Combined anaerobic-aerobic treatment of landfill leachates under mesophilic, submesophilic and psychrophilic conditions

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Abstract As a first step of treatment of landfill leachates (total COD – 1,430–3,810 mg/l, total nitrogen 90–162 mg/l), a performance of laboratory UASB reactors has been investigated under mesophilic (30°C), sub-mesophilic (20°C) and psychrophilic (10°C) conditions. Under hydraulic retention times (HRT) of around 7 h, when the average organic loading rates (OLR) were around 5 g COD/l/day, the total COD removal accounted for 81% (on the average) with the effluent concentrations close to anaerobic biodegradability limit (0.25 g COD/l) for mesophilic and sub-mesophilic regimes. The psychrophilic treatment conducted under the average HRT of 8 h and the average OLR of 4.22 g COD/l/day showed a total COD removal of 47% producing the effluents (0.75 g COD/l) more suitable for subsequent biological 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 sulphides 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.

Keywords Aerobic-anoxic biofilter; denitrification; heavy metals; landfill leachate; nitrification; UASB reactor

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 (Cherp and Vinichenko, 1996). 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 due to its impact on surface and ground waters. Since the main concerns in landfill leachates are usually organic and nitrogenous contaminants as well as heavy metals (Cozzarelli et al., 2000; Lema et al., 1988), the primary objective of this paper was to develop an efficient lab scale technology for removal of these pollutants. As a first step, the UASB reactor for the elimination of the major part of COD and concomitant precipitation of heavy metals (HM) in the form of insoluble sulphides inside the sludge bed was used. Besides the conventional mesophilic regime (30°C), investigations were also carried out at lower temperatures (20 and 10°C) in order to evaluate the possibility of direct treatment without preliminary heating. In a subsequent step, the biofilter operating in an alternative aerobic-anoxic regime at 20 and 10°C was used for the removal of the remaining BOD and nitrogen.

Materials and methods

Landfill leachates

The raw leachates (RL) were taken during December 2001–April 2002 from the leachate collection systems of the operating municipal landfill “Khmet’ yevo” (Moscow province). Some characteristics of the RL used are presented in Table 1.
UASB reactors

Two laboratory UASB reactors (M and P: rectangular cross-section 37–38 cm², height – 85 cm, total working volume – 2.54–2.68 l) made from transparent plastic and equipped with 6 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 thermostat “TS-80” (Mashzavod, Odessa, USSR) or refrigerator “Snaige” (Alitus, Lithuania), respectively. Reactor M (mesophilic) was seeded with mesophilic sludge (40 g VSS, specific aceticlastic activity – 0.67 g COD/g VSS/d at 30°C) originating from an UASB reactor treating starch industry wastewater (Sklyar et al., 2002). Reactor P (psychrophilic) was seeded with psychrophilic sludge (12.2 g VSS, specific aceticlastic activity – 0.12 g COD/g VSS/d at 10°C) originating from an UASB reactor treating winery wastewater (Kalyuzhnyi et al., 2001). To mitigate mass transfer limitations usually observed under psychrophilic conditions (Kalyuzhnyi et al., 2001), a recycle of effluent was applied (recycle ratio – 2.5:1). The submesophilic conditions were imposed by keeping the reactor M under ambient temperature in the laboratory (20±1°C). Assessment of aceticlastic activity of the sludges used was performed under their working temperatures as described by Lettinga and Hulshof Pol (1992). Determination of anaerobic biodegradability and toxicity of the RL was conducted at 30°C according to recommendations of Lettinga and Hulshof Pol (1992) using the same sludge as for seeding of mesophilic UASB reactor.

Aerobic-anoxic biofilter

The tubular biofilter (diameter – 5 cm, height – 55 cm) was made from transparent plastics and packed by road metal (0.5–2 cm fraction). It had a working volume of 0.7 l and functioned in an alternating aerobic/anoxic regime for treatment of the anaerobic effluents. The operation scheme included a sequencing process with a one-hour cycle consisting of 4 phases. During the first unfed phase (duration – 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 an adequate mixing and a complete consumption of resting soluble oxygen in the biofilter. During these 2 phases, nitrification and oxidation of resting BOD proceeded. Then the feeding (this is the only period when the system was fed) was performed during 15–20 min under the same recycle rate of effluent (0.125 l/min) was applied to ensure an adequate mixing and a complete consumption of resting soluble oxygen in the biofilter. During these 2 phases, nitrification and oxidation of resting BOD proceeded. Then the feeding (this is the only period when the system was fed) was performed during 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 the programmable multi-channel timer which controlled all 3 (air, recycle, feeding) pumps used. During the last 2 phases, denitrification proceeded. In the middle of the external loop of the biofilter, an electronic sensor (“Datchik”, Russia) was inserted for on-line 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. The excess of sludge was periodically withdrawn.
from the top of biofilter. The submesophilic and psychrophilic conditions were imposed by keeping the biofilter under ambient temperature in the laboratory (20 ± 1°C) or inside refrigerator “Snaige” (Alitus, Lithuania) at 10 ± 1°C. The determination of nitrification and oxygen uptake rates (OUR) was performed as described by Klapwijk and Rensink (1996).

Analyses
Sampling of treated wastewater for analysis was usually started after 3 hydraulic retention times (HRT) after change of working regime for each reactor in order to ensure its operation in quasi-steady-state conditions. COD was analysed spectrophotometrically using Hach tubes. The HM (Fe, Zn, Cu, Pb, Cd) in the RL, the treated effluents and the reactor sludge were analysed on a regular basis by atomic absorption spectroscopy. Some samples (e.g. for Ca and Mg determinations) were analysed with the ICP-AES. The samples were dried (<40°C) and pre-treated with concentrated HNO$_3$ and H$_2$O$_2$ (30%), thereafter the metal content was measured from the eluate. All other analyses were performed 3–5 times per week by standard methods (APHA, 1992) or as described previously (Kalyuzhnyi et al., 2001). All gas measurements are recalculated to standard conditions (1 atm, 0°C). Statistical analysis of data was performed using Microsoft Excel.

Results and discussion
COD and heavy metals removal using a mesophilic UASB reactor
In the preliminary experiments, it was found that all leachate samples were non-toxic for anaerobic sludge even in undiluted samples and had a high anaerobic biodegradability (>91% on COD basis). Some results of the mesophilic UASB treatment of the RL under quasi-steady state operation are shown in Figure 1a. It can be seen that a stepwise decrease of HRT from 46 to 7 h (organic loading rate (OLR) finally exceeded 5 g COD/l/d) practically did not influence the effluent COD concentrations that oscillated around 400 mg COD/l and were close to the anaerobic biodegradability limit (200–250 mg COD/l for various leachate samples). Only traces of volatile fatty acids (VFA) were detected in the effluents (total VFA < 100 mg COD/l). However, such exhaustion of easily biodegradable COD (e.g., VFA) in the anaerobic effluents might create COD deficiency problems for subsequent biological nitrogen removal. The total COD removal varied from 75 till 91% depending on the initial strength of the RL (Figure 1a). In spite of slightly acidic influent pH (Table 1), the effluent pH was close to 8 as a result of VFA consumption and almost complete nitrogen mineralisation to ammonia (Figure 2a). The specific methane production was somehow below (Figure 2b) the theoretically expected value taking into account the observed COD removal (Figure 1a). This discrepancy can be attributed to entrapment of some part of the undigested SS by the reactor sludge bed and development of the process of

![Figure 1: Total COD removal and effluent total COD concentrations versus HRT under quasi-steady state operation of mesophilic (a) and submesophilic (b) UASB reactors treating the RL (figures on the graphs – influent COD concentrations in mg/l)](https://iwaponline.com/wst/article-pdf/48/6/311/423596/311.pdf)
biological sulphate reduction consuming some part of the COD. The latter can be witnessed by a significant drop of sulphate concentrations in the effluents compared to the influents (Figure 2b). Though the concentrations of phosphate increased in the effluents (data not shown) due to mineralisation of organic phosphorus, the total phosphorus concentration slightly decreased during anaerobic treatment of RL (Figure 2a). 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 mesophilic UASB reactor was quite efficient for removal of HM (Table 2) due to their concomitant precipitation/entrapment of the sludge presumably in the form of sulphides and hydroxides. The HM content (except Fe) in the anaerobically treated effluents was far below the Russian limits for drinking water. The accumulation of HM in the reactor was confirmed by direct measurement of HM sludge content at the start and at the end of the mesophilic experiment (data not shown). This accumulation roughly corresponded to the HM removal from the liquid phase. The specific aceticlastic activity (30°C) of the UASB sludge increased during the mesophilic run from 0.67 till 0.75 g COD/g VSS/day.

**COD and heavy metals removal using a submesophilic UASB reactor**

Some results of submesophilic treatment of the RL under quasi-steady state operation are shown in Figure 1b. In spite of a significant decrease of working temperature, its efficiency (Figure 1b) was comparable to mesophilic treatment (Figure 1a). All other parameters of process performance including HM removal (Table 2) were also quite similar.

**COD and heavy metals removal using a psychrophilic UASB reactor**

Some results of the psychrophilic treatment of the RL under quasi-steady state operation of the UASB reactor are shown in Figure 3. It is seen that the effluent quality slightly deteriorated (Figure 3a) on decreasing the HRT applied (OLR finally exceeded 4 g COD/l/d). Generally, taking into account the need for easily biodegradable organic matter for subsequent nitrogen removal, the effluent COD characteristics were superior compared to the results of mesophilic and submesophilic effluents (Figure 1) due to the presence of resting VFA (usually in the range of 0.2–0.4 g COD/l). The observed specific methane production rates also showed some discrepancies with the theoretically expected ones (data not shown). Besides, the reasons proposed for such a discrepancy in the mesophilic regime, a supersaturation of psychrophilic effluents by dissolved methane may also be a possibility (Kalyuzhnýi et al., 2001).

**Figure 2** Effluent concentrations of ammonia (a), total phosphorus (a) and sulphate (b) as well as specific methane production (b) versus HRT under quasi-steady state operation of mesophilic UASB reactor treating the RL (figures on the graphs – influent concentrations of total nitrogen/total phosphorus (a) and sulphate (b) in mg/l).
Similar to the mesophilic regime, a drop in total phosphorus concentrations in the psychrophilic effluents was also observed compared to the influents (data not shown) due to precipitation of phosphate minerals inside the UASB reactor. On the contrary, 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 38–48% (Figure 3b). At the same time, significantly lower sulphate concentrations were found in the psychrophilic effluents (Figure 3b) compared to the mesophilic and submesophilic ones (Figure 2b). The possible explanation for these observations may be related to an occurrence of the process of simultaneous anaerobic removal of ammonia and sulphate recently highlighted by Fernandez-Polanco et al. (2001). Increased concentrations of nitrogen (one of the proposed products for interaction between sulphate and ammonia) in the psychrophilic biogas (data not shown) may also support such a hypothesis. However, it is unclear why psychrophilic conditions favour this process during anaerobic treatment of the RL. This and other questions arising from the very interesting phenomenon observed need precise investigations in future.

The HM removal in psychrophilic conditions was a little bit inferior but comparable with higher temperature regimes (Table 2). This fact as well as the general performance of psychrophilic and submesophilic UASB reactors may imply that the Khmet’ yevo leachates can be efficiently treated without any heating in warm periods. However, some energy...
expenses (at least to maintain a working temperature around 10°C) will be necessary for cold periods during a full scale implementation of anaerobic treatment of these leachates.

**Biofilter performance**

A successful start-up of biofilter in the nitrifying mode (at 20°C) was achieved in three weeks using mesophilic and submesophilic anaerobic effluents containing low concentrations of biodegradable COD as a substrate (Table 3, run N1). The nitrification rate of the reactor biofilm determined in a separate experiment at the end of run N1 using ammonium chloride as a substrate was 456 mg N/l reactor/day, i.e. significantly higher than the applied ammonia loading rate (ALR) (Table 3). This nitrification rate was in accordance with the measured OUR (~2,000 mg O₂/l reactor/day) in this experiment.

When the effluent ammonia concentrations reached the values around 2 mg N/l, the biofilter was switched to alternating (aerobic-anoxic) operation using psychrophilic anaerobic effluents having higher COD (runs DN1-DN3). During the DN1 run (Table 3), when the aeration phase was 7 min, the average HRT was 1.09 days while the average OLR was 0.68 g COD/l/d. The average total COD removal accounted for 73% with the total COD effluent concentrations slightly oscillating around 0.19 g COD/l (Table 3, run DN1). This is close to the aerobic biodegradability limit of the RL (0.15 g COD/l). The efficiencies of ammonia removal and denitrification were 93 and 79% (on the average) resulting in the average inorganic nitrogen removal of 73% (Table 3, run DN1).

Further manipulation with the duration of the aeration phase and HRT (e.g., during run DN2, Table 3) did not lead to a significant increase of nitrogen removal compared to run DN1. The effluent ammonia, nitrate and nitrite concentrations oscillated around 4, 11 and 1 mg N/l, respectively (Table 3, run DN2). This is related to an immanent drawback of this relatively simple biofilter construction where wastewater filling and effluent withdrawal

**Table 3** Operational parameters and efficiency of the biofilter treating the anaerobic effluents (average values for the period are given in brackets)

<table>
<thead>
<tr>
<th>Parameter/Run</th>
<th>N1</th>
<th>DN1</th>
<th>DN2</th>
<th>DN3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °C</td>
<td>19–21</td>
<td>19–21</td>
<td>19–21</td>
<td>9–11</td>
</tr>
<tr>
<td>Aeration phase, min</td>
<td>60</td>
<td>7</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>Mixing after aeration, min</td>
<td>0</td>
<td>25</td>
<td>25</td>
<td>19</td>
</tr>
<tr>
<td>Feeding phase, min</td>
<td>60</td>
<td>20</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>Mixing after feeding, min</td>
<td>0</td>
<td>8</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>HRT, days</td>
<td>0.99–1.06 (1.03)</td>
<td>0.9–1.27 (1.09)</td>
<td>0.85–0.91 (0.88)</td>
<td>0.99–1.24 (1.12)</td>
</tr>
<tr>
<td>Sampling period, days</td>
<td>15</td>
<td>5</td>
<td>5</td>
<td>14</td>
</tr>
<tr>
<td>OLR, g COD/l/d</td>
<td>0.24–0.39 (0.31)</td>
<td>0.58–0.78 (0.68)</td>
<td>0.74–0.79 (0.76)</td>
<td>0.50–0.77 (0.64)</td>
</tr>
<tr>
<td>Influent COD_{tot} g/l</td>
<td>0.25–0.40 (0.33)</td>
<td>0.7–0.74 (0.72)</td>
<td>0.66–0.68 (0.67)</td>
<td>0.58–0.77 (0.68)</td>
</tr>
<tr>
<td>Effluent COD_{tot} g/l</td>
<td>0.15–0.32 (0.23)</td>
<td>0.19–0.20 (0.19)</td>
<td>0.17–0.19 (0.18)</td>
<td>0.16–0.20 (0.18)</td>
</tr>
<tr>
<td>COD_{tot} removal, %</td>
<td>19–61 (40)</td>
<td>71–74 (73)</td>
<td>72–75 (73)</td>
<td>69–80 (75)</td>
</tr>
<tr>
<td>Influent pH</td>
<td>7.4–8.0 (7.7)</td>
<td>7.3–7.4 (7.35)</td>
<td>7.24–7.26 (7.25)</td>
<td>7.20–7.66 (7.35)</td>
</tr>
<tr>
<td>ALR, mg N-NH₃/l/d</td>
<td>119–173 (116)</td>
<td>49–70 (60)</td>
<td>79–84 (82)</td>
<td>63–82 (69)</td>
</tr>
<tr>
<td>Influent N-NH₃ mg/l</td>
<td>59–176 (117)</td>
<td>62–63 (63)</td>
<td>71–72 (71)</td>
<td>66–82 (73)</td>
</tr>
<tr>
<td>Effluent N-NH₃ mg/l</td>
<td>1.5–2.7 (2.1)</td>
<td>1.9–8.2 (4.6)</td>
<td>3.3–4.3 (3.6)</td>
<td>2.3–7.7 (6.0)</td>
</tr>
<tr>
<td>N-NH₃ removal, %</td>
<td>95–97 (96)</td>
<td>87–93 (97)</td>
<td>94–95 (95)</td>
<td>91–96 (93)</td>
</tr>
<tr>
<td>Effluent N-NO₃ mg/l</td>
<td>59–119 (89)</td>
<td>4–29 (12)</td>
<td>10–15 (11)</td>
<td>1–18 (9)</td>
</tr>
<tr>
<td>Effluent N-NO₂ mg/l</td>
<td>Traces</td>
<td>1.9–2.0 (1.9)</td>
<td>1.1–1.7 (1.4)</td>
<td>0.4–3.0 (1.7)</td>
</tr>
<tr>
<td>*Denitrific. Effic., %</td>
<td>–</td>
<td>52–93 (79)</td>
<td>76–83 (80)</td>
<td>54–96 (75)</td>
</tr>
<tr>
<td>Effluent total N</td>
<td>59–121 (78)</td>
<td>9–33 (18.5)</td>
<td>13–18 (16.3)</td>
<td>5–29 (16.7)</td>
</tr>
<tr>
<td>#Total N removal, %</td>
<td>1–12 (6)</td>
<td>50–87 (73)</td>
<td>72–78 (76)</td>
<td>51–93 (73)</td>
</tr>
<tr>
<td>Influent P-PO₄ mg/l</td>
<td>9–35 (22)</td>
<td>9.2</td>
<td>9.9</td>
<td>10.2–11.8 (11.0)</td>
</tr>
<tr>
<td>Effluent P-PO₄ mg/l</td>
<td>5–22 (13)</td>
<td>5.1–5.4 (5.2)</td>
<td>5.2–5.5 (5.3)</td>
<td>9.9–10.5 (10.2)</td>
</tr>
</tbody>
</table>

* Calculated as: \( \left(1 - \frac{[\text{N-NH}_3\text{tot} - \text{N-NH}_3\text{in}]}{\text{N-NH}_3\text{in}} \right) \times 100 \)

# Calculated as: \( \left(1 - \frac{[\text{N-NO}_3\text{tot} + \text{N-NH}_3\text{in}]}{\text{N-NH}_3\text{in}} \right) \times 100 \)
were performed simultaneously in a CSTR 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 as in sequencing batch biofilm reactor (SBBR) constructions (Wilderer et al., 2001). However, the total nitrogen concentrations in the biofilter effluents were only a little bit 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 would recommend to keep the biofilter effluents in collection/stabilisation ponds (they are usually available at the landfills) for several days in order to decrease their nitrogen concentrations prior to the discharge into surface waters.

A significant increase of effluent pH (around 1 unit) compared to the influent during all submesophilic runs of biofilter operation should be mentioned (Table 3). This was due to the fact that the anaerobic effluents were (over) saturated with CO₂ and the latter was stripped out during aeration giving a rise in pH. A drop in phosphate concentrations in the effluents was due to further precipitation of phosphate minerals under pH higher than 8 occurring in the biofilter.

A decrease of working temperature of the biofilter till 10°C required an increase of HRT and decrease of the aeration phase because the biofilter OUR decreased substantially in these conditions. The optimal conditions were found, when the aeration phase lasted 6 min and HRT was 1.12 days (run DN3, Table 3). In this regime, the effluent characteristics were quite similar to those from run DN2 with regard to total COD and nitrogen content as well as concentrations of nitrogen species – ammonia, nitrate and nitrite (Table 3).

The results on COD and nitrogen removals obtained in this study for sequencing anaerobic-aerobic treatment of Khmet’yevo leachate, especially under 10°C (Figure 3, Table 3) are superior to those previously reported in the literature (Mennerich, 1987; Kettunen et al., 1996). This is mainly related with the fact that this leachates came from the young landfill where decomposition processes still are in the initial (acidogenic) stage generating easily biodegradable COD.

Conclusions
1. The UASB reactor was quite efficient for removal of bulk COD and heavy metals present in the RL from Khmet’yevo landfill even during operation under submesophilic and psychrophilic conditions (10–20°C).
2. 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 post-treatment step like stabilisation pond or constructed wetland will be probably required to ensure a safe discharge of the treated leachates to surface waters.

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References


