Keywords: Landfill leachate, advanced oxidation processes, Fenton reagent.

Abstract: Treatment of leachate from an exploited since 2004 landfill by using two methods of advanced oxidation processes was performed. Fenton’s reagent with two different doses of hydrogen peroxide and iron and UV/H\textsubscript{2}O\textsubscript{2} process was applied. The removal efficiency of biochemically oxidizable organic compounds (BOD\textsubscript{5}), chemically oxidizable compounds using potassium dichromate (COD\textsubscript{Cr}) and nutrient (nitrogen and phosphorus) was examined. Studies have shown that the greatest degree of organic compounds removal expressed as a BOD\textsubscript{5} index and COD\textsubscript{Cr} index were obtained when Fenton’s reagent with greater dose of hydrogen peroxide was used – efficiency was respectively 72.0% and 69.8%. Moreover, in this case there was observed an increase in the value of ratio of BOD\textsubscript{5}/COD\textsubscript{Cr} in treated leachate in comparison with raw leachate. Application of Fenton’s reagent for leachate treatment also allowed for more effective removal of nutrients in comparison with the UV/H\textsubscript{2}O\textsubscript{2} process.

INTRODUCTION

Leachate coming from the landfill is called the water of precipitation, which penetrated through the bed of waste. Leachate may also be a surface and underground waters, which have been in contact with the deposited waste. Moreover, these are also waters formed in the process of physicochemical and biochemical changes of organic compounds contained in waste [9].

Landfill leachate is characterized by a very high concentration of organic and nitrogen compounds. With the growth of age of landfill the ratio of biodegradable and non-biodegradable organic compounds are changed. Firstly, when the age of deposited wastes is little (less than 5 years), both fractions of organic matter (biodegradable and non-biodegradable) are characterized with high concentration. However, with increasing of landfill age the concentration of biodegradable compounds decreases. The content of non-biodegradable compounds is also reduced, but this is a much smaller decrease than in comparison with biodegradable compounds. Therefore, with the growth of landfill age
the ratio of BOD$_5$/COD decreases from 0.5–0.7 to even 0.1. Moreover, leachate from the “young” landfills is characterized by generally higher concentrations of organic compounds than the “old” landfill leachate. It is due to the fact that organic compounds contained in deposited wastes undergo biochemical degradation by the process of anaerobic digestion [9, 10].

According to the Polish law landfill leachate is classified as industrial wastewater. Therefore, there is an obligation to recognize and treat leachate. The degree of purification of leachate depends on where effluent will be discharged. According to the Polish law, leachate can be discharged into municipal sewage treatment plants, but it cannot cause a negative impact on treatment plant work and deteriorate the efficiency of sewage treatment plants [7, 8].

There are many different methods used for leachate treatment. Both, biological and physicochemical processes can be applied for purification of this kind of industrial wastewater. Biological methods are used for biodegradable compounds removal, therefore, these processes have found an application for treatment of leachate from “young” landfill. Moreover, the aim of aerobic biological methods is to remove nitrogen from leachate through the nitrification and denitrification processes [11, 12].

The application of physicochemical methods may be aimed for pretreatment of leachate before its further biological treatment. These methods can also be used for treatment of leachate after biological process in order to remove residual non-biodegradable compounds.

Advanced oxidation processes, belonging to the physicochemical methods, may be used for these two different purposes listed above. Use of AOPs to leachate pretreatment is mainly intended to improve their biodegradability by increasing the ratio of BOD$_5$/COD [1]. Therefore, the AOPs used for pretreatment are used in the leachate from the “old” landfill, where the ratio of BOD$_5$/COD achieves small values. In this case for leachate pretreatment such methods as O$_3$/H$_2$O$_2$, photo-Fenton, UV/H$_2$O$_2$ and O$_3$/UV are used [3, 13, 16]. The advanced oxidation processes applied to the purification of leachate after biological treatment are used in the case of leachate from “young” landfills [4]. In biological process the biodegradable compounds are removed from leachate, and non-biodegradable compounds are removed by chemical method (AOPs) such as Fenton reagent [2].

In this paper the effectiveness of raw leachate treatment from “young” landfill by two advanced oxidation processes (Fenton reagent and UV/H$_2$O$_2$ process) is shown.

METHODOLOGY

Leachate treatment has been studied using Fenton’s reagent and UV/H$_2$O$_2$ process. Leachate came from an exploited since 2004 municipal landfill. However, it was characterized by relatively low content of oxidizable organic compounds, both biochemically (BOD$_5$) and chemically using potassium dichromate (COD$_{Cr}$) and the low value of the ratio of indexes BOD$_5$/COD$_{Cr}$ (Tab. 1).

Fenton process was carried out in batch reactors with a volume of 1 L, which were located on the magnetic stirrers. Leachate acidified with H$_2$SO$_4$ (1+1), then hydrogen peroxide and FeSO$_4$$\cdot$7H$_2$O was introduced, and then the mixture was stirred for a suitable time. Fenton’s reaction was stopped by increasing pH up to 8.5 with NaOH and the mixture was centrifuged to separate the sludge of Fe(OH)$_2$.
The process of UV/H$_2$O$_2$ was realized in the flow system shown in Figure 1. The system consisted of a UV reactor, leachate tank and a peristaltic pump used to circulate leachate in the system. Leachate was acidified with H$_2$SO$_4$ (1+1) to the appropriate value, then hydrogen peroxide was added and the mixture was fed into the leachate tank. Leachate was purified in an appropriate time. Then leachate was neutralized to pH 7.0 with NaOH.

In the treated leachate the content of chemically oxidizable organic compounds using potassium dichromate – COD$_{Cr}$ [5], the content of biochemically oxidizable organic compounds – BOD$_5$ [15], the total phosphorus concentration [6] and the total nitrogen concentration [14] were determined. In addition, the hydrogen peroxide which did not react was determined in the leachate. The presence of hydrogen peroxide influences the measured value of COD$_{Cr}$ index. Therefore, COD$_{Cr}$ index was calculated according to formula 1.

### Table 1. Landfill leachate characteristic

| Indexes          | value       |
|------------------|-------------|
| COD$_{Cr}$, mg O$_2$/L | 1764–2636   |
| BOD$_5$, mg O$_2$/L    | 350–500     |
| BOD$_5$/COD$_{Cr}$    | 0,157       |
| N$_{total}$, mg N/L   | 1425        |
| P$_{total}$, mg P/L   | 25,81–36,91 |

Fig. 1. Flow system of UV/H$_2$O$_2$ process (1 – reaction tank, 2 – magnetic stirrer, 3 – pump introducing leachate into UV reactor, 4 – UV reactor, 5 – low-pressure UV lamp, 6 – reagents (H$_2$O$_2$, NaOH or H$_2$SO$_4$), 7 – leachate recirculation from UV reactor into
\[ COD(mg/L) = COD_m - f \cdot [H_2O_2] \]
\[ f = 0.4706 \cdot [H_2O_2] - 4.06 \cdot 10^{-5} \cdot [H_2O_2] \]

where:
- \( COD_m \) – value of COD index obtained from titration of sample,
- \( f \) – correction factor.

The parameters used in treatment methods are presented in Table 2. These parameters were determined by authors of the publication in previous preliminary studies.

| Process               | Initial pH | \( H_2O_2 \) dose g/L | \( Fe^{2+} \)/\( H_2O_2 \) | Reaction/radiation time | Final pH |
|-----------------------|------------|------------------------|-----------------------------|-------------------------|----------|
| Fenton’s reagent      | 4.0        | 2.0                    | 0.4                         | 90                      | 8.5      |
| Fenton’s reagent      | 3.0        | 3.5                    | 0.25                        | 120                     | 8.5      |
| UV/H_2O_2             | 4.0        | 3.0                    | 0                           | 90                      | 7.0      |

**RESULTS**

**Organic compounds removal**

The study showed that the highest removal efficiency of biochemically oxidizable compounds (expressed as BOD\(_5\) index) was observed when Fenton’s reagent used with a dose of \( H_2O_2 \) was 2.0 g/L – 75.7% (Fig. 2). The smallest degree of reduction of BOD\(_5\) index was observed during the UV/H\(_2O_2\) process – 62.5%. However, in the case of organic compounds expressed as COD\(_{cr}\) index the greatest effectiveness was observed when the leachate was oxidized by Fenton’s reagent with a higher dose of hydrogen peroxide – 69.8% (Fig. 3). The smallest degree of reduction of COD\(_{cr}\) index value was observed using a second dose of Fenton’s reagent – only 54.2%.

Based on the results the change of ratio of BOD\(_5\)/COD\(_{cr}\) indexes in leachate after the purification process was also calculated. It appeared that only the application of Fenton’s reagent with a higher dose of \( H_2O_2 \) led to a slight increase in this ratio (Fig. 4). In the raw leachate the value of BOD\(_5\)/COD\(_{cr}\) ratio was 0.157, whereas after treatment with Fenton’s reagent with a dose of 3.5 g/L this ratio increased to 0.176. The other two oxidation methods caused additional decrease of value of indexes ratio of BOD\(_5\)/COD\(_{cr}\) up to 0.105 (Fenton’s reagent with a dose of 2.0 g H\(_2O_2\)/L).

Differences in the removal of chemically oxidizable organic compounds (COD\(_{cr}\)) and biodegradable compounds (BOD\(_5\)) using described oxidation methods may be due to the formation of various oxidation products after the treatment process.

Provided that biodegradable organic compounds (BOD\(_5\)) contained in the raw leachate were fully oxidized into final products, it can be assumed that the biodegradable organic compounds contained in the treated leachate come from oxidation process – they were intermediate products of oxidation of non-biodegradable organic compounds.
Probably, a portion of non-biodegradable compounds underwent a partial oxidation resulting in the formation of intermediate products, and only some of these compounds were completely oxidized. As intermediate products of both compounds biodegradable and non-biodegradable could be formed (Fig. 5). In the case of Fenton’s reagent with a higher dose of hydrogen peroxide, through a high dose of oxidant so many biodegradable compounds could occur in relation to the non-biodegradable, that there was observed increase of the value of BOD₅/CODₐ in comparison to the raw leachate. However, for the second dose of Fenton’s reagent and UV/H₂O₂ process this phenomenon could not occur. In the case of Fenton’s reagent it could be due to a much lower dose of H₂O₂, which was insufficient to generate enough radicals which oxidize pollutants. While in the case of UV/H₂O₂ process it could be due to a low level of penetration of UV radiation through the treated leachate, what decreased the purification efficiency.
Nutrients removal

During the study the impact of treatment methods on the efficiency of nitrogen and phosphorus removal was also examined.

In the case of nitrogen compounds it has been observed that only the application of Fenton’s reagent decreased the concentration of total nitrogen by several percent (Fig. 6). That reduction of $N_{\text{total}}$ was not observed during leachate treatment by UV/H$_2$O$_2$ method. The difference in removal efficiency of nitrogen compounds could result from the final pH values used after the oxidation process. In the case of Fenton’s reagent after oxidation process the pH was raised up to 8.5 in order to precipitate iron. Because in the leachate phosphate and magnesium ions were also present it may be possible that at this pH value a struvite (magnesium ammonium phosphate) was precipitated.

This allowed to remove ammonium nitrogen as a struvite which was separated from treated leachate as sludge (together with iron sludge). In the case of UV/H$_2$O$_2$ process the pH value was raised only up to 7.0. Under such conditions there is no precipitation of struvite, and therefore there was no significant reduction of nitrogen in leachate.

![Fig. 4. Changes of ratio of BOD$_5$/COD$_{cr}$ during oxidation leachate processes](image4)

![Fig. 5. Scheme of organic compounds transformation during oxidation process](image5)
In the case of phosphorus removal from leachate it was also noted that greater efficiency was achieved when Fenton’s reagent was used (Fig. 7). There was observed almost twice higher efficiency of phosphorus reduction in the case of Fenton’s reagent in comparison with UV/H$_2$O$_2$ process. It has been proved that after oxidation process by Fenton’s reagent a coagulation process takes place. High removal efficiency of phosphorus compounds by Fenton’s reagent results from the coagulation process, which takes place after the oxidation process. Increasing the pH after Fenton’s oxidation up to 8.5 causes precipitation of iron sludge/suspension. During this process the precipitation of phosphorus and phosphorus sorption on precipitate iron sludge take place. In addition, as described earlier, a part of the phosphorus could be removed as struvite.

Fig. 6. Changes of N$_{\text{total}}$ during oxidation leachate processes

Fig. 7. Changes of P$_{\text{total}}$ during oxidation leachate processes
CONCLUSIONS

1. The most effective leachate treatment method for organic compounds removal was Fenton’s reagent with the following parameters: \( \text{H}_{2}\text{O}_2 = 3.5 \text{ g/L}, \text{Fe}^{2+}/\text{H}_2\text{O}_2 = 0.25, \) initial pH 3.0, reaction time 120 minutes, final pH 8.5. The efficiency of organic compounds removal expressed as COD Cr was 69.8% and biochemically oxidizable expressed as BOD 5 index was 72.0%. Moreover, the use of this process has contributed to the increase of the BOD 5/COD Cr indexes ratio in comparison with raw leachate. Thus there was a slight increase of the susceptibility to biochemical degradation of studied leachate.

2. Application of Fenton’s reagent with a lower dose of \( \text{H}_2\text{O}_2 = 2.0 \text{ g/L}, \text{Fe}^{2+}/\text{H}_2\text{O}_2 = 0.4, \) initial pH 4.0, reaction time 90 minutes, final pH 8.5) and the UV/H\text{H}_2\text{O}_2 process did not lead to the increase of leachate biodegradability. In the case of Fenton’s reaction with a dose of 2.0 g H\text{H}_2\text{O}_2/L it could be due to insufficient value of hydrogen peroxide dose. In the case of UV/H\text{H}_2\text{O}_2 process it could be due to turbidity and color of treated leachate, which reduced the effectiveness of UV radiation penetration and reduced oxidative effectiveness.

3. In the case of nutrients removal from leachate a more effective method was Fenton’s reagent in comparison with the UV/H\text{H}_2\text{O}_2 process. Removal of nitrogen compounds (15%) using Fenton’s reagent could be caused by struvite precipitation from leachate. In the case of phosphorus compounds, the removal efficiency achieved over 70%. That effectiveness of P\text{total}_\text{re} removal was possible due to coagulation process. The reason for such an efficiency of phosphorus removal was the process of coagulation, which took place after Fenton’s reaction (increasing pH value up to 8.5 and precipitating iron as sludge).

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PORÓWNANIE EFEKTYWNOŚCI Oczyszczania Odcieków Składowiskowych za Pomocą Metod Pogłębnego Uteniania

Przeprowadzono badania oczyszczania odcieków pochodzących z eksploatowanego od 2004 roku składowiska odpadów za pomocą dwóch metod pogłębnego utleniania. Wykorzystano odczynnik Fentona z dwoma różnymi dawkami nadtlenku wodoru i żela oraz proces UV/H₂O₂. Sprawdzano efektywność usuwania związków organicznych utlenialnych biochemicznie (BZT₅) i chemicznie za pomocą dwuchromianu potasu (ChZTCr) oraz związków biogenicznych (azotu i fosforu). Badania wykazały, że największy stopień usunięcia związków organicznych wyrażonych zarówno jako wskaźnik BZT₅ jak i ChZTCr uzyskano podczas stosowania odczynnika Fentona z większą dawką nadtlenku wodoru – efektywność odpowiednio wyniosła 72% i 69,8%. Ponadto w tym przypadku odnotowano wzrost wartości stosunku BZT₅/ChZTCr w odciekach oczyszczonych w odniesieniu do odcieków surowych. Zastosowanie oczyszczania odcieków odczynnikiem Fentona pozwoliło również na większą skuteczność usuwania związków biogenicznych w porównaniu z procesem UV/H₂O₂.

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