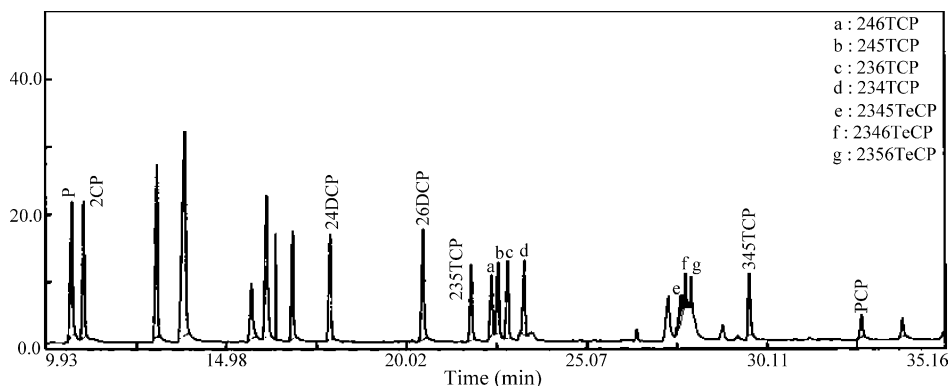


Fig. 1. GC/FID chromatogram of standard mixture containing 13 chlorophenols with an individual concentration of 500  $\mu\text{g/l}$ .

landfill leachates, they reported that chlorophenol derivatives, such as penta-chlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol, 2,4-dichlorophenol and 3,4-dichlorophenol are found in leachate at concentration ranges of 0.01–3000, 0.08–1.87, 0.08–20.4, 0.34–12.8 and 0.27–14.3  $\mu\text{g/l}$ , respectively [24]. Methanogenic leachate of this landfill includes only one chlorophenol derivative of 24DCP at a concentration range of 8–40  $\mu\text{g/l}$ . It is determined that there are no chlorophenol derivatives in aerobic composting leachate (Table 2). Similarly, Reinhart and Grosh [25] examined 55 landfills receiving MSW only and they reported that concentration of 24DCP in acidogenic leachate was 2.83  $\mu\text{g/l}$ , which was the below detection limit in methanogenic leachate. Under anaerobic conditions, more heavily chlorinated phenolic compounds are converted to less chlorinated ones through the reductive dehalogenation [11,26,27]. Absence of more heavily chlorinated phenols in methanogenic leachate led us to think that the occurrence of reductive dechlorination (Table 2), as anaerobic cultures capable of dechlorinating more highly chlorinated com-

pounds have a limited ability to degrade less chlorinated ones [27,28]. Another significant point, which may affect the fate of contaminants, is the extent of interaction with the solid phase. More heavily chlorinated phenols having higher the octanol–water partition coefficient ( $K_{ow}$ ) [29], indicates the higher tendency to sorb, which may increase detection time of those compounds in landfill, in turn, may increase the possibility of dehalogenation. As for leachate originated from composting plant, chlorophenols were observed to be below detection limits. Two conclusions can be drawn from these observations. First, MSW disposed to composting plant may devoid of chlorophenols. Second, even MSW may include chlorophenols, they can be easily degraded even at high concentrations (>50 mg/l) under aerobic conditions as complete removal of mono [30,31], di [32–34] and poly [35]. Saéz and Rittmann [36,37], chlorophenols have also been reported in the literature. Absence of chlorophenol in leachate originated from the composting plant lead us to think that chlorophenols within the waste may be degraded under aerobic conditions. Complete removal of mono, di and

Table 2  
Chlorophenol concentrations in leachate samples

Compound	Detects	Mean	Minimum	Maximum	Standard deviation
Acidogenic leachate					
24DCP	4	40	BDL	130	51.70
26DCP	2	17	BDL	65	28.16
234TCP	3	12	BDL	40	16.49
2345TeCP	2	5	BDL	20	8.66
2346TeCP	2	7	BDL	25	10.95
Methanogenic leachate					
24DCP	4	14	BDL	40	15.23
26DCP	0	BDL	BDL	–	0
234TCP	0	BDL	BDL	–	0
2345TeCP	0	BDL	BDL	–	0
2346TeCP	0	BDL	BDL	–	0
Composting leachate					
24DCP	0	BDL	BDL	–	0
26DCP	0	BDL	BDL	–	0
234TCP	0	BDL	BDL	–	0
2345TeCP	0	BDL	BDL	–	0
2346TeCP	0	BDL	BDL	–	0

BDL, below detection limits.

poly chlorophenols has also been reported in the literature [38].

The chlorophenolic pollutants in acidogenic leachate from Odayeri landfill may originate from hazardous household wastes, such as paints, solvents, oils, cleaning compounds, pesticides and small-scale industrial wastes. Odayeri landfill is on the European side of Istanbul, which is densely industrialized and over populated. Also, the origin of these pollutants is thought to be hazardous waste illegally dumped degradation compounds. Hence, this landfill can contaminate groundwater, if leaks in the insulation system occur. The state of the art of landfilling includes the use of geomembrane (high density polyethylene), and geotextile liners over clay layers. However, volatile organic compounds were found to permeate geomembranes in a matter of days [39] and clay liners without much retardation [40]. Also, geomembrane do little to inhibit the transport of volatile organic carbons (VOCs), because VOCs diffuse readily through geomembrane polymers [39,41–43]. Furthermore, temperature rising during organic matter biotransformation can deteriorate isolation system of landfill [24,44]. Therefore, the effectiveness of modern landfill liner systems to attenuate the migration of such contaminants into surrounding soil and ground water is of concern.

#### 4. Conclusion

Chlorophenols are highly toxic, poorly biodegradable and present carcinogenic and recalcitrant properties. The objective of this study is to investigate chlorophenol derivatives in different leachate (methanogenic, acidogenic and aerobic composting). It is determined that acidogenic leachate percolates from landfill with more species of chlorinated phenols at higher concentration. In order to avoid the ultimate escape of organic pollutants into the environment, a landfill must be operated to optimize the biological stabilization process, to minimize excessive leachate generation, and to isolate the landfill from the groundwater by proper site selection, site preparation, leachate and gas management, liner use and post-closure procedures which may include the ultimate removal of accumulated leachate. Leachate recirculation should be considered in this strategy because of its ability to retain mobile compounds and distribution nutrients until biodegradation is efficiently established. Leachates originated from OSL are currently treated using sequential anaerobic and aerobic reactors. Based on the findings and the literature data it can be concluded that chlorophenols in leachate are low enough concentrations not to adversely affect their biological way of treatment.

#### References

[1] A. Demir, B. Ozkaya, M.S. Bilgili, Effect of leachate recirculation on methane production and storage capacity in landfill, *Fresenius Environ. Bull.* 12 (1) (2003) 29–38.

[2] D.R. Reinhart, A review of recent studies on the sources of hazardous compounds emitted from solid waste landfills: a U.S. experience, *Waste Manage. Res.* 11 (1993) 257–268.

[3] N. Paxéus, Organic compounds in municipal landfill leachates, *Water Sci. Technol.* 42 (7–8) (2000) 323–333.

[4] A. Ribeiro, M.H. Neves, M.F. Almeida, A. Alves, L. Santos, Direct determination of chlorophenols in landfill leachates by solid-phase micro-extraction-gas-chromatography–mass spectrometry, *J. Chromatogr. A* 975 (2002) 267–274.

[5] C. Öman, P.-A. Hynning, Identification of organic compounds in municipal landfill leachates, *Environ. Pollut.* 80 (1993) 265–271.

[6] E. Benfenati, P. Pierucci, R. Fanelli, A. Preiss, M. Godejohann, M. Astratov, K. Levsen, D. Barcello, Comparative studies of the leachate of an industrial landfill by gas chromatography–mass spectrometry, liquid chromatography–nuclear magnetic resonance and liquid chromatography–mass spectrometry, *J. Chromatogr. A* 831 (2) (1999) 243–256.

[7] K.W. Brown, K.C. Donnelly, An estimation of the risk associated with the organic constituents of hazardous and municipal waste landfill leachates, *J. Hazard. Waste Hazard. Mater.* 5 (1) (1988) 3–15.

[8] D.R. Reinhart, F.G. Pohland, The assimilation of organic hazardous wastes by municipal solid waste landfills, *J. Ind. Microbiol.* 8 (1991) 193–200.

[9] C. Grøn, J.B. Christensen, D.L. Jensen, P. Kjeldsen, P. Østfeldt, Organic halogens in landfill leachates, *Water Air Soil Pollut.* 120 (2000) 331–345.

[10] P. Jin, S.K. Bhattacharya, Toxicity and biodegradation of chlorophenols in anaerobic propionate enrichment culture, *Water Environ. Res.* 69 (5) (1997) 938–947.

[11] P.M. Armenante, D. Kafjewitz, A. Lewandowski, C. Jou, Anaerobic–aerobic treatment of halogenated phenolic compounds, *Water Res.* 33 (3) (1999) 681–692.

[12] K.D. Buchholz, J. Pawliszyn, Optimization of solid-phase microextraction (SPME) conditions for phenol analysis, *Anal. Chem.* 66 (1994) 160–167.

[13] M. Llompart, M. Lourido, P. Landin, C. Garcia-Jares, R. Cela, Optimization of a derivatization solid phase microextraction method for the analysis of thirty phenolic pollutants in water samples, *J. Chromatogr. A* 963 (2002) 137–148.

[14] P. Bartak, L. Cap, Determination of phenols by solid-phase microextraction, *J. Chromatogr. A* 767 (1997) 171–175.

[15] M.F. Alpendurada, Solid-phase microextraction: a promising technique for sample preparation in environmental analysis, *J. Chromatogr. A* 889 (1–2) (2000) 3–14.

[16] L.A. Reitzel, A. Ledin, Determination of phenols in landfill leachate-contaminated groundwaters by solid-phase extraction, *J. Chromatogr. A* 972 (2002) 175–182.

[17] M. Lee, Y. Yeh, W. Hsiang, B. Hwang, Solid-phase microextraction and gas chromatography–mass spectrometry for determining chlorophenols from landfill leachates and soil, *J. Chromatogr. A* 806 (2) (1998) 317–324.

[18] B. Ozkaya, A. Demir, A. Başturk, M.S. Bilgili, Investigation of leachate recirculation effects in Istanbul Odayeri sanitary landfill, *J. Environ. Sci. Health A* A39 (4) (2004) 869–879.

[19] G. Kanat, A. Demir, B. Ozkaya, M.S. Bilgili, Optimization of operation in a waste recycling and composting plant, *Fresenius Environ. Bull.* 13 (10) (2004) 956–958.

[20] APHA (American Public Health Association), *Standard Methods for the Examination of Water and Wastewater*, 19th ed., APHA, Washington, DC, 1995.

[21] L. Jirovetz, G. Buchbauer, N.B. Ngassoum, M. Geissler, Analysis of the headspace aroma compounds of the seeds of the Cameroonian “garlic plant” *Hua gabonii* using SPME/GC/FID, SPME/GC/MS and olfactometry, *Eur. Food Res. Technol.* 214 (3) (2002) 212–215.

[22] F.G. Pohland, S.R. Harper, *Critical Review and Summary of Leachate and Gas Production from Landfills*, EPA/600/2-86/073, US Environmental Protection Agency, 1985.

- [23] F.G. Pohland, S.R. Harper, K.C. Chang, J.T. Dertien, E.S.K. Chian, Leachate generation and control at landfill disposal sites, *Water Pollut. Res. J. Can.* 20 (3) (1985) 10–24.
- [24] L. Jimenez, R. Alzaga, J.M. Bayona, Determination of organic contaminants in landfill leachates: a review, *Int. J. Environ. Anal. Chem.* 82 (7) (2002) 415–430.
- [25] D.R. Reinhart, C.J. Grosh, Analysis of Florida MSW Landfill Leachate Quality, Florida Center For Solid and Hazardous Waste Management, Final Report #97-3, 1998.
- [26] J.R.V. Flora, M.T. Suidan, A.M. Wuellner, T.K. Boyer, Anaerobic treatment of a simulated high strength industrial wastewater containing chlorophenols, *Water Environ. Res.* 66 (1994) 21–31.
- [27] J.A. Puhakka, P.M. Makinen, M. Lundin, J.F. Ferguson, Aerobic and anaerobic biotransformations and treatment of chlorinated pulp bleach waste constituents, *Water Sci. Technol.* 29 (5–6) (1994) 73–80.
- [28] M.T. Suidan, J.R.V. Flora, T.K. Boyer, A.M. Wuellner, Anaerobic dechlorination using a fluidized-bed GAC reactor, *Water Res.* 30 (1996) 160–170.
- [29] E. Sahinkaya, Toxicity and treatability of chlorophenols under aerobic and anoxic conditions, Middle East Technical University, M.Sc. Thesis, 2001.
- [30] E. Sahinkaya, F.B. Dilek, Biodegradation of 4-chlorophenol by acclimated and unacclimated activated sludge-evaluation of biokinetic coefficients. *Environ. Res.*, in press.
- [31] U. Bali, F. Şengül, Performance of a fed-batch reactor treating a wastewater containing 4-chlorophenol, *Process Biochem.* 37 (2002) 1317–1323.
- [32] E. Sahinkaya, F.B. Dilek, Effects of 2,4-dichlorophenol on activated sludge, *Appl. Microbiol. Biotechnol.* 59 (2002) 361–367.
- [33] G. Buitron, A. Gonzalez, Characterization of the microorganisms from an acclimated activated sludge degrading phenolic compounds, *Water Sci. Technol.* 34 (5–6) (1996) 289–294.
- [34] G. Buitron, A. Gonzalez, L.M. Lopez-Marin, Biodegradation of phenolic compounds by an acclimated activated sludge and isolated bacteria, *Water Sci. Technol.* 37 (1998) 371–378.
- [35] J.A. Puhakka, W.K. Shieh, K. Jarvinen, E. Melin, Chlorophenol degradation under oxic and anoxic conditions, *Water Sci. Technol.* 25 (1992) 147–152.
- [36] P.B. Saéz, B.E. Rittmann, Biodegradation kinetics of 4-chlorophenol, an inhibitory co-metabolite, *Res. J. Water Pollut. C.* 63 (1991) 838–847.
- [37] P.B. Saéz, B.E. Rittmann, Biodegradation kinetics of a mixture containing a primary substrate (phenol) and an inhibitory co-metabolite (4-chlorophenol), *Biodegradation* 4 (1993) 3–21.
- [38] B.E. Rittmann, P.L. McCarty, *Environmental Biotechnology: Principles and Applications*, McGraw-Hill, New York, 2001.
- [39] J.K. Park, J.B. Sakti, J.A. Hoopes, Transport of organic compounds in thermoplastic geomembranes I: mathematical model, *J. Environ. Eng. ASCE* 122 (9) (1996) 800–806.
- [40] J.Y. Kim, T.B. Edil, J.K. Park, Volatile organic compound (VOC) transport through compacted clay, *J. Geotech. Geoenviron. ASCE* 127 (2) (2001) 126–134.
- [41] T.B. Edil, A review of aqueous-phase VOC transport in modern landfill liners, *Waste Manage.* 23 (2003) 561–571.
- [42] G.J. Foose, C.H. Benson, T.B. Edil, Comparison of solute transport in three composite liners, *J. Geotech. Geoenviron. ASCE* 128 (5) (2002) 391–403.
- [43] K. Brown, J. Thomas, A comparison of the convective and diffusive flux of organic contaminants through landfill liner systems, *Waste Manage. Res.* 16 (3) (1998) 296–301.
- [44] T.H. Christensen, P. Kjeldsen, H.J. Albrechtsen, G. Heron, P.H. Nielsen, P.L. Bijerg, P.E. Holm, Attenuation of landfill leachate pollutants in aquifers, *Crit. Rev. Env. Sci. Technol.* 24 (1994) 119–202.