LANDFILL LEACHATE TREATMENT BY BATCH MULTI-STAGE PROCESS USING NATURAL ZEOLITE

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ABSTRACT
Leachate from the Bikarac landfill of the Šibenik-Knin County in Croatia has been treated by batch multi-stage process consisted of few steps: treatment with lime with pH adjustment, aeration during 24 hours and sorption by natural zeolite. Overall process shows very good removal efficiency for Kjeldahl nitrogen, even 78.60 %, Chemical oxygen demand 55.34 %, turbidity 64.09 % and el. conductivity 38.12 %. All steps in multi-stage process contributed to decrease of these parameters, where the highest contribution achieves the treatment with lime and aeration. Analysis of results obtained by desorption shows high ability of zeolite to retain pollutants particularly at pH 6.65. This can be attributed to the high affinity of zeolite towards Kjeldahl nitrogen, e.g. ammonia in landfill leachates. Results indicate possible use of the natural zeolite as a permeable reactive barrier for prevention of groundwater pollution.

Keywords: waste landfill, landfill leachate, multi-stage treatment processes, natural zeolite.

INTRODUCTION
Controlled and uncontrolled solid waste disposal cause a production of leachate due to solid waste decomposition in a presence of moisture. The Bikarac landfill represents a sanitary active landfill equipped with basin for leachate collection and treatment with sequencing batch reactor (SBR) [1]. Chemical composition of treated leachate has shown that SBR technology is not adequate for treatment since obtained results does not satisfy values for leachate discharge into sewage systems [1,2]. Preliminary investigations with lime addition combined with natural and modified natural zeolite, has shown guidelines for development of the multi-stage leachate treatment [3]. Each stage of this process should contribute to reduction of complex chemical composition of the leachate. This paper presents an alternatively treatment process consisted of several steps. Selection of natural zeolite as adsorbent in the last phase should be effective due to high affinity for nitrogen compounds [4-7].

EXPERIMENTAL
The 24-hour average sample was collected during 16th and 17th March of 2018 from the basin of landfill leachate of municipal solid waste of landfill site Bikarac. Every two hours, a volume of 0.5 L is taken from the basin and transferred to the 10 L plastic bottle stored in a cooler box before transportation to the laboratory. The collected sample is filtered in order to remove the dispersed matter and preserved in refrigerator before analysing. The following parameters have been determined: the pH value, turbidity, chemical oxygen demand (CODC₅), biochemical oxygen demand (BOD₅) and Kjeldahl nitrogen (NKjeldahl). The 5 L of the raw leachate sample has been treated with slow addition of lime up to pH = 12.26 under continuous mixing. Suspension has been aerated during next 24 hours and supernatant has been analysed [3]. After filtration, supernatant has been treated by natural zeolite using two-stage batch method at solid/liquid ratio 1/100. First stage has been performed by shaking the suspension during 24 hours, then suspension is filtrated, and filtrate is analysed for the same
parameters. Then it is equilibrated with fresh zeolite for the second stage during next 24 hours. After filtration, solution is analysed and results are compared with previous determinations [3,4]. Used natural zeolite sample originates from Vranjska Banja deposit (Serbia), milled for particle size 0.6-0.8 mm and dried at 40°C.

Zeolite samples remained after each stage has been leached with ultrapure water with adjusted pH values of 2.98 or 6.65. The pH adjustment is achieved by small addition of 0.1mol/l HNO₃. Equilibration is performed in shaker at 1/100 solid/liquid ratio during 24 hours [4]. The obtained leachates (4 solutions) are analysed for the same parameters (pH, turbidity, el. conductivity, COD₇, N₆Kjeldahl) after filtration and ability of pollution retention onto natural zeolite has been concluded.

RESULTS AND DISCUSSION

A physical, chemical and microbiological characteristic of landfill leachate depend on the waste composition, the climatic conditions and the age of the landfill. The physico-chemical analysis of leachate from landfill Bikaracis performed few times in different period [1]. Current results are presented in Table 1.

The results are compared with the maximum permissible levels prescribed by Croatian law for their discharged of leachate into the natural surface waters or sewage systems [2]. It is obvious from the results presented in Table 1 that the values of parameters BOD₅, COD₇, Kjeldahl nitrogen after SBR treatment (initial sample) are above permissible limits. It was found that the leachate sample had a dark brown colour, turbidity and mainly contains non-biodegradable compounds (BOD₅/COD₇=0.03). Obtained results indicate that leachate needs to be treated appropriately before discharging into the receiving systems. Biological treatment is not promising method and physico-chemical treatment seems much better option [10,11]. Having this in mind, the sample was processed through the lime treatment and aeration and results are presented in Table 1.

Table 1. Results of parameters for initial sample compared to Croatian law for discharge [2].

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Measure unit</th>
<th>Initial sample</th>
<th>After lime treatment (pH=12.26) and aeration</th>
<th>Maximum level for natural waters</th>
<th>Maximum level for sewage systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>-</td>
<td>8.31</td>
<td>12.26</td>
<td>6.5-9</td>
<td>6.5-9.5</td>
</tr>
<tr>
<td>Turbidity</td>
<td>NTU</td>
<td>40.60</td>
<td>2.34</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>El. conductivity</td>
<td>mS/cm</td>
<td>8.84</td>
<td>9.25</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>COD₇</td>
<td>mg O₂/l</td>
<td>1254</td>
<td>642</td>
<td>125</td>
<td>700</td>
</tr>
<tr>
<td>BOD₅</td>
<td>mg O₂/l</td>
<td>39</td>
<td>-</td>
<td>25</td>
<td>250</td>
</tr>
<tr>
<td>N₆Kjeldahl</td>
<td>mg N/l</td>
<td>270</td>
<td>73</td>
<td>10</td>
<td>50</td>
</tr>
</tbody>
</table>

Note: * not prescribed by Croatian law.

Treatment with lime combined with aeration significantly changed colour and transparency of the landfill leachate as shown in Figure 1. Removal efficiency during lime treatment and aeration is 48.7 % for COD₇ and even 73 % for Kjeldahl nitrogen with significant decrease of turbidity [2]. Decrease of Kjeldahl nitrogen and COD₇ values occur due to settling of the suspended organic matter and releasing of NH₃ due to air stripping. BOD₅ is not determined in this phase of experiments because of high pH value and very low concentration in the initial sample. However, this treatment did not achieve levels for discharge into natural waters, therefore the two-stage treatment with natural zeolite has been applied and results are shown in Table 2.
Treatment with natural zeolite has shown decrease in parameters only in the first stage where COD$_{Cr}$ value is additionally decreased for 13% and Kjeldahl nitrogen for 16.2%. Second stage did not have effect on the main parameters. The pH values remained in alkaline range which is not allowed for discharge into natural waters and sewage systems [2]. Zeolites usually have neutralising effect of suspensions, but in these experiments the concentration of hydroxide was obviously overdosed and expected neutralisation did not occur.

Zeolite treatment decrease COD$_{Cr}$ into range available for discharge into sewage systems what is promising for their application in leachate wastewater treatment.

![Figure 1. Comparison of the raw leachate sample (left) and after treatment with lime and aeration (right) [3-5].](image)

![Table 2. Results of parameters after two-stage zeolite treatment and leaching of the zeolite [3-5].](table)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Measure unit</th>
<th>1$^{st}$ stage zeolite treatment</th>
<th>2$^{nd}$ stage zeolite treatment</th>
<th>Leaching of zeolite after 1$^{st}$ stage pH=2.98</th>
<th>Leaching of zeolite after 2$^{nd}$ stage pH=6.65</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>-</td>
<td>12.3</td>
<td>11.68</td>
<td>9.22</td>
<td>9.72</td>
</tr>
<tr>
<td>Turbidity</td>
<td>NTU</td>
<td>21.65</td>
<td>14.58</td>
<td>9.35</td>
<td>9.03</td>
</tr>
<tr>
<td>El. conductivity</td>
<td>mS/cm</td>
<td>7.55</td>
<td>5.47</td>
<td>0.33</td>
<td>0.23</td>
</tr>
<tr>
<td>COD$_{Cr}$</td>
<td>mg O$_2$/l</td>
<td>561</td>
<td>560</td>
<td>16</td>
<td>0</td>
</tr>
<tr>
<td>N$_{Kjeldahl}$</td>
<td>mg N/l</td>
<td>61</td>
<td>58</td>
<td>1</td>
<td>10</td>
</tr>
</tbody>
</table>

Low biodegradability of these waters limits selection of treatment procedures. In the case of their discharge into sewage systems, need to care about volume ratio of these waters in biodegradable streams, to avoid stress of microbial cultures. The overall effect of the multi-stage treatment of the landfill leachate is given in Figure 2.

![Figure 2. Overall removal efficiencies of the multi-stage leachate treatment.](chart)
Leaching of each zeolite sample used in treatments is shown in Table 2 for two examined pH values. Acidic medium shows release of compounds which increase measured parameters, while weak acidic to neutral medium generally retains pollutants [5].

CONCLUSION

Application of the batch multi-stage process consisted of treatment with lime with pH adjustment, aeration during 24 hours and two-stage sorption by natural zeolite has shown significant contribution to investigations of the landfill leachate treatment. Overall multi-stage process shows good removal efficiency for COD$_\text{Cr}$ and turbidity where achieved values are for discharge into sewage systems. Leaching of the saturated zeolite shows good retain of sorbed harmful compounds and confirms possible application for permeable reactive barriers for in situ remediation of groundwater and contaminated soils.

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REFERENCES


