Ultrasound as a pre-oxidation for biological landfill leachate treatment

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Abstract In this study, the effects of low energy ultrasound irradiation on landfill leachate treatment by means of sequencing bath reactor were investigated. The aim of this work was to estimate the influence of leachate irradiation time on aerobic treatment efficiency. The sonification of the leachate was carried out in static conditions using the disintegrator UD-20. The field frequency of 22 kHz (the power output equals to 180 W) and amplitude of 12 μm was applied. The sonification time was changed in the range of 30–140 s. It was found that ultrasonic pretreatment enhances the subsequent aerobic digestion resulting in a better degradation of landfill leachate. The sonification of raw leachate leads to enhancement of COD and ammonia removal as compare to experiment without ultrasound.

Keywords Landfill leachate; SBR reactor; ultrasound

Introduction

For several decades, the ultrasonic process has been considered as a new possibility in the water and wastewater treatment field (Ince et al., 2001). Ultrasound (US) between 20 and several hundred kHz is known to create resonant cavities which release energy during collapse in the process called cavitation. It is able to remove pollutants through the production of radicals in the bubble of cavitation that can react with refractory compounds. The impact of ultrasound waves on liquid causes the periodical compression and rarefaction of the medium. Cavitation occurs above a certain intensity threshold, when gas bubbles are created which first grow in size before violently collapsing within a few microseconds. The violent collapse produces very powerful hydromechanical shear forces in the bulk liquid surrounding the bubble. Cavitation is accomplished by high pressure gradients and extreme increase of the temperature inside the bubble. These extreme conditions can lead to the thermal destruction of compounds present in the cavitation bubbles and to the generation of very reactive species including H₂O₂, H⁺, OH⁺, which potentially can give rise to radical chain reactions throughout sonolysed media. The effects that can be observed when cavitation is generated in aqueous solution can be summarised as: high mechanical shear stress, radical reactions, chemical transformation of substances and thermal breakdown of volatile substances.

Treatment of pollutants using acoustic irradiation can lead to the structural decomposition of some toxic chemicals and to the generation of compounds with lower molecular weight and lower toxicity (Guo et al., 2005). Destruction or mineralisation of organic compounds by ultrasound process is based on oxidative degradation, particularly by the hydroxyl radical attack, which is a far more powerful oxidising agent than all commonly known oxidants.

Landfill leachate has been generally known as a high-strength wastewater. Due to their high content in non-biodegradable organics, inorganics as well as toxic compounds leachate is most difficult to deal with (Lema et al., 1988). High loading of landfill
leachate, divergent composition and different volume of leachate in particular seasons of the year make the treatment of such wastewater very complicated (Park et al., 2001). Biological methods including aerobic and anaerobic process have been shown to be very effective for the treatment of landfill leachate with high BOD/COD ratio. However, the biological treatment process became ineffective in the treatment of old landfill leachates mainly due to presence of non biodegradable compounds (Kennedy and Lentz, 2000).

In this study, the effects of low energy ultrasound irradiation on landfill leachate treatment by means of sequencing bath reactor were investigated. The aim of this work was to estimate the influence of leachate irradiation time on aerobic treatment efficiency.

**Materials and methods**

The landfill leachate used for the experiments was obtained from Sobuczyna sanitary landfill site in southern Poland. The COD strength of the leachate varied between 4,200 and 4,850 mg/L, while the BOD concentration was less than 480 mg/L. This gives BOD/COD ratio of about 0.1 and means that most of the organic compounds in the leachate are non-biodegradable. One of the major pollutants in leachate was ammonium and its strength was 750–830 mg/L. The concentration of chloride was also high, in the level of 2,800–3,200 mg/L.

The disintegration of leachate was carried out in static conditions using disintegrator UD 20 with a “Sandwich” concentrator (TECHPAN, Warsaw). The field frequency of 22 kHz (the power output equals to 180 W) and amplitude of 12 \( \mu \)m was applied. The sonification time was changed in the range of 30–140 s.

Two identical laboratory-scale sequencing batch reactors (SBR) were used for the examination of leachate ultrasound pretreatment on biological treatment efficiency. Each reactor with 15 cm diameter and 30 cm height had a total volume of 5 L. Wastewater in the tank was aerated by using an air pump and diffuser to keep dissolved oxygen concentration above 2 mg/L in the oxic phase. Magnetic stirrers were used for mixing. A set of two peristaltic pumps was used to feed and discharge the effluent, respectively, in both reactors. The reactor was operated at room temperature (18–20°C). Each SBR cycle consisted of the following phase: aerobic fill (0.15 h), aerobic react (2.0), anoxic react (1.0), settle (0.3) and draw (0.08 h). Samples were withdrawn from the reactor at the beginning and at the end of each cycle for analysis. The SBR systems were operated at feeding conditions of leachate dilution of 25% by volume with a synthetic wastewater and with 4 g/L sludge concentration. Both systems were inoculated with sludge collected from the municipal wastewater treatment plant in Czestochowa. The initial volume of the culture in the tank was 1 L which was completed to 4 L with the addition of diluted leachate at the beginning of each cycle. A fraction (1/10) of the culture was removed from the reactor every day to adjust the sludge age to days.

The following parameters were analysed: BOD\(_5\), pH, nitrate, ammonia, total Kjeldahl nitrogen (TKN), total phosphorus. All analyses were carried out according to Standard Methods (APHA, 1992). Chemical oxygen demand (COD) was determined by the dichromate method using DR/4000 spectrophotometer (Hach Company, USA). Raw samples were used for COD\(_0\), 4.4 \( \mu \)m folded paper-filtered samples for COD\(_t\) and 0.45 \( \mu \)m membrane-filtered samples for COD\(_{dis}\) respectively. The COD\(_{ss}\) and COD\(_{col}\) were calculated by the difference between COD\(_t\) and COD\(_{dis}\) respectively (Elmitwalli et al., 2002).

**Results and discussion**

In the first phase of this study the optimal sonification time for leachate conditioning was evaluated. Ultrasound amplitude and dilution ratio of landfill leachate were determined.
during previous investigation (Neczaj et al., 2005). Performances with sonification times of 30, 45, 60, 75, 90, 105, 120 and 140 s were investigated to evaluate biodegradability of leachate in the same conditions. Table 1 shows the influence of sonification time on COD removal and changes in concentration of different COD fractions after irradiation.

Chemical oxygen demand (CODt) of raw landfill leachate used in that part of our experiment had a constant value of 4,500 mg O2/L. A gradual increase of CODt removals with sonification time up to 90 s was observed. It was found that an increase of ultrasound irradiation time over 90 s did not cause improvement of organic compounds degradation. COD removal efficiency was on the same level and achieved a value of 17%. It implies that CODt degradation is accompanied by the formation of liquid-phase organic by-products that are resistant to sonochemical degradation (Emery et al., 2005). A decrease in solution pH indicates the formation of acidic compounds, presumably due to occurrence of hydroxyl radical-mediated reactions to the liquid.

The sonification leads to a gradual increase of the BOD5 up to an irradiation time of 90 s. Those phenomena can be attributed to the transformation of non-biodegradable species in more biodegradable forms. A significant change in concentration of different COD forms was observed after ultrasound pretreatment. CODcol changes from 810 mgO2/L for untreated leachate to about 355 mg mgO2/L for US conditioned leachate, i.e. a decrease of 57%. At the same time, an increase of CODdis concentration was observed. That means that colloidal organic compounds were transformed to dissolved forms.

Significant representation of biodegradability is given by the ratio of BOD5 to COD. This ratio increased when sonification time increased from 30 to 90 s and remained stable for longer irradiation time (Figure 1). In these experiments, this value was initially equal to 0.1 for raw leachate, reaching about 0.3 at the end of the experiment which indicates an increase of the biodegradability.

Although the BOD/COD ratio of the leachate effluent from the ultrasound pre-oxidation process was much improved to 0.3, it was still not sufficient for effective biological treatment. That is why the leachate was mixed with synthetic wastewater to a ratio of 1:4 before it was subjected to SBR treatment. Initially after start up of each reactor (15 days), one reactor was operated with the mixture of synthetic wastewater and raw leachate while the second one with diluted landfill leachate conditioned by ultrasound. The reactor performance was assessed by monitoring carbon (CODt) and ammonia removal during the sequence operation and also through the reactor operation. Initial concentration of COD in influent was of the level 2,000 mgO2/L.

The variation of COD removal (at the end of the reaction phase) with the function of landfill irradiation time is depicted in Figure 2. With an increase of leachate irradiation time, a higher COD removal efficiency was observed. COD removal rates over 60% were maintained with sonification time of leachate up to 60 s and a gradual increase in organic

<table>
<thead>
<tr>
<th>Item</th>
<th>0</th>
<th>30</th>
<th>45</th>
<th>60</th>
<th>75</th>
<th>90</th>
<th>105</th>
<th>120</th>
<th>140</th>
</tr>
</thead>
<tbody>
<tr>
<td>CODt, mgO2/L</td>
<td>4,500</td>
<td>4,275</td>
<td>4,185</td>
<td>4,082</td>
<td>3,915</td>
<td>3,735</td>
<td>3,740</td>
<td>3,739</td>
<td>3,734</td>
</tr>
<tr>
<td>CODss, mgO2/L</td>
<td>2,025</td>
<td>1,796</td>
<td>1,716</td>
<td>1,633</td>
<td>1,527</td>
<td>1,419</td>
<td>1,421</td>
<td>1,420</td>
<td>1,418</td>
</tr>
<tr>
<td>CODcol, mgO2/L</td>
<td>810</td>
<td>665</td>
<td>584</td>
<td>490</td>
<td>428</td>
<td>355</td>
<td>356</td>
<td>353</td>
<td>354</td>
</tr>
<tr>
<td>CODdis, mgO2/L</td>
<td>1,215</td>
<td>1,131</td>
<td>1,132</td>
<td>1,143</td>
<td>1,099</td>
<td>1,064</td>
<td>1,066</td>
<td>1,067</td>
<td>1,064</td>
</tr>
<tr>
<td>BOD5, mgO2/L</td>
<td>450</td>
<td>641</td>
<td>837</td>
<td>980</td>
<td>1,096</td>
<td>1,121</td>
<td>1,159</td>
<td>1,122</td>
<td>1,083</td>
</tr>
<tr>
<td>CODrem, %</td>
<td>–</td>
<td>5</td>
<td>7</td>
<td>10</td>
<td>13</td>
<td>17</td>
<td>17</td>
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<td>pH</td>
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<td>7.9</td>
<td>7.4</td>
<td>6.9</td>
<td>6.5</td>
<td>6.4</td>
<td>6.5</td>
<td>6.5</td>
<td>6.4</td>
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</table>
compounds removals was observed as sonification time increased from 75 to 90 s. It was found that an increase of sonification time over 90 s did not cause improvement of SBR process efficiency. COD removal was on the same level and achieved a value of about 90%. It can be concluded from the reactors performance data obtained that SBR operated with ultrasound conditioned landfill leachate showed relatively better performance with respect to COD removal when compared to the SBR operated with non-conditioned leachate. In that case organic compounds mineralisation was significant lower and achieved a value of 50%. The relatively poor performance of that SBR reactor can be attributed to the presence of high concentrations of non-biodegradable compounds as well as toxic and inhibitory substances in the raw landfill leachate.

Percent ammonium-N removal was also improved by using ultrasound as a pre-oxidation method resulting in 63 and 55% NH$_4$–N removals in the presence and absence of leachate ultrasound irradiation, respectively (Figure 3). Ammonia removal efficiency was on the same level when sonification time in the range of 30–75 s was applied. An increase of irradiation time to 90 s resulted in a significant improvement in NH$_4$–N removal of over 70%. The effluent N–NH$_4$ dropped from 90 mg/L for SBR operated with untreated raw leachate to 56 mg/L when irradiation time in the range of 90–140 s was applied. The results clearly indicated that ultrasound irradiation improves the treatability of the landfill leachate resulting in higher percent ammonia removals and lower effluent
NH4–N levels. However, this leachate pre-treatment method does not allow ammonia concentrations in the effluent below the required limits. Hence, further studies should be carried out to optimise the SBR process in order to improve nitrogen removal (Figure 3).

Conclusions
The aim of this work was to estimate the influence of different leachate irradiation time on aerobic treatment efficiency. It was found that ultrasonic pretreatment enhances the subsequent aerobic digestion resulting in a better degradation of landfill leachate. Increase of sonification time over 90 s did not cause improvement of SBR process efficiency. COD removal was on the same level and achieved a value of about 90%. For the same ultrasound irradiation time, improvement of ammonia removal efficiency (over 70%) was observed. Therefore, sonification time 90 s seems to be a practical upper limit for leachate conditioning to the SBR process. However, effluent NH4–N concentration was below the required limits and additional studies should be carried out in order to improve nitrogen removal in the SBR process.

References

Figure 3 Ammonia removal efficiency versus ultrasound irradiation time