

Use of advanced oxidation processes to improve the biodegradability of mature landfill leachates

Josmaria Lopes de Moraes, Patricio Peralta Zamora*

Grupo de Desenvolvimento de Técnicas Avançadas para Tratamento de Resíduos (TECNOTRATER), Departamento de Química, Universidade Federal do Paraná, P.O. Box 19081, 81531-990 Curitiba, Brazil

Received 25 January 2005; received in revised form 28 March 2005; accepted 29 March 2005

Available online 4 May 2005

Abstract

Two advanced oxidative processes ($\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ and $\text{H}_2\text{O}_2/\text{UV}$ systems) were used for the pre-treatment of mature landfill leachate with the objective of improving its overall biodegradability, evaluated in terms of BOD_5/COD ratio, up to a value compatible with biological treatment. At optimized experimental conditions (2000 mg L^{-1} of H_2O_2 and 10 mg L^{-1} of Fe^{2+} for the photo-Fenton system, and 3000 mg L^{-1} of H_2O_2 for the $\text{H}_2\text{O}_2/\text{UV}$ system), both methods showed suitability for partial removal of chemical oxygen demand (COD), total organic carbon (TOC) and color. The biodegradability was significantly improved (BOD_5/COD from 0.13 to 0.37 or 0.42) which allowed an almost total removal of COD and color by a sequential activated sludge process. In addition, gel permeation chromatography (GPC) has showed a substantial agreement on the cleavage of large organic compound into smaller ones.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Landfill leachate; Biodegradability enhancement; Photo-Fenton; $\text{UV}/\text{H}_2\text{O}_2$

1. Introduction

Leachates may contain large amounts of recalcitrant organic matter, where humic-type constituents represent an important group [1,2] as well as ammonia–nitrogen, heavy metals, chlorinated organic and inorganic salts [3]. The composition and concentration of contaminants are influenced by the type of deposited waste, the quality of the refuse, the hydrogeological factors and mainly by the age of the landfill [4,5]. In general, the leachates originated from recent domestic waste landfill have high BOD_5 values (which can reach thousands $\text{mg O}_2/\text{L}$) and even higher chemical oxygen demand (COD) content [5–7]. The mature leachate is very complex consisting of high concentrations of humic and fulvic acids as well as salts and low BOD_5/COD ratio (less than 0.1).

Biological treatment of wastewater is often the most cost-effective alternative when compared to other treatment options [8–10]. Nevertheless, mature leachate effluents are

known to contain recalcitrant and/or non-biodegradable organic substances and biological processes are not efficient in these cases [11,12]. Studies have demonstrated that the major fraction of dissolved organic carbon (DOC) in biologically pre-treated landfill leachates consists of humic substances, mainly in humic and fulvic acids [13,14].

Traditionally, the degradation of organic compounds and the removal of nitrogen can be achieved by advanced oxidation processes (AOP) [15,16]. AOP have been used to enhance the biotreatability of wastewaters containing various organic compounds that are non-biodegradable and/or toxic to common microorganisms [17–20].

AOP involve the generation of the hydroxyl radical ($\bullet\text{OH}$), which has a very high oxidation potential and is able to oxidize almost all organic pollutants. Although these processes are very effective in completing mineralization of pollutants, if they are applied as the only treatment process, they will be expensive. A promising alternative to complete oxidation of biorecalcitrant wastewater is the use of an AOP as pre-treatment to convert initially biorecalcitrant compounds to more readily biodegradable intermediates,

* Corresponding author. Tel.: +55 41 3613176; fax: +55 41 3613186.

E-mail address: zamora@quimica.ufpr.br (P.P. Zamora).

followed by biological oxidation of these intermediates to biomass and water [21,22].

Wu et al. [23] demonstrated the efficiency of ozone-based AOP enhancing the biodegradability and eliminating the color of leachate. Koh et al. [24] studied the integration of processes for the treatment of complex leachates from both domestic and industrial landfills. This work reports that the environmental parameters were reduced to the values demanded by the German legislation by using a three steps treatment: biological, photochemical and biological.

This study focused on the remediation of a typical mature landfill leachate, through an integrated photoassisted-biological reactor without addition of other electron acceptor than O_2 . The following topics are also studied in this paper: (a) the characterization of mature leachate samples; (b) the comparison between the photochemical treatments use process UV/ H_2O_2 and photo-Fenton using parameters such as COD, DOC, inorganic carbon (IC), BOD/COD ratio; (c) the comparison between the leachate treatment just for biological process and use photochemical process as a pre-treatment step in the integrated photochemical biological reactor in a laboratory scale.

2. Experimental

2.1. Wastewater, organisms and reagents

Samples of landfill leachate were obtained from a municipal landfill site (over 14 years old) located in Curitiba (Paraná State, Brazil). This landfill receives, exclusively, municipal solid waste. The samples were collected in teflon bottles and maintained at 4 °C, protected from light.

Samples of activated sludge inoculum were collected directly from the aeration tank of the municipal wastewater treatment plant. The sludge was continuously aerated using aeration pumps.

Ferrous sulphate ($FeSO_4 \cdot 7H_2O$), sulphuric acid and hydrogen peroxide (Merck, 30 wt.%) were of analytical grade.

2.2. Experimental setup

After the optimization by factorial design, the AOPs were applied in the treatment of raw leachates using a batchwise mode. To evaluate differences on the biodegradability of raw and photochemically pre-treated leachates, both samples were submitted to an activated sludge system, also operated in a batchwise mode.

2.3. Photochemical procedure

The experiments were carried out in a 100 mL closed batch reactor (internal diameter: 5 cm, external diameter: 7.5 cm, total height: 15 cm) equipped with water refrigeration and magnetic stirrer. Ultraviolet radiation was provided by a medium-pressure mercury vapor lamp (125 W, Philips), with-

out the original glass-bulb, located at the center of the reactor by using a quartz bulb. The incident light flux of the UV lamp was determined by actinometry (uranyl/oxalate system [25]) as 3.2×10^{-3} Einstein $L^{-1} s^{-1}$. Adequate amounts of photocatalysts (H_2O_2 or Fe^{2+}/H_2O_2) were added to the samples of leachate, which were stirred and irradiated in determined times (by optimization). Commercial oxygen was bubbled through a sintered glass placed at the bottom of the reactor at flows of about 45 $mL min^{-1}$. For analytical control, samples were taken at convenient intervals and filtered through a 0.45 μm Millipore filter. In general, the photochemical treatment time was extended up to absence of residual H_2O_2 .

2.4. Biological procedure

The activated sludge system was applied in cylindrical aeration glass-vessels (5 cm of internal diameter and 25 cm of height) with a total volume of about 500 mL. The system was aerated by using air pumps and diffusers coupled at the bottom of the reactors. The initial volume of the culture was 200 mL, which was completed to 400 mL with substrates (leachate, pre-treated leachate or glucose) at the beginning of each cycle. The pH was controlled by a probe and adjusted at 7.0 by using H_2SO_4 or NaOH. The oxygen concentration was monitored by using an O_2 probe, located at the top of the reactor. All the experiments were carried out in duplicate and at room temperature (20–25 °C) by periods of 72 h. Physic characteristics of the sludge were periodically monitored by sludge volume index (SVI) determination and microscopic observation. For COD determinations, samples (5 ml each) were taken every 12 h, after they had been centrifuged and filtered through a 0.45 μm Millipore filter.

2.5. Analytical methods

2.5.1. Characterization of the raw landfill leachate

Determinations of chemical and biochemical oxygen demand (COD and BOD), total solids (TS), total Kjeldhal nitrogen (TKN), chloride (Cl^-) and alkalinity were carried out according to standard methods [26]. Selected metals were determined with an AVANTA-GBC flame atomic absorption spectrophotometer (GBC Scientific Equipment). The UV–vis absorption was measured with a SINCO S-1150 spectrophotometer, using quartz cells. The analysis of total organic carbon (TOC) and inorganic carbon was carried out by using a Shimadzu TOC-VCPH analyzer.

2.5.2. Analytical control

The analytical control of the processes included determinations of the COD, BOD, TOC, IC, color (expressed as integrated spectral area between 400 and 700 nm) and residual H_2O_2 (spectrophotometrically measured at 441 nm using the reaction with vanadate according to Oliveira et al. [27]). In order to better understand the change of molecular weight distribution after treatments, gel permeation chromatograph (GPC) was used. GPC was performed using a Shimadzu

LC-10 HPLC system, equipped with a TSK-HXL column (TOSOH Co.) and a refractive-index detector operated at 280 nm.

2.5.3. Sludge characterization

The activated sludge system was characterized by determining the total suspended solids (TSS), volatile suspended solids (VSS), settled volume after 30 min (V30), sludge volume index and pH according to the procedures described by standard methods [26].

3. Results and discussion

3.1. Characterization of the raw landfill leachate

From the main chemical characteristics summarized in Table 1, it is possible to confirm the complex character of the leachate samples. With biodegradability ratio (DBO/DQO) lower than 0.13 and a pH higher than 8, the samples can be considered as mature or stabilized leachates [5,7,12], normally classified as refractory to conventional biodegradation processes. In most cases, intensive and sophisticated physico-chemical processes are necessary for the treatment of aged leachates.

3.2. Optimization of photochemical processes

3.2.1. UV/H₂O₂ system

Radiation with wavelength lower than 400 nm is able to photolyse the H₂O₂ molecule. The mechanism accepted for the photolysis of hydrogen peroxide is the cleavage of the molecule into hydroxyl radicals with a quantum yield of two •OH radicals formed per quantum of absorbed radiation [28], according to the following reaction:



The optimization of relevant variables (pH and H₂O₂ concentration) was carried out by the 2² factorial experimental design complemented with a central point [29] showed in

Table 1
Chemical characteristics of the studied landfill leachates

Parameters	Values	Parameters	Values
pH	8.4 ± 0.1	Calcium	10.61 ± 0.2
COD	5200 ± 27	Sodium	1512 ± 47
BOD	720 ± 81	Potassium	1480 ± 3.5
TOC	1058 ± 2.7	Barium	3.6 ± 0.23
IC	1088 ± 2.7	Iron	13.212
TS	1212 ± 97	Magnesium	9.365
TKN	1114 ± 42	Zinc	1.059
Chloride	2590 ± 95	Nickel	1.429
Alkalinity as CaCO ₃	1240 ± 45	Lead	0.278
PO ₄ -P	11.3 ± 0.7	Copper	0.362
Boro	2.15 ± 0.23	Chromium	0.451
Sulphur	316 ± 23	Manganese	0.298

Values (except pH) in mg L⁻¹.

Table 2
2² Factorial design for optimization of the H₂O₂/UV system

Variable	Level (-)	Level (0)	Level (+)
pH	7.0	8.0	9.0
H ₂ O ₂ (mg L ⁻¹)	2500	3000	3500
Experiment	Variable		COD removal (%)
	pH	H ₂ O ₂	
1	-	-	35 ± 2.5
2	-	+	53 ± 3.6
3	+	-	29 ± 2.2
4	+	+	31 ± 2.8
5	0	0	55 ± 4.1

Reaction time: 60 min; O₂: 45 mL min⁻¹. Main effects: pH: -14 ± 3.0; H₂O₂: 10 ± 3.0; COD removal (%) = 40.6 - 7 (pH) + 5 (H₂O₂).

Table 2. The analytical response corresponds to the COD reduction (%) at a 60 min reaction time.

The results indicated that the system operates with great efficiency in low pH values and high hydrogen peroxide concentration. However, it is important to remark that a similarity can be observed between the best experimental conditions (represented by the low level of pH and the high level of H₂O₂) and the conditions defined by the central point. There is an interesting peculiarity that allows an optimized response in an extended range of experimental conditions.

Additionally, it was observed an important dependence between the kinetics of the peroxide consumption process and the pH of the media. Normally, the pH 7 leads to a gradual decomposition of H₂O₂, which prolongs the degradation reaction for a longer time. On the other hand, in pH 8, the largest degradation gradient happens between 0 and 30 min, for all the studied H₂O₂ concentrations. This is an important fact, taking into account that the presence of residual peroxide makes the use of the pre-treated leachate in biological studies unfeasible. In view of these arguments, the high concentration of hydrogen peroxide (3500 mg L⁻¹) and the natural pH of the leachate (8.4) were selected as experimental conditions for further studies.

At the assayed experimental conditions, the effect of single UV-light, hydrogen peroxide or oxygenation was negligible.

3.2.2. Fe²⁺/UV/H₂O₂ system

The Fenton process has attracted great interest in recent years in view of this high efficiency to generate hydroxyl radicals through decomposition of H₂O₂ by Fe²⁺ in acidic conditions (Eq. (2)). Combined with UV-vis irradiation, the oxidation power is increased due to the photoreduction of Fe³⁺ to Fe²⁺ (Eq. (3)) and the generation of a catalytic cycle that involves the formation of two hydroxyl mol per mol of H₂O₂ initially decomposed. The so-called photo-Fenton system shows the great advantage of working even with visible light, which facilitates the development of low-cost treatment procedures.

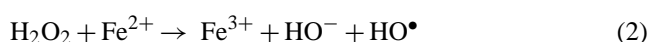
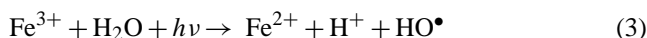


Table 3
2³ Factorial design for optimization of the Fe²⁺/UV/H₂O₂ system

Variable	Level (-)	Level (0)	Level (+)
pH	2.8	3.3	3.8
H ₂ O ₂ (mg L ⁻¹)	1000	1500	2000
Fe ²⁺ (mg L ⁻¹)	10	15	20

Experiment	Variable			COD removal (%)
	Fe ²⁺	H ₂ O ₂	pH	
1	-	-	-	27 ± 1.9
2	-	-	+	23 ± 1.8
3	-	+	-	47 ± 2.2
4	-	+	+	35 ± 2.8
5	+	-	-	32 ± 2.5
6	+	-	+	26 ± 1.9
7	+	+	-	49 ± 3.2
8	+	+	+	39 ± 3.1
9	0	0	0	41 ± 3.7

Reaction time: 60 min; O₂: 45 mL min⁻¹. Main effects: Fe²⁺: 3.5 ± 2.6; H₂O₂: 16 ± 2.6; pH: -8 ± 2.6; COD removal (%) = 35.4 + 1.7 (Fe²⁺) + 7.8 (H₂O₂) - 4 (pH).



The optimization of the main experimental variables (pH, H₂O₂ and Fe²⁺ concentrations) was carried out by the 2³ factorial design showed in Table 3. The results resemble the ones observed by the Fenton system. That is, higher degradation efficiency at low pH levels and high H₂O₂ concentrations. In contrast, changes on the iron II concentration induce negligible effects on the degradation capacity of the system, probably due to the high iron content in the raw samples. Considering these preliminary results, the high concentration of hydrogen peroxide (2000 mg L⁻¹), the low iron II concentration (10 mg L⁻¹) and a pH of 2.8 were selected as experimental conditions for further studies.

3.3. Comparative evaluation of AOPs

Using the previously optimized experimental conditions, the efficiency of both photochemical processes was evaluated toward the removal of COD and COT. The results (Table 4) demonstrated that the total organic carbon content can be efficiently removed in lower than 60 min reaction times, fact that confirms the great degradation capacity of both photochemical processes. Normally, the residual TOC (lower than 10%) is represented by resistant species that accumulate at the

Table 4
COD and TOC removal (%) by photochemical treatments

Treatment	Time (min)	Removed (%)	
		COD	TOC
UV/H ₂ O ₂	30	40.9	80.7
	60	55.5	97.2
Photo-Fenton	30	46.4	33.7
	60	57.5	89.9

end of the process, mainly carboxylic acids and short-chain aldehydes.

The COD evolved according to a least favorable kinetics, resulting in a total elimination of about 50%. At first, the differences between TOC and COD removal can appear as analytical inconsistencies. However, in view of the unselective character of the COD determination procedure, it is possible to assume that the residual COD content correspond to interfering reduced inorganic substances.

In both photochemical systems, the hydrogen peroxide was quickly consumed, resulting in an almost total decomposition at the end of the processes.

The evolution of the molecular weight of the leachate during the photochemical treatments was evaluated by gel permeation chromatography. For untreated samples, the molecular weight is distributed between 6 and 35 kDa with predominance of values between 10 and 35 kDa (Fig. 1). This result is in agreement with the current literature [13,23,30,31], which admits that, for mature leachates, the predominance of molecular weight higher than 10 kDa is related to the presence of humic and fulvic substances.

The effect of both photochemical processes is very obvious (Fig. 1), since it involves the fragmentation of large organic compounds into smaller and probably more biodegradable molecular fragments.

3.4. Biodegradability changes during photocatalytic decomposition

Initially, the biodegradability of the leachates was evaluated through the evolution of the BOD/COD ratio. For untreated samples, this parameter attains values of about 0.13 while UV/H₂O₂ and photo-Fenton treatments of 60 min permit its enhancement up to values near 0.4, which represent substantial biodegradability according to the current literature [32–34]. This result indicates that the photochemical processes can break down or rearrange

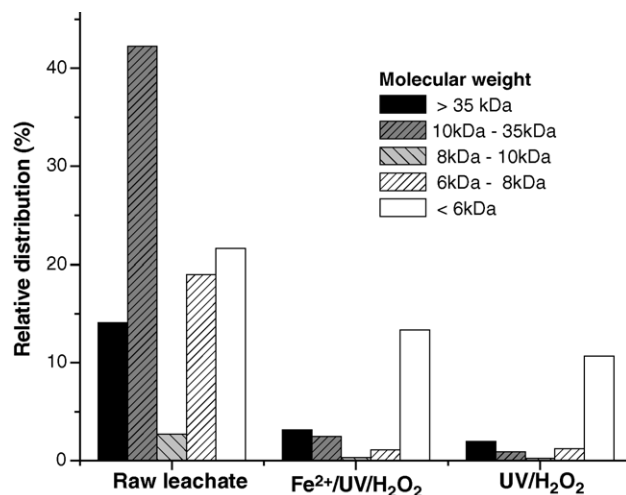


Fig. 1. Distribution of molecular weight during the photochemical treatment of the leachate.

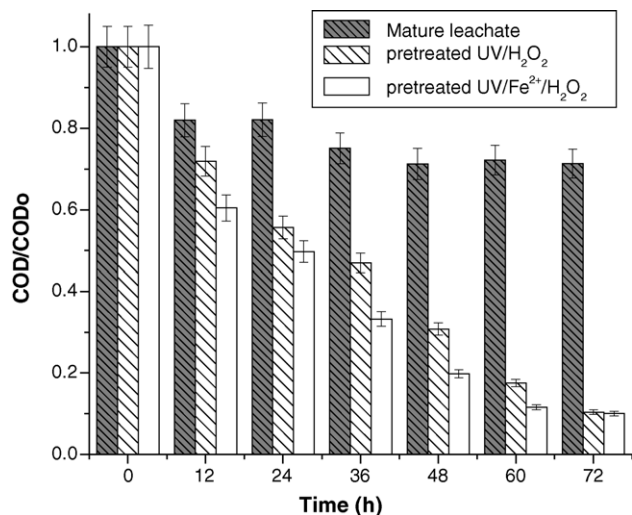


Fig. 2. Evolution of COD during biological treatment of the leachates.

molecular structures of organic matter and convert the non-biodegradable organics to more biodegradable forms. This is a fact of remarkable importance in the case of the application of photochemical–biological integrated system to wastewater treatment [35].

In general, it is admitted that photochemical processes can transform organic recalcitrant compounds into easily

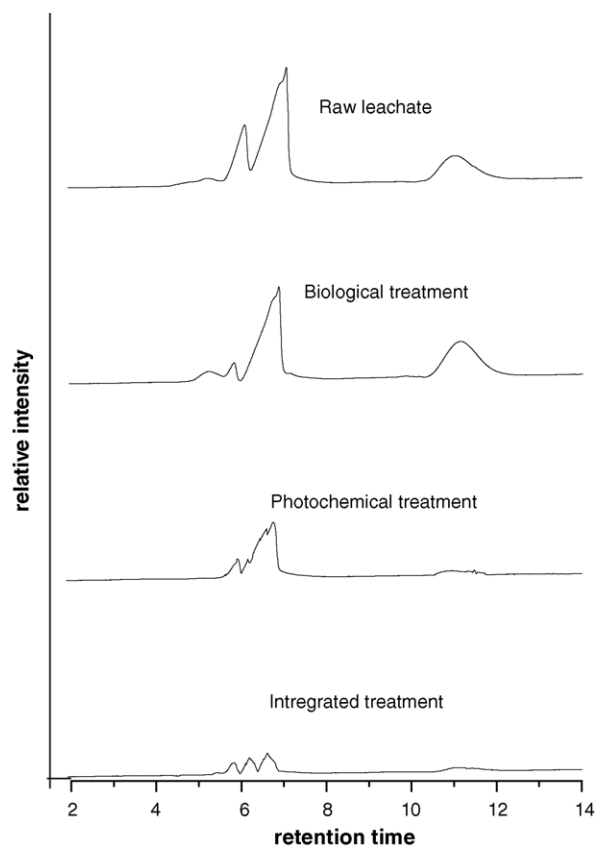


Fig. 3. GPC analysis of leachate before and after treatments. The retention time is shown in minutes.

biodegradable products, improving the efficiency and reducing the cost of further biological steps.

In a second phase, raw and pre-treated leachate was submitted to a biological degradation process using a sequential batch reactor. The evolution of COD during the biological treatment (Fig. 2) confirms the low biodegradability of raw mature leachates, which achieve a maximal COD removal of about 30% at 72 h treatment times. On the other hand, the COD of pre-treated leachates fades progressively attaining COD removal higher than 90% at the end of the 72-h cycle. Additionally, the use of photochemically pre-treated samples favored the preservation of physical characteristics of the biological sludge, which could be corroborated by the measurement of traditional physical parameters and microscopic observation.

The significant differences induced in the leachate samples, by using the isolated and integrated processes, can be confirmed by the evolution of molecular weight showed in Fig. 3.

4. Conclusions

Mature landfill leachates contain some macromolecular organic substances that are resistant to biological degradation. With very low biodegradability ratios (BOD/COD), usually lower than 0.1, these complex matrixes show a recognized resistance toward conventional activated sludge systems. When applied as relatively brief pre-treatment systems, the UV/H₂O₂ and photo-Fenton processes induce several modifications of the matrix, which results in significant enhancement of its biodegradability. For this reason, the integrated photochemical–biological systems proposed here represent a suitable solution for the treatment of mature landfill leachate samples with an efficient remediation of the relevant parameters (COD, TOC).

References

- [1] P. Kjeldsen, A.B. Morton, A.P. Rooker, A. Bauns, A. Ledin, T.H. Christensen, Present and long-term composition of MSW landfill leachate, *Environ. Sci. Technol.* 32 (4) (2002) 297–336.
- [2] K.H. Kang, H.S. Shin, H. Park, Characterization of humic substances present in landfill leachates with different landfill ages and its implications, *Water Res.* 36 (16) (2002) 4023–4032.
- [3] Z.P. Wang, Z. Zhang, Y.-J. Lin, N.-S. Deng, T. Tao, K. Zhuo, Landfill leachate treatment by a coagulation-photooxidation process, *J. Hazard. Mater.* 2887 (2002) 1–7.
- [4] A.A. Tasi, A.I. Zouboulis, K.A. Matis, P. Samaras, Coagulation-flocculation pretreatment of sanitary landfill leachates, *Chemosphere* 53 (2003) 737–744.
- [5] M. El Fadel, E. Douseid, W. Chahine, B. Alaylic, Factors influencing solid waste generation and management, *Waste Manage.* 22 (2002) 269–283.
- [6] T.H. Christensen, P. Kjeldsen, P.L. Bjerg, D.L. Jensen, J. Christensen, A. Baun, J. Albrechtsen, G. Heron, Biogeochemistry of landfill leachate plumes, *Appl. Geochem.* 16 (2001) 659–718.

- [7] S. Baig, I. Coulomb, P. Courant, P. Liechti, Treatment of landfill leachates: Lapeyrouse and Satrod case studies, *Ozone Sci. Eng.* 21 (1999) 1–22.
- [8] O.N. Akgdag, D.T. Sponza, Anaerobic/aerobic treatment of municipal landfill leachate in sequential two-stage up-flow anaerobic sludge blanket reactor (UASB)/completely stirred tank reactor (CSTR) systems, *Process Biochem.* 40 (2005) 895–902.
- [9] P. Gogate, B. Aniruddha, A. Pandit, Review of imperative technologies for wastewater treatment. II. Hybrid methods, *Adv. Environ. Res.* 8 (2004) 553–597.
- [10] V. Sarria, S. Parra, N. Adler, P. Péringier, N. Benitez, C. Pulgarin, Recent developments in the coupling of photoassisted and aerobic biological processes for the treatment of biorecalcitrant compounds, *Catal. Today* 76 (2002) 301–315.
- [11] S.P. Cho, S.C. Hong, S.-I. Hong, Photocatalytic degradation of the landfill leachate containing refractory matters and nitrogen compounds, *Appl. Catal. B39* (2002) 125–133.
- [12] A. Lopez, M. Pagano, A. Volpe, A.C. Di Pinto, Fenton's pretreatment of mature landfill leachate, *Chemosphere* 54 (2004) 1005–1010.
- [13] J.B. Christensen, D.L. Jensen, C. Geron, Z. Filip, T.H. Christensen, Characterization of the dissolved organic carbon in landfill leachate-polluted groundwater, *Water Res.* 32 (1998) 125–135.
- [14] M.A. Nanny, N. Ratasuk, Characterization and comparison of hydrophobic neutral and hydrophobic acid dissolved organic carbon isolated from three municipal landfill leachates, *Water Res.* 36 (2002) 1577–1584.
- [15] R. Bauer, G. Waldner, H. Fallmann, S. Hager, M. Klare, T. Krutzler, S. Malato, P. Maltzky, The photo-Fenton reaction and the TiO_2/UV process for waste water treatment—novel developments, *Catal. Today* 53 (1999) 131–144.
- [16] Z.P. Wang, Z. Zhang, Y.-J. Lin, N.S. Deng, T. Tao, K. Zhuo, Landfill leachate treatment by a coagulation–photooxidation process, *J. Hazard. Mater.* 2887 (2002) 1–7.
- [17] D.M. Bila, F. Montalvão, A.C. Silva, M. Dezotti, Ozonation of a landfill leachate: evaluation of toxicity removal and biodegradability improvement, *J. Hazard. Mater.* 117 (2/3) (2005) 235–242.
- [18] A.C. Silva, M. Dezotti, G.L. Sant'anna Jr., Treatment and detoxification of a sanitary landfill leachate, *Chemosphere* 55 (2004) 207–214.
- [19] N.J. Karrer, G. Ryhiner, E. Hinzle, Applicability test for combined biological-chemical treatment of wastewaters containing biorefractory compounds, *Water Res.* 31 (1997) 1013–1020.
- [20] G. Yu, W. Zhu, Z. Yang, Pretreatment and biodegradability enhancement of DSD acid manufacturing wastewater, *Chemosphere* 37 (3) (1998) 487–494.
- [21] V. Sarria, P. Péringier, J. Cáceres, J. Blanco, S. Malato, C. Pulgarin, Solar degradation of 5-amino-6-methyl-2-benzimidazolone by TiO_2 and iron(III) catalyst with H_2O_2 and O_2 as electron acceptors, *Energy* 29 (2004) 853–860.
- [22] S.H. Lin, C.D. Kiang, Combined physical, chemical and biological treatments of wastewater containing organics from a semiconductor plant, *J. Hazard. Mater. B97* (2003) 159–171.
- [23] J.J. Wu, C.-C. Wu, H.-W. Ma, C.-C. Chang, Treatment of landfill leachate by ozone-based advanced oxidation processes, *Chemosphere* 54 (2004) 997–1003.
- [24] I.-O. Koh, X. Chen-Hamacher, K. Hicke, W. Thiermann, Leachate treatment by the combination of photochemical oxidation with biological process, *J. Photochem. Photobiol. A162* (2004) 261–271.
- [25] D. Curc6, S. Malato, J. Blanco, J. Gimenez, P. Marco, Photocatalytic degradation of phenol: comparison between pilot-plant-scale and laboratory results, *Solar Energy* 56 (1996) 387–400.
- [26] APHA, AWWA, Standard Methods for Examination of Water and Wastewater, 19th ed., WPCF, New York, 1995.
- [27] M.C. Oliveira, R.F.P. Nogueira, J.A. Gomes-Neto, W.F. Jardim, J.J.R. Rohwedder, Sistema de injeção em fluxo espectrofotométrico para monitorar peróxido de hidrogênio em processo de fotodegradação por reação foto-fenton, *Quim. Nova* 24 (2001) 188–193.
- [28] S. Esplugas, J. Giménez, S. Contreras, E. Pascual, M. Rodrigues, Comparison of different advanced oxidation processes for phenol degradation, *Water Res.* 36 (2002) 1034–1042.
- [29] G.E.P. Box, W.G. Hunter, J.S. Hunter, Statistics for experimenters—an introduction to design, in: *Data Analysis and Model Building*, John Wiley and Sons, New York, 1978.
- [30] N. Milloti, C. Granet, A. Wicker, G.M. Faup, Application of GPC processing system to landfill leachates, *Water Res.* 21 (6) (1987) 709–715.
- [31] N. Calace, B.M. Petronio, Characterization of high molecular weight organic compounds in landfill leachate: humic substances, *J. Environ. Sci. Health A* 32 (1997) 2229–2244.
- [32] J. Metcalf, Eddy, *Wastewater Engineering*, third ed., Mc Graw-Hill Series in Water Resources and Environmental Engineering, New York, 1991.
- [33] A. Marco, S. Esplugas, G. Saum, How and why to combine and biological processes for wastewater treatment, *Water Sci. Technol.* 35 (1997) 321–327.
- [34] S. Esplugas, S. Contreras, D.F. Ollis, Engineering aspects of the integration of chemical and biological oxidation: simple mechanistic models for the oxidation treatment, *J. Environ. Eng.* 130 (2004) 967–974.
- [35] J. Wiszniowski, D. Robert, J. Surmacz-Gorska, K. Miksch, S. Malato, J.V. Weber, Solar photocatalytic degradation of humic acids as a model of organic compounds of landfill leachate in pilot-plant experiments: influence of inorganic salts, *Appl. Catal. B53* (2004) 127–137.