0273-2289/03/109/0181/$20.00

Removal of Chemical Oxygen Demand, Nitrogen, and Heavy Metals Using a Sequenced Anaerobic–Aerobic Treatment of Landfill Leachates at 10–30°C

SERGEY KALYUZHNYI,*,[1] MARINA GLADCHENKO,[1] ANDREY EPOV,[1] AND VASU APPANNA[2]

[1]*Department of Chemical Enzymology, Chemistry Faculty, Moscow State University, 119899 Moscow, Russia,*
E-mail: svk@enz.chem.msu.ru;
and [2]Department of Chemistry and Biochemistry, Laurentian University, Ramsey Lake Road, Sudbury, Ontario, P3E 2C6, Canada

Abstract

As a first step of treatment of landfill leachates (total chemical oxygen demand [COD]: 1.43–3.81 g/L; total nitrogen: 90–162 mg/L), performance of laboratory upflow anaerobic sludge bed reactors was investigated under mesophilic (30°C), submesophilic (20°C), and psychrophilic (10°C) conditions. Under hydraulic retention times (HRTs) of about 0.3 d, when the average organic loading rates (OLRs) were about 5 g of COD/(L·d), the total COD removal accounted for 81% (on average) with the effluent concentrations close to the anaerobic biodegradability limit (0.25 g of COD/L) for mesophilic and submesophilic regimes. The psychrophilic treatment conducted under an average HRT of 0.34 d and an average OLR of 4.22 g of COD/(L·d) showed a total COD removal of 47%, giving effluents (0.75 g of COD/L) more suitable for subsequent biologic nitrogen removal. All three anaerobic regimes used for leachate treatment were quite efficient for elimination of heavy metals (Fe, Zn, Cu, Pb, Cd) by concomitant precipitation in the form of insoluble sulfides inside the sludge bed. The application of aerobic/anoxic biofilter as a sole polishing step for psychrophilic anaerobic effluents was acceptable for elimination of biodegradable COD and nitrogen approaching the current standards for direct discharge of treated wastewater.

---

*Author to whom all correspondence and reprint requests should be addressed.

Index Entries: Landfill leachate; upflow anaerobic sludge bed reactor; heavy metals; simultaneous anaerobic removal of ammonia and sulfate; aerobic-anoxic biofilter; nitrification; denitrification.

Introduction

The total annual production of municipal solid wastes in Russia accounts for 37.5 million tons from which more than 96% are currently disposed of via landfilling *(1)*. As a result of microbial activity within a landfill, compression, and water flows, a leachate containing a wide variety of intermediate organic degradation products and inorganic (including metallic) contaminants is produced. This leachate (if not collected and treated) poses dangerous environmental and health risks owing to its impact on surface waters and groundwaters *(2)*. Since the main concerns in landfill leachates are usually organic and nitrogenous contaminants as well as heavy metals *(3)*, the primary objective of the present study was to develop an efficient laboratory-scale technology for removal of these pollutants. Although some physicochemical methods have been suggested as perspective ones *(4,5)*, microbiologic methods have proved efficient for the treatment of municipal landfill leachates *(3)*. Various aerobic *(6–8)*, anaerobic *(9–11)*, and combined anaerobic-aerobic *(12,13)* treatments have been researched and applied for this purpose. In our study, as a first step, the UASB reactor for the elimination of the major part of chemical oxygen demand (COD) and concomitant precipitation of heavy metals in the form of insoluble sulfides inside the sludge bed was used. In addition to conventional mesophilic regime (30°C) investigations were carried out at lower temperatures (20 and 10°C) in order to evaluate the possibility of direct treatment without preliminary heating. This option is especially attractive in Russia because of the moderate/cold climate. In a subsequent step, the biofilter operating in alternative aerobic-anoxic regime at 20 and 10°C was used for removal of the remaining biodegradable COD (biochemical oxygen demand [BOD] was not measured) and nitrogen.

Materials and Methods

Landfill Leachates

The raw leachates were taken from December 2001 to April 2002 from the leachate collection systems of two operating municipal landfills located in different regions receiving mainly municipal wastes with limited disposal of industrial refuses: landfill Khmet'yevo (Moscow province, central part of Russia) and landfill Severo-Zapadnaya (Rostov-on-Don, southern part of Russia). Some of the characteristics of the raw leachates used and the number of samples taken are presented in Table 1. The experiments were mostly carried out with the Khmet'yevo leachate, but data on the Rostov leachates are also presented in Table 1.

Table 1
Range of Variation in Some Characteristics of Raw Leachates (mg/L)[a]

Parameter	Khmet'yevo[b]	Severo-Zapadnaya[c]
COD_{tot}	1430–3810 (2620)	560–4860 (2710)
COD_{SS}	110–480 (295)	ND
COD_{col}	20–360 (190)	ND
COD_{sol}	1230–2970 (2100)	ND
pH	6.53–6.7 (6.62)	7.88–8.13 (8.0)
VFA-COD	718–1020 (869)	11–68 (40)
Total nitrogen	90–162 (126)	ND
N_{NH3}	63–80 (72)	70–1115 (574)
N_{NO3}	0–1.2 (0.6)	14–33 (24)
Total phosphorus	20–38 (29)	ND
$P\text{-}PO_4$	3.7–7.5 (5.6)	1.0–21.0 (9.1)
SO_4	61–128 (95)	189–572 (409)
Fe	4.08–13.58 (8.83)	ND
Zn	1.08–1.92 (1.50)	ND
Cu	0.04–0.24 (0.14)	ND
Pb	0.038–0.1 (0.067)	ND
Cd	0.0008–0.0054 (0.0031)	ND

[a] Average values are given in parentheses. ND, not determined.
[b] Ten samples.
[c] Four samples.

Assessment of Anaerobic Biodegradability and Toxicity of Leachates

Both assays were conducted at 30°C as described in ref. *14* using the same sludge as for seeding the mesophilic UASB reactor (discussed next).

UASB Reactors

Two laboratory UASB reactors (M and P) (rectangular cross-section: 37 to 38 cm^2; height: 85 cm; total working volume: 2.54–2.68 L) made from transparent plastic and equipped with six sampling ports along the reactor height were used. Operating temperatures of 30 ± 1 and 10 ± 1°C were maintained by placing the corresponding reactor into a TS-80 thermostat (Mashzavod, Odessa, USSR) or a Snaige refrigerator (Alitus, Lithuania), respectively. Reactor M (mesophilic) was seeded with mesophilic sludge (40 g of volatile suspended solids [VSS]; specific aceticlastic activity: 0.67 g of COD/[g of VSS·d] at 30°C) originating from a UASB reactor treating starch industry wastewater *(15)*. Reactor P (psychrophilic) was seeded with psychrophilic sludge (12.2 g of VSS; specific aceticlastic activity: 0.12 g of COD/[g of VSS·d] at 10°C) originating from a UASB reactor treating winery wastewater *(16)*. To mitigate the mass-transfer limitations usually observed under psychrophilic conditions *(16)*, a recycle of effluent was applied (recycle ratio of 2.5:1). The submesophilic conditions were imposed by keeping reactor M under ambient temperature in the laboratory (20 ± 1°C).

Biofilter

The tubular biofilter (5-cm diameter, 55-cm height) was made from transparent plastics and packed with road metal (0.5- to 2-cm fraction). It had a working volume of 0.7 L and functioned in an alternating aerobic/anoxic regime for treatment of anaerobic effluents. The operation scheme included a sequencing process with a 1-h cycle consisting of four phases. During the first unfed phase (duration of 3–10 min), air at a flow rate of 0.8 L/min was pumped through an external loop of the biofilter. Aeration was switched off throughout the second unfed phase (22–27 min) while the high recycle rate of effluent (0.125 L/min) was applied to ensure adequate mixing and complete consumption of resting soluble oxygen in the biofilter. During these two phases, nitrification and oxidation of resting BOD proceeded. Then the feeding (this is the only period when the system was fed) was performed for 15–20 min under the same recycle rate of effluent. The third unfed phase included only mixing (by effluent recycle) and was variable (5–17 min) to close the 1-h working cycle of a programmable multichannel timer controlled all three (air, recycle, feeding) pumps used. During the last two phases, denitrification proceeded. In the middle of the external loop of biofilter, an electronic sensor (Datchik, Russia) was inserted for online monitoring of soluble oxygen. The electric signal from this sensor was transferred to a programmable data-logger system. The data were recorded every 30 s and were averaged (when necessary) over 3-min intervals. A personal computer programmed to function as a terminal emulator was used to communicate with the data logger. Secondary sludge from Kur'yanovskaya sewage treatment plant (Moscow) was used as a seed sludge for formation of the attached biofilm. Excess sludge was periodically withdrawn from the top of the biofilter. The submesophilic and psychrophilic conditions were imposed by keeping the biofilter under ambient temperature in the laboratory (20 ± 1°C) or inside the Snaige refrigerator (Alitus) at 10 ± 1°C. Determination of nitrification and oxygen uptake rates (OURs) was performed as described in ref. *17*.

Sampling and Analyses

Sampling of treated wastewater for analysis was usually started after three hydraulic retention times (sHRT) after changing the working regime for each reactor in order to ensure its operation in quasi-steady-state conditions *(18)*. COD was analyzed spectrophotometrically using Hach tubes. Raw samples of influents or effluents were used to determine total COD (COD_{tot}), 4.4-µm-folded-paper-filtered (Schleicher & Schuell $595_{1/2}$, Germany) samples to determine filtrated COD (COD_{filt}), and 0.45-µm-membrane-filtered (Schleicher & Schuell ME 25, Germany) samples to determine soluble COD (COD_{sol}). Suspended solids COD (COD_{SS}) and colloidal COD (COD_{col}) were calculated by the differences between COD_{tot} and COD_{filt}, and between COD_{filt} and COD_{sol}, respectively. Heavy metals (Fe, Zn, Cu, Pb, Cd) in the raw leachates, treated effluents, and reactor sludge were analyzed on a regular basis by atomic absorption spectroscopy. Some samples (e.g., for Ca and Mg determinations) were analyzed with the ICP-AES. Samples were dried (<40°C) and pretreated with concentrated HNO_3 and H_2O_2 (30%), and then the metal content was measured from the eluate *(19)*. All other analyses were performed three to five times per week by standard methods *(20)* or as described previously *(16)*. All gas measurements were recalculated to standard conditions (1 atm, 0°C). Statistical analyses of data was performed using Microsoft Excel.

Results and Discussion

Anaerobic Biodegradability and Toxicity of Leachates

It can be seen (Table 1) that though the both leachates had more-or-less the same strength, the Khmet'yevo leachate had lower pH and more VFA, which are typical for acidogenic phase leachate, whereas Rostov leachate is more typical for methanogenic phase leachate. This is probably related with younger age of Khmet'yevo landfill compared to Rostov one and more humid and warm climate in Rostov (this city is located in the coastal area of Azov sea) favoring to a better development of methanogenic phase inside landfill. All leachates were found to be nontoxic for anaerobic sludge even in undiluted samples (data not shown). The Khmet'yevo leachate had a high anaerobic biodegradability (>91% on COD basis) whereas the Rostov leachates were more persistent (~50% of anaerobic biodegradability on the COD basis).

Removal of COD and Heavy Metals Using Mesophilic UASB Reactor

The results of the UASB treatment of the raw leachates under mesophilic conditions are summarized in Table 2. It can be seen that a stepwise decrease in HRT from 2 to 0.28 d for UASB treatment of Khmet'yevo leachate during runs 1M–5M (organic loading rate [OLR] finally exceeded 5 g of COD/[L·d]) practically did not influence the effluent COD concentrations, which were close to the anaerobic biodegradability limit (0.19–0.25 g of COD/L for various leachate samples). Only traces of volatile fatty acids (VFA) were detected in the effluents (total VFA < 100 mg of COD/L). However, such exhaustion of easily biodegradable COD (e.g., VFA) in the anaerobic effluents might create COD deficiency problems for subsequent biologic nitrogen removal. Total COD removal varied from 74 to 93%, depending on the initial strength of the raw leachates (Table 2). In spite of slightly acidic influent pH, the effluent pH was close to 8.0 owing to consumption of VFA and release of ammonia (Table 2). The specific methane production was somehow below the theoretically expected value, taking into account the observed COD removal. This discrepancy can be attributed to entrapment of some part of the undigested suspended solids by the reactor sludge bed and development of the process of biologic sulfate reduction consuming some part of the COD. The latter can be witnessed by

Table 2
Operational Parameters and Efficiency of UASB Reactor Treating Raw Leachates at 30°C[a]

Parameter	1M	2M	3M	4M	5M	6M[b]
HRT (d)	1.77–2.06 (1.93)	1.32–1.49 (1.38)	0.79–1.06 (0.92)	0.60–0.62 (0.61)	0.28–0.29 (0.285)	0.24–0.26 (0.25)
Sampling period (d)	6	5	4	3	3	3
OLR (g COD/[L·d])	1.85–2.15 (1.97)	2.56–2.89 (2.76)	3.59–4.82 (4.14)	2.97–3.07 (3.02)	5.0–5.18 (5.09)	2.03–2.21 (2.12)
Influent COD_{tot} (g/L)	3.81	3.81	3.81	1.84	1.45	0.53
Effluent COD_{tot} (g/L)	0.42–0.43 (0.425)	0.25–0.42 (0.36)	0.39–0.41 (0.4)	0.45–0.47 (0.46)	0.22–0.28 (0.25)	0.32–0.34 (0.33)
Total COD removal (%)	89	89–93 (91)	89–90 (90)	74–76 (75)	81–85 (83)	36–40 (38)
Influent pH	6.7	6.7	6.7	6.53	6.53	7.88
Effluent pH	8–8.3 (8.17)	7.95–8.2 (8.01)	7.83–7.87 (7.85)	7.9–7.93 (7.92)	7.48–7.5 (7.49)	7.79–7.86 (7.83)
CH_4 in biogas (%)	57–78 (70)	60–83 (75)	79–81 (80)	82–83 (82)	79–82 (81)	48–55 (53)
CH_4 (nL/[$L_{reactor}$·d])	0.24–0.28 (0.26)	0.38–0.45 (0.42)	0.61–0.73 (0.67)	0.64–0.7 (0.67)	1.0–1.27 (1.14)	0.25–0.34 (0.3)
Influent total N (mg/L)	162	162	162	128	128	ND
Effluent total N (mg/L)	159–161 (160)	156–160 (159)	151–157 (155)	124–125 (125)	103–105 (104)	ND
Influent N-NH_3 (mg/L)	80	80	80	63	63	70
Effluent N-NH_3 (mg/L)	153–159 (156)	156–159 (158)	150–156 (153)	120–126 (123)	95–107 (101)	121–179 (150)
Influent total P (mg/L)	38	38	38	21	21	ND
Effluent total P (mg/L)	36–37 (36)	34–36 (35)	28–30 (29)	14–15 (15)	13–18 (15)	ND
Influent P-PO_4 (mg/L)	8	8	8	7	7	1
Effluent P-PO_4 (mg/L)	36–37 (36)	34–35 (34)	27–28 (27)	12–13 (13)	11–18 (15)	31–40 (35)
Influent SO_4 (mg/L)	128	128	128	106	106	189
Effluent SO_4 (mg/L)	ND	125–129 (127)	63–65 (64)	74–76 (75)	58–61 (60)	70–105 (88)

[a] Average values are given in parentheses. ND, not determined.
[b] The Rostov leachate.

a significant drop in sulfate concentrations in the effluents compared to the influents (runs 3M–5M, Table 2). Although the concentrations of phosphate increased in the effluents owing to mineralization of organic phosphorus, the total concentration of phosphorus slightly decreased during anaerobic treatment of raw leachates (Table 2). This was attributed to a partial precipitation of phosphate minerals (presumably hydroxyapatite and struvite) inside the UASB reactor because calcium and magnesium concentrations in the effluents were significantly lower compared to the influents (data not shown).

The UASB treatment of Rostov leachate followed the regularities of Khmet'yevo leachate treatment (run 6M, Table 2); however, the efficiency of COD removal was inferior owing to low anaerobic biodegradability of this leachate. Taking into account a low strength and a (relatively) high nitrogen concentration of such leachates, the application of direct aerobic-anoxic biotechnology for their treatment, skipping an anaerobic step, is recommended.

The mesophilic UASB reactor was quite efficient for removal of heavy metals (Table 3) owing to their concomitant precipitation/entrapment on the sludge presumably in the form of sulfides and hydroxides. Heavy metals content (except Fe) in the anaerobically treated effluents was far below the Russian limits for drinking water. The accumulation of heavy metals in the reactor was confirmed by direct measurement of heavy metals sludge content at the start and end of the mesophilic experiment (Table 4). This accumulation roughly corresponded to the removal of heavy metals from the liquid phase. The specific aceticlastic activity (30°C) of the UASB sludge increased during the mesophilic run from 0.67 to 0.75 g of COD/(g of VSS·d) (Table 4).

Removal of COD and Heavy Metals Using Submesophilic UASB Reactor

The results of submesophilic treatment of the raw leachates are given in Table 5. In spite of a significant decrease in working temperature, the efficiency of submesophilic treatment (Table 5) was comparable with that of mesophilic treatment (Table 2) because of a relatively high activity of sludge in the UASB reactor (Table 4). All other parameters of process performance including removal of heavy metals were also quite similar (Tables 2–5).

Removal of COD and Heavy Metals Using Psychrophilic UASB Reactor

The results of the UASB treatment of the raw leachates under psychrophilic conditions are shown in Table 6. The effluent quality slightly deteriorated with an increase in OLR. Generally, taking into account a need in easily biodegradable organic matter for subsequent nitrogen removal, the effluent COD characteristics were superior compared to the results of

Table 3
Removal of Heavy Metals by Mesophilic, Submesophilic, and Psychrophilic UASB Reactors Treating Raw Leachates
(at end of corresponding run)

	Mesophilic			Submesophilic	Psychrophilic		
Parameter	1M	2M	5M	3SM	1P	4P	7P
Influent Fe (mg/L)	13.58	13.58	4.08	6.32	13.58	4.08	6.32
Effluent Fe (mg/L)	1.73	0.26	0.46	0.36	0.54	0.8	0.94
Fe removal (%)	87	98	89	94	96	80	85
Influent Zn (mg/L)	1.92	1.92	1.08	1.2	1.92	1.08	1.2
Effluent Zn (mg/L)	0.94	0.2	0.24	0.08	0.16	0.3	0.26
Zn removal (%)	51	90	78	93	92	72	78
Influent Cu (mg/L)	0.24	0.24	0.08	0.04	0.24	0.08	0.04
Effluent Cu (mg/L)	0.097	0.02	0.02	0.02	0.02	0.02	0.02
Cu removal (%)	60	92	75	50	92	75	50
Influent Pb (mg/L)	0.1	0.1	0.046	0.038	0.1	0.046	0.038
Effluent Pb (mg/L)	0.06	0.025	0.014	0.002	0.024	0.038	0.003
Pb removal (%)	40	75	70	95	76	17	92
Influent Cd (mg/L)	0.0008	0.0008	0.0054	0.001	0.0008	0.0054	0.001
Effluent Cd (mg/L)	0.0001	0.0001	0.0009	0.0001	0.0002	0.0034	0.0001
Cd removal (%)	87.5	87.5	83	90	75	37	90

Table 4
Some Sludge Characteristics of Mesophilic, Submesophilic, and Psychrophilic UASB Reactors Treating Raw Leachates

	Mesophilic		Submesophilic[b]		Psychrophilic	
Parameter[a]	Start	End	Start	End	Start	End
VSS in reactor (g)	40.0	45.1	42.2	43.6	12.2	17.5
TSS in reactor (gL)	86.9	95.4	89.4	95.1	21.9	26.7
Aceticlastic activity (g COD/[g VSS·d])[c]	0.67	0.75	0.31	0.32	0.13	0.15
Fe content (μg/g TSS)	5269	6271	ND	ND	1757	10,158
Zn content (μg/g TSS)	1639	2834	ND	ND	509	819
Cu content (μg/g TSS)	207.3	308.2	ND	ND	83.3	98.4
Pb content (μg/g TSS)	2.81	12.41	ND	ND	5.54	7.80
Cd content (μg/g TSS)	0.011	0.017	ND	ND	0.020	0.032

[a] TSS, total suspended solids.
[b] ND, not determined.
[c] Values were obtained at working temperatures of 30, 20, and 10°C, respectively.

Table 5
Operational Parameters and Efficiency of UASB Reactor Treating Raw Leachates at 20°C[a]

Parameter	1SM	2SM	3SM
HRT (d)	0.79–0.94 (0.87)	0.48–0.60 (0.54)	0.29–0.31 (0.30)
Sampling period (d)	5	4	3
OLR (g COD/[L·d])	1.52–1.81 (1.67)	2.39–2.97 (2.68)	4.55–4.85 (4.70)
Influent COD_{tot} (g/L)	1.43	1.43	1.43
Effluent COD_{tot} (g/L)	0.17–0.2 (0.19)	0.19–0.23 (0.21)	0.26–0.28 (0.27)
Total COD removal (%)	86–88 (87)	84–87 (85)	80–82 (81)
Influent pH	6.58	6.58	6.58
Effluent pH	7.78–8.16 (7.97)	7.73–7.74 (7.74)	7.49–7.60 (7.55)
CH_4 in biogas (%)	75–81 (78)	82–84 (83)	84–85 (85)
CH_4 (nL/[$L_{reactor}$·d])	0.32–0.38 (0.35)	0.43–0.44 (0.44)	0.91–1.01 (0.96)
Influent total N (mg/L)	90	90	90
Effluent total N (mg/L)	84–86 (85)	78–81 (80)	79–80 (79)
Influent N-NH_3 (mg/L)	70	70	70
Effluent N-NH_3 (mg/L)	81–85 (83)	76–80 (78)	71–76 (73)
Influent total P (mg/L)	15	15	15
Effluent total P (mg/L)	14–15 (14)	14–15 (15)	13–15 (14)
Influent P-PO_4 (mg/L)	4	4	4
Effluent P-PO_4 (mg/L)	13–14 (14)	14–15 (14)	13–14 (14)
Influent SO_4 (mg/L)	61	61	61
Effluent SO_4 (mg/L)	37–43 (40)	51–53 (52)	50–52 (51)

[a] Average values are given in parentheses.

mesophilic and submesophilic effluents (Tables 2 and 5) owing to the presence of resting VFA (usually in the range of 0.2–0.4 g of COD/L). This may also explain the slightly lower pH values of these effluents (Table 6) com-

Table 6

Operational Parameters and Efficiency of UASB Reactor Treating Raw Leachates at 10°C[a]

Parameter	1P	2P	3P	4P	5P	6P	7P
HRT (d)	2.33–2.92 (2.61)	1.55–1.60 (1.58)	1.02–1.40 (1.21)	0.55–0.63 (0.59)	0.83–1.00 (0.91)	0.62–0.64 (0.63)	0.31–0.37 (0.34)
Sampling period (d)	9	6	5	4	4	3	5
OLR (g COD/[L·d])	1.32–1.56 (1.51)	2.31–2.42 (2.37)	1.31–1.42 (1.37)	2.31–2.64 (2.48)	1.43–1.73 (1.58)	2.23–2.31 (2.27)	3.87–4.57 (4.22)
Influent COD_{tot} (g/L)	3.81	3.81	1.45–1.84	1.45	1.43	1.43	1.43
Effluent COD_{tot} (g/L)	0.38–0.69 (0.51)	0.52–0.86 (0.69)	0.49–0.54 (0.52)	0.38–0.53 (0.46)	0.42–0.50 (0.46)	0.51–0.62 (0.57)	0.74–0.77 (0.75)
COD_{tot} removal (%)	82–90 (87)	77–86 (82)	66–71 (69)	63–74 (69)	65–71 (68)	57–64 (61)	46–48 (47)
Influent pH	6.7	6.7	6.53	6.53	6.58	6.58	6.58
Effluent pH	7.71–8.3 (7.93)	7.56–7.8 (7.67)	7.48–7.79 (7.64)	7.45–7.53 (7.49)	7.46–7.79 (7.62)	7.56–7.61 (7.59)	7.39–7.41 (7.40)
CH_4 in biogas (%)	68–76 (73)	63–77 (72)	69–71 (70)	72–74 (73)	71–73 (72)	72–73 (72)	72–74 (73)
CH_4 (nL/[$L_{reactor}$·d])	0.08–0.11 (0.10)	0.11–0.13 (0.12)	0.09–0.20 (0.15)	0.28–0.31 (0.30)	0.30–0.33 (0.32)	0.33–0.34 (0.34)	0.39–0.40 (0.40)
Influent N_{tot} (mg/L)	162	162	128–162	128	90	90	90
Effluent N_{tot} (mg/L)	78–92 (85)	82–86 (84)	79–80 (80)	76–78 (77)	71–72 (72)	71–73 (72)	68–71 (70)
Influent N-NH_3 (mg/L)	80	80	63	63	70	70	70
Effluent N-NH_3 (mg/L)	71–93 (81)	67–69(68)	58–86 (62)	51–62 (57)	68–72 (70)	69–71 (70)	63–68 (65)
Influent P_{tot} (mg/L)	38	38	20–38	20	15	15	15
Effluent P_{tot} (mg/L)	12–36 (24)	19–21 (20)	15–16 (16)	11–13 (12)	11–12 (12)	10–11 (11)	9–10 (10)
Influent P-PO_4 (mg/L)	8	8	7	7	4	4	4
Effluent P-PO_4 (mg/L)	16–36 (24)	11–13 (12)	13–16 (15)	8–12 (10)	9–10 (9)	9–10 (10)	9–10 (9)
Influent SO_4 (mg/L)	128	128	106	106	61	61	61
Effluent SO_4 (mg/L)	35–40 (37)	19–20 (20)	29–37 (33)	22–24 (23)	29–31 (30)	38–39 (38)	33–36 (34)

[a] Average values are given in parentheses.

pared to mesophilic and submesophilic ones (Tables 2 and 5). The observed specific methane production rates (Table 6) also showed some discrepancies with the theoretically expected ones. A possible reason for such discrepancies in mesophilic regime is a supersaturation of psychrophilic effluents by dissolved methane *(21)*.

Similar to the mesophilic regime, a drop in total phosphorous concentrations in the psychrophilic effluents was also observed compared to the influents (Table 6) owing to precipitation of phosphate minerals inside the UASB reactor. By contrast, the psychrophilic regime did not show an increase in ammonia concentrations, as was observed for higher temperature regimes. Moreover, the total nitrogen concentrations decreased by 20–50% (Table 6). Furthermore, significantly higher sulfate removals were found in the psychrophilic effluents (Table 6) compared with the mesophilic and submesophilic ones (Tables 2 and 5). A possible explanation for these observations may be related to an occurrence of the process of simultaneous anaerobic removal of ammonia and sulfate recently highlighted in ref. *22*. Increased concentrations of nitrogen (one of the proposed products for interaction between sulfate and ammonia *[22]*) in the psychrophilic biogas (data not shown) may also support such a hypothesis. However, it is unclear why this process favors psychrophilic conditions during anaerobic treatment of the raw leachates. This and other areas of question arising from the very interesting phenomenon observed need precise investigations in future.

The removal of heavy metals in psychrophilic conditions was a slightly inferior but comparable to higher-temperature regimes (Table 3). This fact, as well as a general performance of psychrophilic and submesophilic UASB reactors, may imply that the Khmet'yevo leachates can be efficiently treated without any heating in summertime. However, some energy expenses (at least to maintain a working temperature of about 10°C) will be necessary for cold periods during full-scale implementation of anaerobic treatment of these leachates.

Biofilter Performance

Successful startup of the biofilter in the nitrifying mode (at 20°C) was achieved in 3 wk using mesophilic and submesophilic anaerobic effluents containing low concentrations of biodegradable COD as a substrate (run N1, Table 7). The nitrification rate of the reactor biofilm determined in a separate experiment in the end of run N1 using ammonia chloride as a substrate was 456 mg N/(L reactor·d), significantly higher than the applied ammonia loading rate (ALR) (Table 7). This nitrification rate was in accordance with the measured OUR (~2000 mg of O_2/[L·d]) in this experiment.

When the effluent ammonia concentrations reached values of about 2 mg of N/L, the biofilter was switched on alternating (aerobic-anoxic) operation using psychrophilic anaerobic effluents having higher COD (run DN1). The typical dynamics of targeted pollutants and oxygen concentra-

Table 7
Operational Parameters and Efficiency of Biofilter Treating Anaerobic Effluents[a]

Parameter	N1	DN1	DN2	DN3
Temperature (°C)	19–21	19–21	19–21	9–11
Aeration phase (min)	60	7	10	6
Mixing after aeration (min)	0	25	25	19
Feeding phase (min)	60	20	20	15
Mixing after feeding (min)	0	8	5	20
HRT (d)	0.99–1.06 (1.03)	0.9–1.27 (1.09)	0.85–0.91 (0.88)	0.99–1.24 (1.12)
Sampling period (d)	15	5	5	14
OLR (g COD/[L·d])	0.24–0.39 (0.31)	0.58–0.78 (0.68)	0.74–0.79 (0.76)	0.50–0.77 (0.64)
Influent COD_{tot} (g/L)	0.25–0.40 (0.33)	0.7–0.74 (0.72)	0.66–0.68 (0.67)	0.58–0.77 (0.68)
Effluent COD_{tot} (g/L)	0.15–0.32 (0.23)	0.19–0.20 (0.19)	0.17–0.19 (0.18)	0.16–0.20 (0.18)
COD_{tot} removal (%)	19–61 (40)	71–74 (73)	72–75 (73)	69–80 (75)
Influent pH	7.4–8.0 (7.7)	7.3–7.4 (7.35)	7.24–7.26 (7.25)	7.20–7.66 (7.35)
Effluent pH	8.17–8.73 (8.45)	8.3–8.34 (8.32)	8.4–8.5 (8.45)	8.14–8.35 (8.23)
ALR (mg $N-NH_3$/[L·d])	119–173 (116)	49–70 (60)	79–84 (82)	63–82 (69)
Influent $N-NH_3$ (mg/L)	59–176 (117)	62–63 (63)	71–72 (71)	66–82 (73)
Effluent $N-NH_3$ (mg/L)	1.5–2.7 (2.1)	1.9–8.2 (4.6)	3.3–4.3 (3.6)	2.3–7.7 (5.0)
$N-NH_3$ removal (%)	95–97 (96)	87–97 (93)	94–95 (95)	91–96 (93)
Effluent $N-NO_3$ (mg/L)	59–119 (89)	4–29 (12)	10–15 (11)	1–18 (9)
Effluent $N-NO_2$ (mg/L)	Traces	1.9–2.0 (1.9)	1.1–1.7 (1.4)	0.4–3.0 (1.7)
Denitrification efficiency (%)[b]	—	52–93 (79)	76–83 (80)	54–96 (75)
Effluent total N	59–121 (78)	9–33 (18.5)	13–18 (16.3)	5–29 (16.7)
Total N removal (%)[c]	1–12 (6)	50–87 (73)	72–78 (76)	51–93 (73)
Influent $P-PO_4$ (mg/L)	9–35 (22)	9.2	9.9	10.2–11.8 (11.0)
Effluent $P-PO_4$ (mg/L)	5–22 (13)	5.1–5.4 (5.2)	5.2–5.5 (5.3)	9.9–10.5 (10.2)

[a] Average values for the period are given in parentheses.

[b] Calculated as follows: $\{1 - ([N-NO_3]_{ef} + [N-NO_2]_{ef})/([N-NH_3]_{in} - [N-NH_3]_{ef})\} \times 100$.

[c] Calculated as follows: $\{1 - ([N-NO_3]_{ef} + [N-NH_3]_{ef} + [N-NO_2]_{ef})/([N-NH_3]_{in})\} \times 100$.

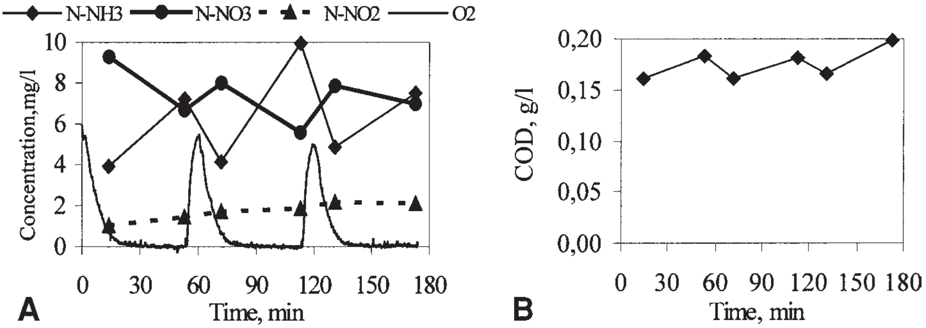

Fig. 1. Dynamics of nitrogen species, soluble oxygen, and COD concentrations during alternating operation of biofilter (Table 7, run DN1).

tion inside the biofilter during three consecutive cycles is presented in Fig. 1. During the DN1 run (Table 7), when the aeration phase was 7 min, the average HRT was 1.09 d while the average OLR was 0.68 g of COD/(L·d). The average COD_{tot} removal accounted for 73% with the COD_{tot} effluent concentrations slightly oscillating at about 0.19 g of COD/L (run DN1, Table 7), close to the aerobic biodegradability limit of the raw leachates (0.15 g of COD/L). The efficiencies of ammonia removal and denitrification were 93 and 79% (on average), resulting in average inorganic nitrogen removal of 73% (run DN1, Table 7).

Further manipulation of the duration of aeration phase and HRT (e.g., during run DN2, Table 7) did not lead to a significant increase in nitrogen removal compared to run DN1. The effluent ammonia, nitrate, and nitrite concentrations oscillated at about 4, 11, and 1 mg N/L, respectively (run DN2, Table 7). This is related to an imminent drawback of this relatively simple biofilter construction in which wastewater filling and effluent withdrawal were performed simultaneously in a continuous-flow stirred tank reactor regime. In this way, it is hardly possible to reach a zero discharge of ammonia. The better performance can be expected under disruption of filling and withdrawal phases in the biofilter like in sequencing batch biofilm reactor constructions *(23)*. However, the total nitrogen concentrations in the biofilter effluents were only slightly above the Russian limits (10 mg N/L) for discharge into surface waters. Hence, to be within the safe regulatory limits under full-scale implementation of leachate treatment, we recommend keeping the biofilter effluents in collection/stabilization ponds (they are usually available at the landfills) for several days in order to decrease their nitrogen concentrations prior to discharge into surface waters.

There was a significant increase in effluent pH (about one unit) compared to the influent during all submesophilic runs of biofilter operation (Table 7). This was owing to the fact that the anaerobic effluents were (over)saturated with CO_2 and the latter was stripped out during aeration, causing a rise in pH. A drop in phosphate concentrations in the effluents was owing to further precipitation of phosphate minerals at a pH higher than 8.0 occurring in the biofilter.

A decrease in working temperature of the biofilter to 10°C required a decrease in HRT and a decrease in aeration phase because the biofilter OUR decreased substantially in these conditions. Optimal conditions were found when the aeration phase lasted 6 min and HRT was 1.12 d (run DN3, Table 7). In this regime, the effluent characteristics were quite similar to those from run DN2 regarding COD_{tot} and nitrogen content as well as concentrations of nitrogen species—ammonia, nitrate, and nitrite (Table 7).

The results on the removal of COD and nitrogen for sequencing anaerobic-aerobic treatment of Khmet'yevo leachate, especially under 10°C (Tables 6 and 7), are superior to those previously reported in the literature *(12,13)*. This is mainly related to the fact that this leachate came from a young landfill where decomposition processes are still in the initial (acidogenic) stage, generating easily biodegradable COD. By contrast, the leachate from the more aged Rostov landfill was less biodegradable, resulting in relatively poor COD removals at the anaerobic stage, even under mesophilic conditions (run 6M, Table 2) comparable with the other studies *(12,13)*. In addition, the quantity and quality of resting COD in generated effluents after anaerobic treatment of Rostov leachate were not favorable for subsequent nitrogen removal (data not shown).

Conclusion

The UASB reactor was quite efficient for removal of bulk COD and heavy metals presented in the raw leachates from Khmet'yevo landfill even during operation under submesophilic and psychrophilic conditions (10–20°C). The application of aerobic/anoxic biofilter as a sole polishing step at 10–20°C was acceptable for elimination of biodegradable COD and nitrogen from the anaerobic effluents approaching the current national standards for direct discharge of treated wastewater. A simple and cheap posttreatment step such as a stabilization pond or constructed wetland will probably be required to ensure a safe discharge of the treated leachates to surface waters.

Acknowledgments

We thank Ecotechprom (Moscow) and Ecological Laboratory (Rostov-on-Don) for delivering the landfill leachates. We gratefully acknowledge the financial support of INCO Copernicus (contract no. ICA2-CT-2001-10001) and NATO (collaborative linkage grant LST.CLG.977867).

References

1. Cherp, O. M. and Vinichenko, V. N. (1996), *Problem of Municipal Solid Waste: Integrated Approach*, Ecoline-Ecologia, Moscow (in Russian).
2. Cozzarelli, I. M., Suflita, J. M., Ulrich, G. A., Harris, S. H., Scholl, M. A., Schlottmann, J. L., and Christenson S. (2000), *Environ. Sci. Technol.* **34,** 4025–4033.

3. Lema, J. M., Mendez, R., and Blazquez, R. (1988), *Water Air Soil Pollut.* **40,** 223–250.
4. Trebouet, D., Schlumpf, J. P., Jaouen, P., and Quemeneur, F. (2001), *Water Res.* **35,** 2935–2942.
5. Marttinen, S. K., Kettunen, R. H., Sormunen, K. M., Soimasuo, R. M., and Rintala, J. A. (2002), *Chemosphere* **46,** 851–858.
6. Boyle, W. C. and Ham, R. K. (1974), *J. Water Pollut. Control Fed.* **48,** 860–872.
7. Robinson, H. D. and Grantham, G. (1988), *Water Res.* **22,** 733–747.
8. Lin, S. H. and Chang, C. C. (2000), *Water Res.* **34,** 4243–4249.
9. Kennedy, K. J., Hamoda, M. F., and Guiot, S. G. (1988), *J. Water Pollut. Control Fed.* **60,** 1675–1683.
10. Keenan, P. J., Iza, J., and Switzenbaum, M. S. (1993), *Water Environ. Res.* **65,** 181–188.
11. Kennedy, K. J. and Lentz, E. M. (2000), *Water Res.* **34,** 3640–3656.
12. Kettunen, R. H., Hoilijoki, T. H., and Rintala, J. A. (1996), *Bioresour. Technol.* **58,** 31–40.
13. Mennerich, A. (1987), in *The Tenth Annual Madison Waste Conference*, University of Wisconsin, Madison.
14. Lettinga, G. and Hulshoff Pol, L. W. (1992), *Anaerobic Reactor Technology*, Wageningen Agricultural University, Wageningen, The Netherlands.
15. Sklyar, V., Epov, A., Gladchenko, M., Danilovich, D., and Kalyzhnyi, S. (2003), *Appl. Biochem. Biotechnol.* **109,** 253–262.
16. Kalyuzhnyi, S. V., Gladchenko, M. A., Sklyar, V. I., Kizimenko, Y. S., and Shcherbakov, S. S. (2001), *Water Sci. Technol.* **44(4),** 23–31.
17. Klapwijk, A. and Rensink, J. H. (1996), *Aerobic Wastewater Treatment, Lecture Notes*, Department of Environmental Technology, Wageningen Agricultural University, Wageningen, The Netherlands.
18. Kalyuzhnyi, S. V., Sklyar, V. I., Davlyatshina, M. A., Parshina, S. N., Simankova, M. V., Kostrikina, N. A., and Nozhevnikova, A. N. (1996), *Bioresour. Technol.* **55,** 47–54.
19. Kettunen, R. (1997), PhD thesis, Tampere University of Technology, Tampere, Finland.
20. APHA. (1992), *Standard Methods for Water and Wastewater Examination*, 17th ed., American Public Health Association, Washington, DC.
21. Rebac, S. (1998), PhD thesis, Wageningen Agricultural University, Wageningen, The Netherlands.
22. Fernandez-Polanco, F., Fernandez-Polanco, M., Fernandez, N., Uruena, M., Garcia, P. A., and Villaverde, S. (2001), *Water Res.* **35(4),** 259–262.
23. Wilderer, P. A., Irvine, R. L., Goronszy, M. C., Artan, N., Demoulin, G., Keller, J., Morgenroth, E., Nyhuis, G., Tanaka, K., and Torrijos, M. (2001), IWA Scientific and Technical Report no. 10, IWA, London.