Heavy metal pollution from Russian landfill leachates and its elimination together with other contaminants

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Abstract Systematic monitoring of raw leachates (RL) from the operating landfill "Khmet'yevo" during December, 2001–June, 2002 with regard to heavy metals (HM) revealed that these RL were moderately contaminated with Fe, Zn, Pb and Cd (Cu is present in non-dangerous concentrations). This contamination depends on season — the winter leachates are less polluted compared to the summer ones. For removal of HM together with removal of bulk COD, the UASB reactors were applied where, besides elimination of the major part of organic matter, concomitant precipitation of HM in the form of insoluble sulphides inside the sludge bed occurred due to development of the process of biological sulphate reduction. Both removal processes were quite efficient even during operation under submesophilic and psychrophilic conditions (20–10°C). The subsequent submesophilic aerobic-anoxic treatment of submesophilic anaerobic effluents led to only 75% of total inorganic N removal due to COD deficiency for denitrification created by a too efficient anaerobic step. On the contrary, psychrophilic anaerobic effluents (richer in COD compared to the submesophilic ones) were more suitable for subsequent aerobic-anoxic treatment giving the total N removal of 95 and 92% at 20 and 10°C, respectively. The final effluent is approaching the current national standards for direct discharge of treated wastewater.

Keywords Aerobic-anoxic biofilter; biological sulphate reduction; heavy metals; landfill leachate; UASB reactor

Introduction

According to available statistics, between 130 and 150 mln. m³ (~27–37.5 mln. tonnes considering a density coefficient of 0.2–0.25) of municipal solid wastes (MSW) are annually generated in Russia and more than 96% of these MSW are currently disposed of via landfilling (Cherp and Vinichenko, 1996; Saveliev, 2003). The exact number of landfills in our country is unknown because of its huge territory, not very comprehensive statistics and existence of thousands of non-sanctioned sites for waste disposal. However, the estimates show that, in total, Russian landfills occupy 0.8 mln. ha, i.e., an area equivalent to 8 cities of the size of Moscow. By the end of the eighties, 88% of landfill sites, according to the inspection of the USSR State Committee of Nature (1989), were in unsatisfactory sanitary conditions producing many dangerous emissions to the environment (Cherp and Vinichenko, 1996). Besides landfill gas, the main concern is a leachate generated due to microbial activity within a landfill, compression and water flows and containing a wide variety of intermediate organic degradation products and inorganic (including metallic) contaminants. The data about flows and compositions of landfill leachates are limited in Russia. This is related with the fact that the leachate collection systems are still not widely implemented throughout the country. The typical composition of leachates from operating Russian landfills is the following (mg/l, except pH): COD – 370–20,000; BOD – 72–13,300; carbonates (hardness salts) – 890–7,600; Ca – 240–2,330; Mg – 64–410; Na – 85–1,700; K – 28–1,700; Fe – 0.5–8.7; chlorides – 96–2,350; sulphates 84–730; phosphates – 0.3–29; organic nitrogen – 0.3–29; organic nitrogen – 0.3–29; ammonia nitrogen – 0.22–480; pH – 4.5–8.6 (Pan, 2001; Kalyuzhnyi et al., 2003a). Besides the above mentioned bulk pollutants, the landfill leachates usually contain heavy metals (HM) and other micropollutants (phenols etc). These leachates (if not collected and treated (the typical
situation for Russia)) pose dangerous environmental and health risks due to its impact on surface and ground waters. Since the data on HM contamination of Russian landfill leachates are very scare, the primary objective of this paper was to perform systematic monitoring of leachates from one of the operating Russian landfills with regard to 5 major troublesome HM (Fe, Zn, Cu, Pb and Cd). The second objective was to develop an efficient lab scale technology for removal of these micropollutants together with removal of bulk biodegradable COD. For this, the UASB reactors were applied where, besides elimination of the major part of organic matter, a concomitant precipitation of HM in the form of insoluble sulphides inside the sludge bed was expected due to the development of the process of biological sulphate reduction. In addition to 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. This option is especially attractive in Russia due to a moderate/cold climate. Finally, as a post-treatment option for anaerobic effluents, the biofilter operating in an alternative aerobic-anoxic regime was investigated at 10 and 20°C for the removal of remaining BOD and nitrogen, which are also a concern for discharge into surface water.

Materials and methods
Leachate sampling
The raw leachates (RL) were sampled during December, 2001–June 2002 from the leachate collection system of the operating municipal landfill “Khmet’yevo” (Moscow province).

Laboratory reactors
2 UASB reactors with rectangular cross-section of 37–38 cm², height of 85 cm, and total working volume of 2.54–2.68 l were used. They were 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., 2003) and 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 tubular biofilter (diameter – 5 cm, height – 55 cm, packed by 0.5–2 cm fraction of road metal) had a working volume of 0.7 l and functioned in 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, 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 while the high recycle rate of effluent (0.125 l/min) was applied to ensure an adequate mixing and a complete consumption of remaining soluble oxygen in the biofilter. During these 2 phases, nitrification and oxidation of remaining BOD proceeded. Then the feeding was performed during the 3rd phase under the same recycle rate of effluent. The last phase included only mixing (by effluent recycle) and was variable to close the 1 h working cycle of the programmable multi-channel timer controlling all 3 (air, recycle, feeding) pumps used. During the last 2 phases, denitrification proceeded. In the middle of the external loop of biofilter, an electronic sensor was inserted for on-line monitoring of soluble oxygen. Secondary sludge from Kur’yanovskaya sewage treatment plant (Moscow) was used as seed sludge for the formation of the attached biofilm. The excess of sludge was periodically withdrawn by intensive backwash of the biofilter. The mesophilic, submesophilic and psychrophilic conditions were imposed by keeping the laboratory reactors inside a thermostat (30 ± 1°C), under ambient temperature in the laboratory (20 ± 3°C) or inside refrigerator (10 ± 2°C).
Analyses

Sampling of treated wastewater for analysis was usually started after 3 hydraulic retention times (HRT) after the change of working regime for each reactor in order to ensure its operation in quasi steady-state conditions. 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. The samples were dried (<40°C) and pre-treated with concentrated HNO₃ and H₂O₂ (30%); thereafter the metal content was measured from the eluate. Some samples (for other HM determinations) were analysed with the ICP-AES. COD, total N and P were analysed spectrophotometrically using Hach tubes. All other analyses were performed by Standard Methods (1995) or as described previously (Kalyuzhnyi et al., 2003b). All gas measurements were recalculated to standard conditions (1 atm, 0°C). Statistical analysis of data was performed using Microsoft Excel.

Results and discussion

Monitoring of HM contamination of landfill leachates

From data presented in Table 1, it is seen that HM contamination of the RL was very variable and there was a noticeable difference between the winter and summer RL - the latter ones are more contaminated compared to the former ones. It is probably related to different water flows through the landfill body during these 2 seasons. However, generally the RL were moderately contaminated with Fe, Zn, Pb and Cd (Cu is present in non-dangerous concentrations). Also the concentrations of sulphate and COD were more than sufficient to run biological sulphate reduction for the generation of sulphide for HM precipitation.

UASB elimination of HM from the RL

From the data of Table 2, it is seen that UASB treatment was quite efficient for removal of HM under all temperature regimes investigated due to their concomitant precipitation/entrapment on the sludge presumably in the form of sulphides and hydroxides. The HM content (except Fe and sometimes Pb) in the anaerobically treated effluents approached 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 each operational regime (Table 3). This accumulation roughly corresponded to the HM removal from the liquid phase for mesophilic and psychrophilic regimes and apparently did not inhibit specific acetilastic activity of these sludges (Table 3). However, after 4.5 months of continuous experiments, the sludge inside the submesophilic UASB reactor became heavy - its ash content increased to 70% (Table 3). Under full-scale implementation of UASB treatment of

Table 1  HM contamination of RL from landfill "Khmet'yevo" (mg/l, except pH)

<table>
<thead>
<tr>
<th></th>
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<tbody>
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<td>Fe</td>
<td>13.58</td>
<td>4.08</td>
<td>6.32</td>
<td>170.4</td>
<td>17.28</td>
<td>79.2</td>
</tr>
<tr>
<td>Zn</td>
<td>1.92</td>
<td>1.08</td>
<td>1.2</td>
<td>28.8</td>
<td>0.86</td>
<td>2.4</td>
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<tr>
<td>Cu</td>
<td>0.24</td>
<td>0.08</td>
<td>0.04</td>
<td>0.168</td>
<td>0.048</td>
<td>0.096</td>
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<tr>
<td>Pb</td>
<td>0.1</td>
<td>0.046</td>
<td>0.038</td>
<td>0.072</td>
<td>0.077</td>
<td>0.058</td>
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<tr>
<td>Cd</td>
<td>0.00008</td>
<td>0.0054</td>
<td>0.001</td>
<td>0.001</td>
<td>0.024</td>
<td>0.006</td>
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<tr>
<td>Total COD</td>
<td>3,810</td>
<td>1,450</td>
<td>1,430</td>
<td>20,560</td>
<td>4,180</td>
<td>9,660</td>
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<td>Total N</td>
<td>162</td>
<td>128</td>
<td>ND</td>
<td>781</td>
<td>ND</td>
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<td>Ammoniac N</td>
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<td>63</td>
<td>70</td>
<td>562</td>
<td>164</td>
<td>822</td>
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<tr>
<td>Total P</td>
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<td>ND</td>
<td>ND</td>
<td>51</td>
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<td>21</td>
<td>8</td>
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<tr>
<td>SO₄²⁻</td>
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<td>106</td>
<td>61</td>
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<td>174</td>
<td>213</td>
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<tr>
<td>pH</td>
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<td>6.53</td>
<td>6.58</td>
<td>5.99</td>
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<td>7.52</td>
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ND - not determined
Table 2 Influent and effluent HM concentrations (mg/l) for mesophilic, submesophilic and psychrophilic UASB reactors treating the RL (steady-state data)

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<tr>
<th>HRT, h</th>
<th>Fe_in</th>
<th>Fe_ef</th>
<th>Zn_in</th>
<th>Zn_ef</th>
<th>Cu_in</th>
<th>Cu_ef</th>
<th>Pb_in</th>
<th>Pb_ef</th>
<th>Cd_in</th>
<th>Cd_ef</th>
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<tr>
<td>46</td>
<td>13.58</td>
<td>1.73</td>
<td>1.92</td>
<td>0.94</td>
<td>0.24</td>
<td>0.097</td>
<td>0.100</td>
<td>0.060</td>
<td>0.0008</td>
<td>0.0001</td>
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<tr>
<td>33</td>
<td>13.58</td>
<td>0.26</td>
<td>1.92</td>
<td>0.20</td>
<td>0.24</td>
<td>0.020</td>
<td>0.100</td>
<td>0.025</td>
<td>0.0008</td>
<td>0.0001</td>
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<tr>
<td>7</td>
<td>4.08</td>
<td>0.46</td>
<td>1.08</td>
<td>0.24</td>
<td>0.080</td>
<td>0.020</td>
<td>0.046</td>
<td>0.014</td>
<td>0.0054</td>
<td>0.0009</td>
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<tr>
<td>80</td>
<td>170.4</td>
<td>1.3</td>
<td>28.8</td>
<td>2.40</td>
<td>0.168</td>
<td>0.048</td>
<td>0.072</td>
<td>0.046</td>
<td>0.0010</td>
<td>0.0005</td>
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<td>29</td>
<td>79.2</td>
<td>5.9</td>
<td>2.4</td>
<td>0.04</td>
<td>0.096</td>
<td>0.020</td>
<td>0.058</td>
<td>0.010</td>
<td>0.0080</td>
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<tr>
<td>7</td>
<td>6.32</td>
<td>0.36</td>
<td>1.2</td>
<td>0.08</td>
<td>0.040</td>
<td>0.020</td>
<td>0.038</td>
<td>0.002</td>
<td>0.0010</td>
<td>0.0001</td>
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<tr>
<td>126</td>
<td>170.4</td>
<td>1.6</td>
<td>28.8</td>
<td>1.60</td>
<td>0.168</td>
<td>0.043</td>
<td>0.072</td>
<td>0.015</td>
<td>0.0010</td>
<td>0.0005</td>
</tr>
<tr>
<td>63</td>
<td>13.58</td>
<td>0.54</td>
<td>1.92</td>
<td>0.16</td>
<td>0.240</td>
<td>0.020</td>
<td>0.100</td>
<td>0.024</td>
<td>0.0008</td>
<td>0.0002</td>
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<td>59</td>
<td>79.2</td>
<td>16.0</td>
<td>2.4</td>
<td>2.00</td>
<td>0.096</td>
<td>0.060</td>
<td>0.058</td>
<td>0.010</td>
<td>0.0080</td>
<td>0.0010</td>
</tr>
<tr>
<td>15</td>
<td>4.08</td>
<td>0.8</td>
<td>1.08</td>
<td>0.30</td>
<td>0.008</td>
<td>0.020</td>
<td>0.046</td>
<td>0.038</td>
<td>0.0054</td>
<td>0.0034</td>
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<td>8</td>
<td>6.32</td>
<td>0.94</td>
<td>1.2</td>
<td>0.26</td>
<td>0.040</td>
<td>0.020</td>
<td>0.038</td>
<td>0.003</td>
<td>0.0010</td>
<td>0.0001</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>5</td>
<td>1</td>
<td>0.03</td>
<td>0.0001</td>
<td>0.0010</td>
<td>0.000</td>
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</tr>
</tbody>
</table>

* RLDW – Russian limit for drinking water

Table 3 Some sludge characteristics of mesophilic, submesophilic and psychrophilic UASB reactors treating the RL

<table>
<thead>
<tr>
<th>Parameter/regime</th>
<th>Day of operation</th>
<th>Mesophilic</th>
<th>Submesophilic</th>
<th>Psychrophilic</th>
</tr>
</thead>
<tbody>
<tr>
<td>VSS in the reactor, g</td>
<td>0</td>
<td>40.0</td>
<td>45.1</td>
<td>42.2</td>
</tr>
<tr>
<td>TSS in the reactor, g</td>
<td></td>
<td>86.9</td>
<td>95.4</td>
<td>89.4</td>
</tr>
<tr>
<td>VSS/TSS, %</td>
<td></td>
<td>46</td>
<td>47.3</td>
<td>47.2</td>
</tr>
<tr>
<td>Aceticlastic activity, g COD/g</td>
<td></td>
<td>0.67</td>
<td>0.75</td>
<td>0.31</td>
</tr>
<tr>
<td>VSS/day*</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe content, µg/g TSS</td>
<td></td>
<td>5,269</td>
<td>6,271</td>
<td>ND</td>
</tr>
<tr>
<td>Zn content, µg/g TSS</td>
<td></td>
<td>1,639</td>
<td>2,834</td>
<td>ND</td>
</tr>
<tr>
<td>Cu content, µg/g TSS</td>
<td></td>
<td>207.3</td>
<td>308.2</td>
<td>ND</td>
</tr>
<tr>
<td>Pb content, µg/g TSS</td>
<td></td>
<td>2.81</td>
<td>12.41</td>
<td>ND</td>
</tr>
<tr>
<td>Cd content, µg/g TSS</td>
<td></td>
<td>0.011</td>
<td>0.017</td>
<td>ND</td>
</tr>
</tbody>
</table>

* Values were obtained at working temperatures – 30, 20 and 10°C, respectively
ND – not determined

RL, such sludges should be periodically withdrawn from the reactors and disposed of on special landfills or incinerated.

COD removal during UASB treatment

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 (79–91% on COD basis). The steady-state results of COD removal during UASB treatment under various HRT and temperature regimes applied are generalised in Figures 1–2. It is seen that in mesophilic conditions when the diluted leachates were treated (Figure 1a), the total COD removal varied from 75 to 91% depending on the initial strength of the RL. Only traces of volatile fatty acids (VFA) were detected in the effluents even under the highest organic loading rate (OLR) applied (5.1 g COD/l/d, HRT – 6.8 h). However, such exhaustion of easily biodegradable COD in the anaerobic effluents might create COD deficiency problems for subsequent biological nitrogen removal because the effluent total COD/total N ratio (Figure 1a) was significantly lower than 6 (the practically established COD/N ratio to have a stable denitrification, Henze et al., 1999).
Figure 1: Total COD removal and effluent total COD/total N ratio versus HRT under quasi-steady state operation of mesophilic (a) and submesophilic (b) UASB reactors treating the RL (figures on the graphs – influent total COD concentrations in mg/l).

Figure 2: Total COD removal and effluent total COD/total N ratio versus HRT under quasi-steady state operation of psychrophilic UASB reactor treating the RL (figures on the graphs – influent total COD concentrations in mg/l).

Under submesophilic conditions (Figure 1b), the total COD removal varied from 81 to 87% and from 51 to 70% for diluted and concentrated RL, respectively. The effluent total COD/total N ratio exceeded the targeted value of 6 only during treatment of high strength leachate (HRT of 80 h). Thus, submesophilic anaerobic effluents in the majority of cases will also need an external COD for subsequent nitrogen removal.

A decrease of working temperature of the UASB reactor to 10°C required an increase of HRT and, hence, a decrease of OLR because the bacterial activity dropped substantially at these conditions (Kalyuzhnyi et al., 2001). From Figure 2, it is seen that in spite of higher HRT applied, the total COD removal (Figure 2) slightly dropped compared to mesophilic and submesophilic regimes (Figure 1). However, taking into account a need in easily biodegradable organic matter for subsequent nitrogen removal, the effluent COD characteristics were superior compared to those from mesophilic and submesophilic regimes due to the presence of remaining VFA (data not shown) – the effluent total COD/total N ratio exceeded 6 during all HRT applied independently on the strength of the RL (Figure 2).

A 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.

Aerobic-anoxic post-treatment of anaerobic effluents

A successful start-up of the 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. When the effluent ammonia
concentrations reached values around 2 mg N/l, the biofilter was switched on in alternating (aerobic-anoxic) operation. During run SM1 (Table 4), when anaerobically treated (in psychrophilic regime) diluted RL were fed, the average total COD removal accounted for 73% with the total COD effluent concentrations slightly oscillating around 0.19 g COD/l. It is close to the aerobic biodegradability limit of these RL (0.15 g COD/l). The efficiencies of ammonia removal and denitrification were 93 and 80% (on the average) resulting in the average inorganic nitrogen removal of 75% (Table 4, run SM1). The effluent ammonia, nitrate and nitrite concentrations oscillated around 4, 12 and 1.5 mg N/l, respectively (Table 4, run SM1).

During runs SM2-SM4, the biofilter was fed with strong nitrogenous anaerobic effluents that required a longer aeration phase and HRT (Table 4). During run SM2, the average total COD removal accounted for 85% with the total COD effluent concentrations oscillating around 1.5 g COD/l (Table 4). The efficiencies of ammonia removal and denitrification were 73 and 99% (on the average) resulting in the average inorganic nitrogen removal of 72% (Table 4, run SM2). Insufficient nitrification probably was due to the high COD/N ratio (15.2) of anaerobic effluent used for feeding during this run. An excess of COD leads to intensive development of heterotrophs making the reactor biofilm thick (mass transfer limitations and clogging) as well as to inhibition of autotrophic nitrifiers (Henze et al., 1999). In order to avoid such undesired phenomena, the submesophilic anaerobic effluents with lower COD/N ratio were used during run SM3. The average efficiency of ammonia removal increased (to 90%) but the average efficiency of denitrification decreased (to 83%) compared to the corresponding values obtained during run SM2 (Table 4). The total inorganic nitrogen removal increased to 75% (on the average) giving the total effluent inorganic nitrogen concentrations around 196 mg N/l (run SM3, Table 4). The elevated total nitrogen concentrations in the effluents were related with both incomplete nitrification and

Table 4 Operational parameters and efficiency of the biofilter treating the anaerobic effluents (mean ± standard deviation)

<table>
<thead>
<tr>
<th>Parameter/run</th>
<th>SM1</th>
<th>SM2</th>
<th>SM3</th>
<th>SM4</th>
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<th>P2</th>
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<td>18-22</td>
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<tr>
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<td>1st mixing, min</td>
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<td>10</td>
<td>4</td>
<td>19</td>
<td>8</td>
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<tr>
<td>Feeding phase, min</td>
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<td>13</td>
<td>20</td>
<td>15</td>
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<tr>
<td>HRT, days</td>
<td>0.98 ± 0.1</td>
<td>3.81 ± 0.47</td>
<td>4.29 ± 0.07</td>
<td>5.09 ± 0.06</td>
<td>1.12 ± 0.1</td>
<td>7.10 ± 0.17</td>
</tr>
<tr>
<td>Influent COD/N</td>
<td>10.3</td>
<td>15.2</td>
<td>4.9</td>
<td>7.4</td>
<td>9.3</td>
<td>7.9</td>
</tr>
<tr>
<td>OLR, g COD/l/d</td>
<td>0.71 ± 0.07</td>
<td>2.61 ± 0.35</td>
<td>0.89 ± 0.16</td>
<td>1.12 ± 0.08</td>
<td>0.64 ± 0.01</td>
<td>0.86 ± 0.08</td>
</tr>
<tr>
<td>Influent COD tot, g/l</td>
<td>0.70 ± 0.03</td>
<td>10</td>
<td>3.81 ± 0.70</td>
<td>5.72 ± 0.38</td>
<td>0.68 ± 0.08</td>
<td>5.95 ± 0.52</td>
</tr>
<tr>
<td>Effluent COD tot, g/l</td>
<td>0.18 ± 0.01</td>
<td>1.53 ± 0.49</td>
<td>1.47 ± 0.44</td>
<td>1.08 ± 0.08</td>
<td>0.18 ± 0.02</td>
<td>0.89 ± 0.13</td>
</tr>
<tr>
<td>COD tot removal, %</td>
<td>73.0 ± 1.1</td>
<td>84.7 ± 4.9</td>
<td>63.6 ± 5.2</td>
<td>80.5 ± 1.5</td>
<td>75 ± 3</td>
<td>86.5 ± 1.7</td>
</tr>
<tr>
<td>Influent pH</td>
<td>7.30 ± 0.05</td>
<td>7.74 ± 0.23</td>
<td>7.71 ± 0.09</td>
<td>6.9 ± 0.1</td>
<td>7.35 ± 0.1</td>
<td>7.41 ± 0.10</td>
</tr>
<tr>
<td>Effluent pH</td>
<td>8.37 ± 0.05</td>
<td>7.08 ± 0.11</td>
<td>7.07 ± 0.10</td>
<td>8.04 ± 0.14</td>
<td>8.23 ± 0.09</td>
<td>7.72 ± 0.14</td>
</tr>
<tr>
<td>Infl. N-NH₃, mg/l</td>
<td>67 ± 4</td>
<td>660</td>
<td>784 ± 21</td>
<td>771 ± 2</td>
<td>73 ± 8</td>
<td>78 ± 2</td>
</tr>
<tr>
<td>Eff. N-NH₃, mg/l</td>
<td>4.1 ± 2.0</td>
<td>178 ± 25</td>
<td>78 ± 9</td>
<td>18.8 ± 0.9</td>
<td>5.0 ± 2.5</td>
<td>30 ± 1</td>
</tr>
<tr>
<td>N-NH₃ removal, %</td>
<td>93 ± 3</td>
<td>73.1 ± 3.8</td>
<td>90.1 ± 1.0</td>
<td>97.7 ± 0.1</td>
<td>93 ± 2</td>
<td>96 ± 0.1</td>
</tr>
<tr>
<td>Eff. N-N₂O₃, mg/l</td>
<td>12 ± 5</td>
<td>1 ± 1</td>
<td>117 ± 14</td>
<td>18.0 ± 4.5</td>
<td>9 ± 5</td>
<td>33.3 ± 1.5</td>
</tr>
<tr>
<td>Eff. N-N₂O, mg/l</td>
<td>1.5 ± 0.3</td>
<td>Traces</td>
<td>1.5 ± 1.1</td>
<td>0.4 ± 0.1</td>
<td>1.7 ± 0.9</td>
<td>0.3 ± 0.1</td>
</tr>
<tr>
<td>*Denitrif. effici., %</td>
<td>80 ± 7</td>
<td>99.2 ± 0.3</td>
<td>83.3 ± 2.2</td>
<td>97.6 ± 0.8</td>
<td>75 ± 10</td>
<td>95 ± 4.2</td>
</tr>
<tr>
<td>Eff. N tot,inorg, mg/l</td>
<td>18 ± 5</td>
<td>182 ± 26</td>
<td>196 ± 22</td>
<td>37 ± 5</td>
<td>16.7 ± 8.9</td>
<td>63 ± 2</td>
</tr>
<tr>
<td>*N tot,ino rg removal, %</td>
<td>75.0 ± 8.3</td>
<td>72.4 ± 3.9</td>
<td>75.1 ± 2.6</td>
<td>95.2 ± 0.7</td>
<td>73.2 ± 11.2</td>
<td>91.6 ± 0.3</td>
</tr>
<tr>
<td>Infl. P-PO₄, mg/l</td>
<td>9.4 ± 0.1</td>
<td>17</td>
<td>14.9 ± 5.8</td>
<td>18.9 ± 0.1</td>
<td>11.0 ± 0.7</td>
<td>18.7 ± 0.1</td>
</tr>
<tr>
<td>Eff. P-PO₄, mg/l</td>
<td>5.2 ± 0.1</td>
<td>4.6 ± 0.8</td>
<td>8.1 ± 5.4</td>
<td>9.8 ± 0.5</td>
<td>10.2 ± 0.2</td>
<td>14.9 ± 0.3</td>
</tr>
</tbody>
</table>

*Calculated as: \[1 - \frac{[\text{N-NO}_3\text{ eff} + \text{N-NO}_2\text{ eff} + \text{N-NH}_3\text{ eff}]}{[\text{N-NH}_3\text{ in} - \text{[(N-NH}_3\text{ eff}]}]*100\]
*Calculated as: \[1 - \frac{[\text{N-NO}_3\text{ eff} + \text{N-NO}_2\text{ eff} + \text{N-NH}_3\text{ eff}]}{[\text{N-NH}_3\text{ in}]}]*100\]
COD deficiency to have a stable denitrification (COD/N ratio during run SM2 was around 5). On the contrary, during run SM4 when the COD/N ratio was 7.4 (i.e. between the corresponding values for runs SM2 and SM3), the biofilter was able to remove 95% of total inorganic nitrogen giving the effluent with total inorganic nitrogen concentrations around 37 mg N/l. It seems that it is hardly possible to reach a lower level of ammonia in the effluent due to an imminent drawback of this relatively simple biofilter construction where wastewater filling and effluent withdrawal were performed simultaneously in a CSTR regime. 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).

- A decrease of working temperature of the biofilter to 10°C required an increase of HRT because the nitrifying-denitrifying activity of the biofilm dropped substantially at these conditions (Henze et al., 1999). The optimal conditions for anaerobically treated diluted RL were found when HRT was 1.12 days (run P1, Table 4). In this regime, the effluent characteristics were quite similar to those from run SM1 with regard to total COD and nitrogen content as well as concentrations of nitrogen species – ammonia, nitrate and nitrite (Table 4). Switching of the psychrophilic biofilter on feeding with strong nitrogenous anaerobic effluents required a further decrease of HRT and an increase of duration of the aeration phase (run P2, Table 4). The corresponding process optimisation led to the average total inorganic nitrogen removal accounting for 92% with the total inorganic nitrogen concentrations in the effluents around 63 mg N/l from which only 30 mg N/l was represented by ammonia (run P2, Table 4).

Thus, during all runs, the remaining nitrogen concentrations were above the current national standards (10 mg N/l) for direct discharge of treated wastewater. A simple and inexpensive post-treatment steps like a collection/stabilisation pond (they are usually available at landfills) or constructed wetland will probably be required to ensure a safe discharge of the treated leachates (by proposed sequenced technology) to surface waters.

Conclusions
1. Systematic monitoring of Khmet’yevo landfill leachates during December, 2001–June, 2002 with regard to HM content showed that they were moderately contaminated with Fe, Zn, Pb and Cd (Cu is present in non-dangerous concentrations). This contamination depends on season – the winter leachates are less polluted compared to the summer ones.

2. The UASB reactors were quite efficient for removal of HM (due to their precipitation/entrapment on the sludge) and bulk COD from Khmet’yevo landfill leachates even during operation under submesophilic and psychrophilic conditions (20–10°C).

3. The application of aerobic/anoxic biofilters at 10–20°C allowed an elimination of biodegradable COD and more than 92% of inorganic nitrogen from the anaerobic effluents. However, the remaining nitrogen concentrations were above the current national standards for direct discharge of treated wastewater. A simple and cheap post-treatment step like a stabilisation pond or constructed wetland will probably be required to ensure a safe discharge of the treated leachates to surface waters.

Acknowledgements
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References