

Application of a modified Fenton method for landfill leachate treatment – a case study

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ABSTRACT

The study analyzed the effect of modification of the dosing method of reagents in the Fenton process and the effect of sequential dosing on the reduction of impurities in leachates. Leachate samples were collected from a landfill in Janczyce (Świętokrzyskie Voivodeship), which is a part of the municipal waste disposal plant in Janczyce. Tests were carried out at the initial process pH value of 4 (correction with concentrated H_2SO_4) for various doses of Fe^{2+} catalyst (Fe^{2+} dose within the range of 600–1,400 $mg\ L^{-1}$) at $20^\circ C \pm 1^\circ C$. The effect of oxidant dosing was investigated in different configurations for Fe^{2+} relations: H_2O_2 ratio of 1:8. Prior to and following the treatment process, the values of *inter alia* chemical oxygen demand (COD), total organic carbon (TOC), and selected elements including heavy metals in the leachate were studied. The maximum decrease in the COD indicator was as much as 81.1%, and was obtained in the series for which the conventional Fenton process excluding the sequential dosing at a H_2O_2 dose of 8,000 $mg\ H_2O_2\ L^{-1}$ was run. The maximum decrease in the TOC indicator was as much as 72.6% for 11,200 $mg\ H_2O_2\ L^{-1}$. This time, however, a better result was noted for the series in which the modification was implemented by means of hydrogen peroxide sequencing dosing. It was demonstrated that oxidant sequencing at a constant catalyst dose results in substantial improvement in elimination of TOC in treated leachate samples compared with the results obtained for the reference sample. Significant increase in electrolytic conductivity or improvement in heavy metal removal were not observed.

Keywords: Landfill leachate; AOP; Fenton's reaction; Wastewater treatment

1. Introduction

Every functioning civilization generates waste that needs to be managed. Waste disposal methods include recycling, organic waste composting, biomass anaerobic fermentation, incineration or landfilling. Actions are carried out, at the national level, regional, and local, aimed at reducing the environmental impact (nuisance) of waste and human health and the most efficient use of resources. Despite so many waste management methods, landfilling is still the most

popular one worldwide [1,2]. The amount of waste generated each year is maintained at a similar level, with steady GDP growth, which may indicate positive trends in waste management. In 2004 in Poland, almost 97% of non-hazardous and non-neutral waste were disposed by means of landfilling. On the other hand, in 2014 in the EU, as much as 31% of waste were disposed by means of landfilling. But in 2017, out of the total amount of municipal waste generated in the European Union, 30% was subject to material recycling, 29% was thermally disposed of, 23% was disposed of

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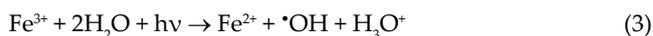
by landfill, 17% was composted. In Poland, 7.1 million tons of municipal waste collected and collected in 2018 were destined for recovery. On the other hand, a total of 5.4 million tons was sent to disposal processes, of which 5.2 million tons (approximately 42% of the municipal waste generated) was destined for storage [3–7].

A waste landfill, both during its operation and following its closure, affects the environment in many ways due to the physical, chemical, and biological transformations occurring within. In addition to emissions of landfill gases, odors, microorganisms, or noise, the resulting landfill leachate deserves special attention. Leachate means “any liquid percolating through the deposited waste and emitted from or contained within a landfill” [8]. It is estimated that the landfilling of 1×10^3 kg t of municipal waste generates from $(0.05\text{--}0.2) \times 10^3$ kg t of landfill leachate [9]. The substances found in landfill leachate originate *inter alia* from fermentation processes and, to a lesser extent, from the dissolution of waste constituents. In certain cases, contaminant concentrations are high; this refers to organic substances, nitrogen compounds, and salinity. In addition, leachate contains potentially hazardous organic substances including heavy metals, chloro-organic compounds, alkyl aromatic hydrocarbons, polycyclic aromatic hydrocarbons, and phthalates. Highly concentrated leachate waters require specialized treatment. When selecting a leachate treatment technology, for example, the changing chemical composition and the volume of leachate need to be taken into account. Moreover, it is necessary to maintain the minimum leachate treatment costs which include *inter alia* the cost of purchasing chemicals, costs of waste treatment plant operation and maintenance, electricity and utility costs, etc. It is also of significance to make maximum use of the existing landfill potential [10]. Conventional waste treatment methods have also been employed for many years for the treatment of landfill leachates. These methods can be generally divided into [1,2,11]: mechanical, biological, chemical, physico-chemical, and combinations of the methods mentioned. Moreover, in order to pre-treat waste and reduce its volume, leachate recirculation onto a landfilled waste pile can be applied [11,12]. However, these methods often fail to satisfactorily eliminate the contaminants found in the leachate, particularly non-biodegradable ones [1,9,13]. An alternative to the conventional treatment methods includes advanced oxidation processes (AOPs) [1,10,13]. A common characteristic of the AOPs is the use of the oxidative potential of $\cdot\text{OH}$ hydroxyl radicals. The generated free hydrogen radicals are non-selective, have a very high oxidative potential (ranging from 1.95 V at the pH of 14–2.80 V at the pH of 0), and the reaction rate, k , amounts to $10^8\text{--}10^{10}$ L mol⁻¹ s⁻¹. For comparison, ozone (O_3) has the oxidative potential of 2.07 V and decomposes organic compounds with the reaction rate constant of $10^0\text{--}10^3$ L mol⁻¹ s⁻¹ [14]. Currently, many processes of the AOPs group are known, including *inter alia* in the homogeneous phase with exposure (O_3/UV , $\text{H}_2\text{O}_2/\text{UV}$, $\text{H}_2\text{O}_2/\text{ultrasounds}$) and without exposure ($\text{O}_3/\text{H}_2\text{O}_2$, O_3/OH^- , $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ – Fenton’s reagent), and in the heterogeneous phase with exposure ($\text{TiO}_2/\text{O}_2/\text{UV}$, $\text{TiO}_2/\text{H}_2\text{O}_2/\text{UV}$) and without exposure (electro-Fenton). Given the numerous advantages (low costs, non-toxicity of Fe^{2+} and H_2O_2 , the ease of running the process, low energy inputs for the

generation of H_2O_2 , no need for UV exposure, high non-selectivity of the $\cdot\text{OH}$ radical, and the elimination of a number of contaminants), the Fenton process is the most popular among the AOPs methods. One of the few disadvantages of this process is the generation of waste which needs to be properly managed. Fenton process involves the formation of hydroxyl radicals $\cdot\text{OH}$ in an acidic environment ($\text{pH} < 5$) as a result of the reaction between Fe^{2+} ions with H_2O_2 (1). The formed Fe^{3+} ions undergo further reactions which result in the restoration of Fe^{2+} ions (2) [13–15]. As for the conventional Fenton process, the method comprises four stages [16]: bringing wastewater to an appropriate pH, the reaction of organic compound oxidation, wastewater neutralization, and the elimination of resulting sediments.



The Fenton process efficiency may be enhanced by modifying the method. The conventional UV-assisted Fenton’s reaction ($\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$) is a photocatalytic Fenton’s reaction (UV-Fenton) [17]. UV radiation regenerates the Fe^{2+} ions, and additional $\cdot\text{OH}$ radicals are formed (3).



The main disadvantages of the UV-Fenton reaction include energy costs and operational problems (e.g., maintaining lamp cleanliness). In addition, the application of the method is limited where wastewater is highly colored or turbid.

In order to reduce the amount of iron ions required for the oxidation process, a reaction using electrochemical processes in the Fenton’s reaction (the electro-Fenton (EF) method) is also applied. Hydrogen peroxide in the electro-Fenton process may be generated on a continuous basis on an appropriate cathode (4). On the other hand, Fe^{2+} is still electro-generated by the Fe^{3+} reduction (5). The electro-Fenton requires pre-acidification of the leachate to the pH of approximately 3.0; as a result of an 8 h process, Fernandes et al. [10] obtained a 40% reduction in the chemical oxygen demand (COD) content at the initial value of 42 g L⁻¹.



The literature also provides examples of running the Fenton process supported by coagulation. According to Gawdzik et al. [18], an effective agent that supports the removal of contaminants is hard coal fly ash. Such an ash serves as an agent supporting the flocculation process. Sorption using ashes and zeolites synthesized from these ashes is considerably efficient in eliminating copper, lead, and organic compounds from the analyzed leachate samples [19]. Ashes obtained from sewage sludge have a highly stable composition, and the heavy metals they contain occur in immobile forms which significantly affects the wastewater being treated [20].

Sequential dosing in the Fenton reaction can be found in the literature in various categories. Mortazavi et al. [21] used sequence Fenton reaction for decreasing phenol formation during benzene chemical conversion in aqueous solutions. Sequence-Fenton reaction was conducted by a sequent H_2O_2 injection in the vials. H_2O_2 oxidant was added to the vial in two steps. Firstly, 200 mL L^{-1} of H_2O_2 (10%) was injected to the vial which contained benzene (870 mg L^{-1}) and FeSO_4 (1 g L^{-1}). After 90 min, different volumes of H_2O_2 were added to vials which contained the reaction products of the first stage. The research carried out showed almost complete mineralization benzene and phenol, but the response time and volume of H_2O_2 were greater than a conventional Fenton reaction. While in the work of Mohanty and Wei [22], sequential dosing was used to remove 2.4 dinitrotoluene (2.4 DNT). To study the effect of sequential addition in detail, three experiments were performed by varying the combination of the addition of oxidant/catalyst (1): H_2O_2 applied in 20 equal steps; (2): Fe^{2+} applied in 20 equal steps, and (2): H_2O_2 and Fe^{2+} applied initially in a single dose. Application of H_2O_2 sequentially rather than one single dose was observed to achieve better oxidation. The presence of oxygen in the reaction mixture decreased the concentration of reaction end products. The total organic carbon (TOC) removal showed that about 30% of the initial TOC could not be removed at a molar ratio of 20:1:2.5 (H_2O_2 :DNT: Fe^{2+}).

Therefore, the authors decided to test the effectiveness of sequential dosing on a more complex matrix – landfill leachate

The conventional Fenton process efficiency may also be increased by the optimization of basic process parameters and the reagents dosing method. As regards the Fenton process, the optimum pH of the process which obtains the best effects in the elimination of contaminants is an acidic pH falling within the range of 2–5 [23,24]. The main chemical reagents used in the Fenton's reaction include hydrogen peroxide and iron(II) ions. An increase in the H_2O_2 dose results in better effects of the contaminant oxidation process, but too high a dose of H_2O_2 in relation to the substrate may cause the $\cdot\text{OH}$ radical binding by H_2O_2 . Moreover, the unused portion of hydrogen peroxide results in an overvaluation of the COD being determined (in a reaction with strong oxidants, for example, potassium dichromate used to determine the COD, hydrogen peroxide acts as a reducing agent). In such a case, it is necessary to check on the residual H_2O_2 content in the treated wastewater. Where the residual H_2O_2 content is found, the COD value needs to be corrected using the following formula [25]:

$$\text{COD} = \text{COD}_M - df \quad \text{mg L}^{-1} \quad (6)$$

COD_M – COD value obtained from titration, mg L^{-1} ; d – residual H_2O_2 concentration in the sample, mg L^{-1} ; f – correction factor of 0.25 (for the range of 20–1,000 $\text{mg H}_2\text{O}_2 \text{ L}^{-1}$).

The rate of contaminant degradation in wastewater is also determined by the Fe^{2+} ion concentration and increases with an increase in Fe^{2+} concentration. Therefore, for each type of landfill leachate, it is necessary to conduct testing on a laboratory scale to determine the optimum doses and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ relations [23]. A high molar ratio above

the stoichiometric reduction may be associated with the formation of a number of side reactions which affect the Fenton's reaction efficiency [24]. According to the research carried out by Barbusiński [17], calcium peroxides (CaO_2), and magnesium peroxides (MgO_2) may be used as an alternative source of H_2O_2 in the Fenton reaction. Another source of hydrogen peroxide may be sodium percarbonate ($2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$). Its advantages include its solid form, which makes it easier to transport and can be used in a wider pH range compared to hydrogen peroxide. When mixed with water, sodium percarbonate can disassociate to hydrogen peroxide and sodium carbonate [26]. Research conducted by Muszyńska et al. [27] demonstrated that sodium percarbonate can be used as an effective alternative to hydrogen peroxide as an oxidant in the Fenton process in leachate treatment. With an optimal catalyst/oxidant ratio of 0.33 and a hydrogen peroxide dose of $7,200 \text{ mg L}^{-1}$, a reduction of more than 50% in the TOC and COD was achieved (the initial value in the leachate was 854 mg L^{-1} for TOC and $3,832 \text{ mg L}^{-1}$ for COD). The best possible process duration of 60 min has been found. It has been proven that the process modified with sodium percarbonate may be effective already at $\text{pH} = 4$. Whereas Pieczykolan et al. [28] applied a modification of the Fenton process with sodium percarbonate as an oxidant for the treatment of sewage containing Acid Green 16 (concentration 100 mg L^{-1}). The process was additionally carried out using UV radiation (low-pressure UV lamp – system I and medium-pressure UV lamp – system II). As a result of the process at $\text{pH} = 3$ the dye content was reduced below 1 mg L^{-1} for sodium percarbonate dose and Fe^{2+} percarbonate ratio of 400 mg L^{-1} and 0.2 (system I) and 200 mg L^{-1} and 0.33 (system II), respectively.

The aim of the study was to comparatively analyze the efficiency of landfill leachate treatment using H_2O_2 oxidation, the conventional Fenton process, and Fenton process with reagent dosage modification.

2. Research scope and methodology

The study on the Fenton process with reagent dosage modification and the effect of sequential dosing in the Fenton process on the contaminant reduction in leachate was conducted on a laboratory scale. The leachate samples were collected and stored, and their chemical composition was studied in accordance with the existing standards PN-ISO 5667-10:1997 [29]. Leachate samples were collected from a landfill in Janczyce (Świętokrzyskie Voivodeship), which is a part of the municipal waste disposal plant in Janczyce. The waste disposal plant in Janczyce has been operating since 2003, and provides services to approximately 150,000 inhabitants. Apart from landfill sites, it includes a mechanical waste processing system and a composting plant. On the landfill (3.64 ha), waste after mechanical processing of mixed municipal waste, sorting remnants, and other non-recyclable waste are deposited. According to estimates, 293 kg waste/inhabitant per year are generated in the region. During the year, the landfill operation generates an average of $6,695 \text{ m}^3$ leachate.

Laboratory tests for the landfill leachate pre-treatment were carried out on leachate samples with a volume of 0.6 L (the sample volume was selected in such a way that

all the parameters being determined could be analyzed). In the tests, the following analytical grade reagents were used: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (used as a 5% solution and converted into a Fe^{2+} dose), 30% H_2O_2 , H_2SO_4 (concentration of 98%), $\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$ (applied in a solid form), and KOH (10%).

In the Fenton process at the Fe^{2+} to H_2O_2 ratio as well as the Fe^{2+} to $\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$ ratio of 1:8, the effect of Fenton process modification was studied. Tests were carried out at the initial process pH value of 4 (correction with concentrated H_2SO_4) for various doses of Fe^{2+} catalyst (Fe^{2+} dose within the range of 600–1,400 mg L^{-1}) at $20^\circ\text{C} \pm 1^\circ\text{C}$. After the pre-defined oxidation time (120 min – the mixing rate during the reaction of 50 revolutions/min) in a Conbest JLT6 flocculator, the samples were neutralized with 10% KOH to the pH of approximately 7.5. Then, the leachate was mixed for 30 min at a rate of 10 revolutions/min, and afterwards sedimented for 30 min. After this stage, the effect of H_2O_2 dosing depending on its dosing duration and the dose with the $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ relation of 1:8 was analyzed. The process was carried out in the following configurations:

- only an H_2O_2 dose was administered (basic oxidation process – A)
- an entire Fe^{2+} and $\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$ dose was added at once (B)
- an entire Fe^{2+} and H_2O_2 dose was added at once (C),
- an entire Fe^{2+} dose was added at once, and an H_2O_2 dose was added in four equal portions every 30 min (D),
- a Fe^{2+} and H_2O_2 dose was added in four equal portions every 30 min (E),
- an entire Fe^{2+} dose was added at once, and an H_2O_2 dose was added in 4 portions with variable dosing time: at once, after 15 min, after 45 min, and after 105 min (the time was measured from the beginning of the process – F),
- an Fe^{2+} and H_2O_2 dose was added in four portions with variable dosing time: at once, after 15 min, after 45 min, and after 105 min (the time was measured from the beginning of the process – G).

Both prior to and following the treatment process, the contents of the following were determined: COD, TOC, selected elements including heavy metals (Al, Ca, Cd, Cu, Cr, Fe, Mg, Na, Ni, K, Pb, and Zn), and their pH, specific conductance, total amount of dissolved substances, salinity, temperature, and the potential were measured. All analyses were conducted in line with the existing standards:

- chemical oxygen demand was determined by the Spectroquant photometric method – determination by cuvette tests using a Merck Spectroquant Nova 60 spectrophotometer after pre-heating in a Merck TR 320 thermoreactor (Merck, Darmstadt, Germany) (120 min at 148°C); depending on the method, the limit of quantification was 10–10,000 mg L^{-1} [30],
- total organic carbon was determined by the UV oxidation with peroxydisulphate method using a StarTOC System apparatus according to PN-EN 1484:1999 [31], depending on the method, the limit of quantification was 50 ppb–1,000 ppm,
- the pH was determined by potentiometric method using a pH meter according to PN-EN ISO 10523:2012 [32],

- total dissolved solids, temperature, and specific conductance were determined using a Mettler Toledo Seven Multi pH meter/conductometer (Greifensee, Switzerland),
- Al, Ca, Cd, Cu, Cr, Fe, Mg, Ni, Pb, and Zn were determined using a Perkin Elmer Optima 8000, (Waltham, MA, USA) ICP inductively coupled plasma optical emission spectrometer according to PN-EN ISO 11885:2009 [33] after previous aqua regia digestion according to PN-EN ISO 15587-1:2005 [34], the limit of quantification ranged from 0.01 to 0.1 ppb.

3. Study results and analysis

For the study, a landfill leachate sample originating from municipal landfill in Janczyce (Świętokrzyskie Voivodeship, Poland) was used. Initially, the landfill leachate susceptibility to oxidation with hydrogen peroxide and sodium percarbonate during a reaction duration of 120 min at the pH of 4.0 was checked (basic oxidation process – A and B). The experiment was repeated with an addition of a catalyst in the form of an iron(II) salt with the catalyst/oxidant mass relation of 1:8. The experiment results are presented in Figs. 1–3 and in Table 1. In raw landfill leachate, the COD value was $(2,859 \pm 12)$ mg L^{-1} , TOC (789 ± 1) mg L^{-1} , and specific conductance (6.89 ± 0.01) mS cm^{-1} . The pH of raw leachate was relatively low: 6.794 ± 0.003 , respectively. During the tests in the A, C, D, E, F, and G series, hydrogen peroxide doses were used, while in the B series, doses of sodium percarbonate ranging from 4,800 to 11,200 were used (Fig. 1).

In the B, C, D, E, F, and G series, catalytic oxidant decomposition using H_2O_2 in doses of 4,800–11,200 mg L^{-1} and was carried out. It was observed that with an increase in the oxidant dose, only a slight decrease in the leachate COD value was obtained. The greatest increase in the COD removal efficiency was observed during increasing this reagent dose from 6,400 to 8,000 mg L^{-1} for the B series (Fig. 1). At this time, the waste COD decreased from 1,740 to 1,420 $\text{mg O}_2 \text{ L}^{-1}$. The maximum decrease in the COD indicator was as much as 81.1%, and was obtained in the C series for which the conventional Fenton process excluding the sequential dosing at a H_2O_2 dose of 8,000 mg L^{-1} was run. For lower oxidant doses, the results obtained for the COD were no longer as promising (Fig. 1). Similarly, increasing the oxidant dose and, thus, the catalyst dose did not enhance the effect of leachate remediation for the COD being measured. In this case, the COD of 550 mg L^{-1} for a dose of 11,200 mg L^{-1} was obtained, which is a significantly better result than that for the other measurement series, including the D series. The study results indicate that parallel sequencing of both the oxidant and catalyst is not justified. The results obtained for the E, F, and G series is the elimination of COD at the levels of 66.4%, 68.9%, and 65.7%, respectively. For the most advantageous variant in the F series, the leachate COD of 890 $\text{mg O}_2 \text{ L}^{-1}$ was obtained, with a rather high catalyst dose, that is, 1,400 $\text{mg of Fe}^{2+} \text{ L}^{-1}$ and 11,200 $\text{mg of H}_2\text{O}_2 \text{ L}^{-1}$ (!) being required. A certain but small improvement can be noted by taking the TOC assessment as the starting point (Fig. 2).

As was the case above, the worst remediation results were obtained for the A series. The maximum TOC elimination degree in this case is 9%, and it decreases with an

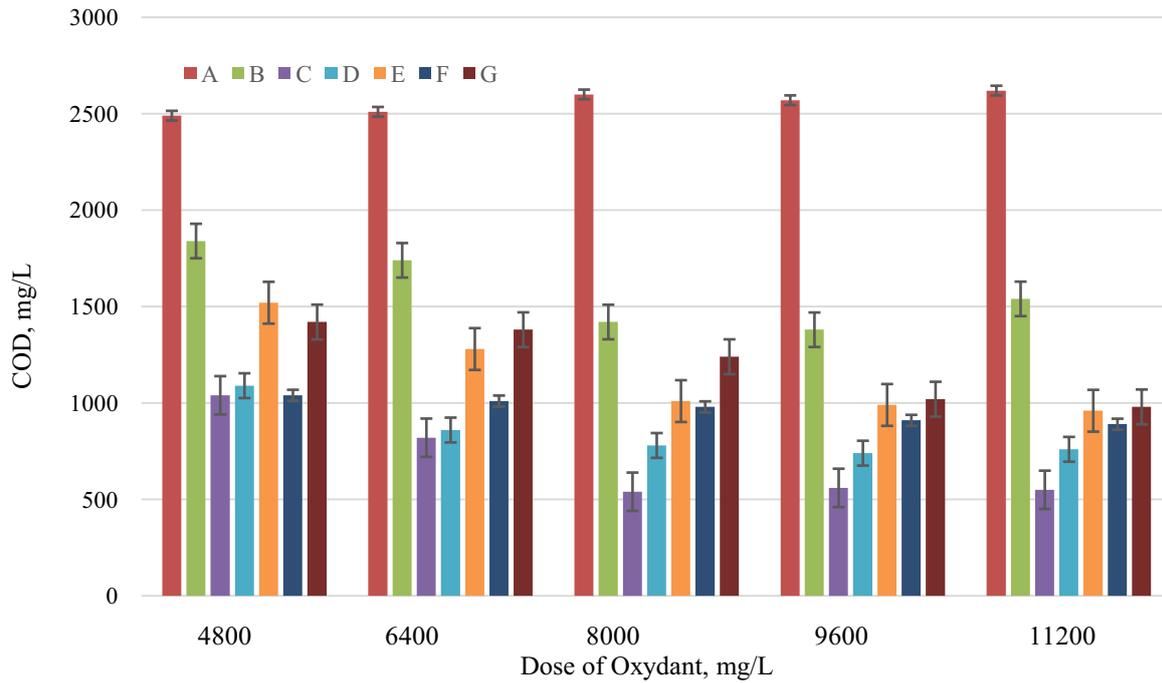


Fig. 1. Effect of oxidant dose on the leachate COD ($\alpha = 0.05$; $df = 4$).

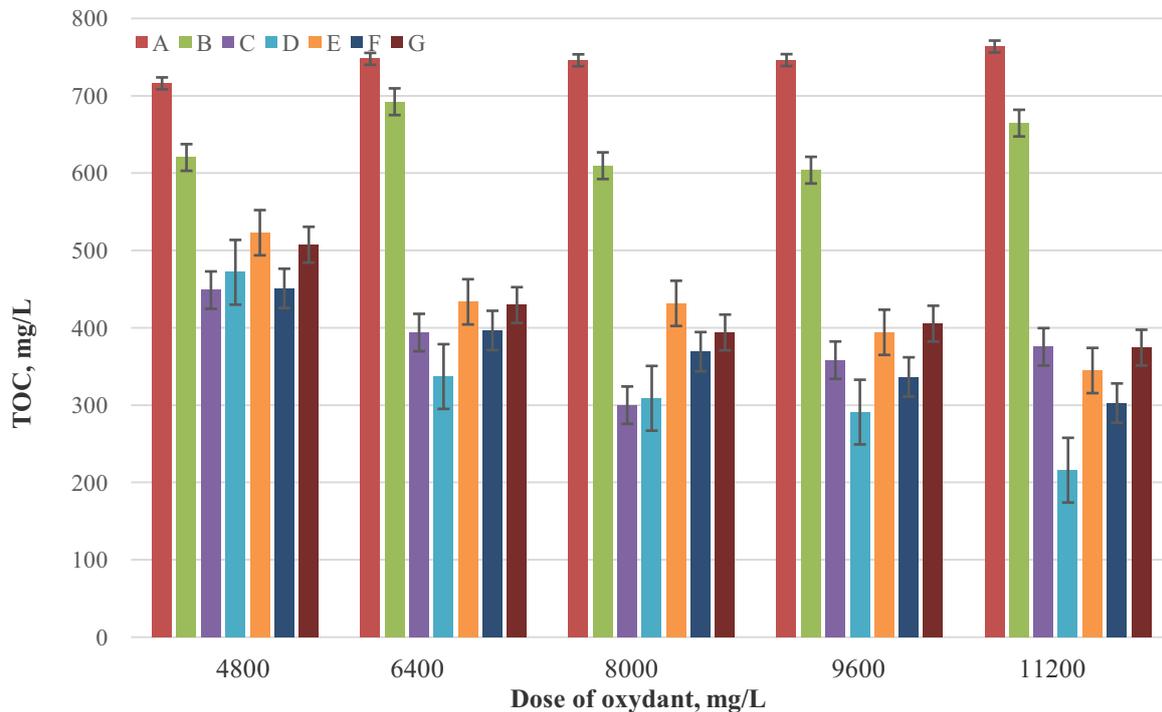


Fig. 2. Effect of oxidant dose on the leachate TOC ($\alpha = 0.05$; $df = 4$).

increase in the hydrogen peroxide dose. Considerably better results were obtained by running the Fenton process modified with sodium percarbonate.

For the B series, a 23.5% level of TOC elimination at an oxidant dose of 8,000 mg L⁻¹ was noted. In the conventionally run Fenton process for the C series, a 62% level of TOC

elimination at a dose of 8,000 mg H₂O₂ L⁻¹ was obtained (Fig. 2). This time, however, a better result was noted for the D series in which the modification was implemented by means of hydrogen peroxide sequencing dosing. Thus, at a dose of 9,600 mg H₂O₂ L⁻¹, a 63% TOC reduction was obtained, while at a dose of 11,200 mg H₂O₂ L⁻¹, a 72.6% reduction

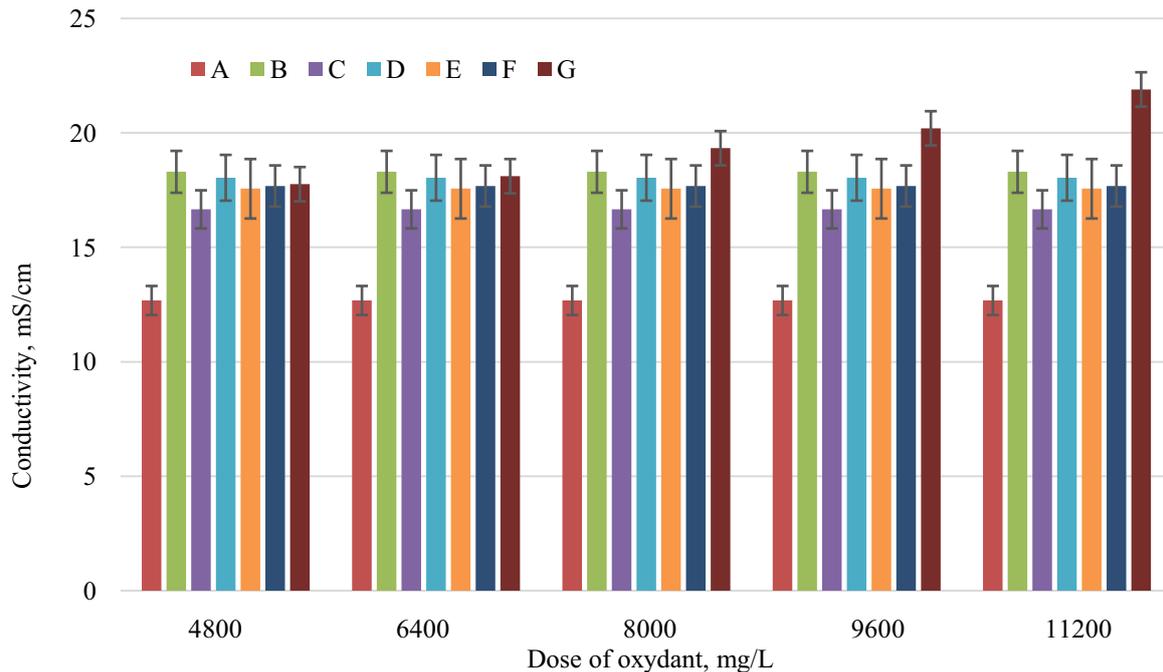


Fig. 3. Effect of oxidant dose on specific conductance of leachate ($\alpha = 0.05$; $df = 4$).

was obtained. Significantly poorer remediation effects were obtained for the E and G series. The levels of 56% and 53%, respectively, were only obtained at the maximum hydrogen peroxide concentration. A very even and rather good effect of the TOC removal was noted for the F series where the entire Fe^{2+} dose was added at once, and an H_2O_2 dose was added in four portions with variable dosing time: at once, after 15 min, after 45 min, and after 105 min. It was not statistically demonstrated, however, that the results obtained for the F series were, in this case, better than those for the C series. The maximum effect of the TOC removal was obtained in the C series at a significantly smaller dose than that for the F series. There is a possibility that at higher catalyst doses, an improvement in the remediation effect would be possible, and the results obtained for the F series would be competitive. However, it is important to bear in mind that the permeate specific conductance significantly increases (Fig. 3). This value is related to the catalyst dose, with the trend towards an increase in conductivity as a function of the Fe^{2+} content becoming evident (Fig. 3). Thus, in the total absence of the catalyst (the A series), the obtained conductance values are significantly lower than those for the other cases (Fig. 3). At this point, the main disadvantage of the Fenton method due to the significant increase in leachate salinity is clearly noticeable. Table 1 presents the determination results for selected metals in raw and treated leachate.

What is worth noting here is the general trend toward a decrease in the metal content following the Fenton process. Even for the A series which used only hydrogen peroxide, the selected metal contents, in particular that of total iron, decreased. For the other cases, even better improvement in the leachate composition in this aspect was obtained. The highest efficiency of iron removal was noted for the D series.

Table 2 presents the paired difference test results for the set of series illustrated in Figs. 1–3.

It was demonstrated that the results obtained in the Fenton process run in the system where both the catalyst and the oxidant entire doses were administered at once (the C series), and in the process with modified oxidant dosing, where the entire Fe^{2+} dose was added at once, and the H_2O_2 dose was added in four equal portions every 30 min (the D series) yielded the best results at a wide dose spectrum. The advantage of the method implemented according to the D scenario involves the lower total organic carbon content in the treated wastewater and is statistically significant ($t = 2.49$; Table 2). In this case, the lowest heavy metal content was noted as well. Only the values which satisfied the Grubbs criterion at $P = 95\%$ were selected for the test.

4. Summary

Landfill operation generates emissions of contaminants, including landfill leachate, which may pose a hazard to the environment. AOPs enable effective mineralization of refractory organic compounds resistant to biodegradation and toxic to humans and the natural environment, provided that the control parameters of the process are properly selected. Highly concentrated landfill leachate requires specialized treatment, and when selecting a treatment technology, for example, the changing chemical composition and the volume of leachate, as well as the capital intensity of the method, need to be taken into account. Advanced oxidation methods which include the Fenton process have increasingly been becoming an alternative to conventional treatment methods. In recent years, more and more studies on modifications of the conventional Fenton method by changing the oxidant, catalyst, or the reagent

Table 1
Content of mg L⁻¹ of metals in leachate samples before and after the Fenton process

Sample		Cu	Cr	Ni	Zn	Mn	Fe	Al
Raw	Mean	0.1389	0.0943	0.0674	0.7670	0.7772	24.492	0.7127
	Minimum	0.1388	0.0941	0.0670	0.7666	0.7770	24.488	0.7122
	Maximum	0.1391	0.0944	0.0678	0.7672	0.7775	24.511	0.7128
	Median	0.1389	0.0942	0.0672	0.7671	0.7772	24.489	0.7125
A	Mean	0.1203	0.0862	0.0552	0.3378	0.4685	4.5352	0.6089
	Minimum	0.1166	0.0794	0.0551	0.3198	0.4666	4.3417	0.6033
	Maximum	0.1207	0.0881	0.0557	0.3710	0.4701	4.7191	0.6487
	Median	0.1191	0.0850	0.0553	0.3301	0.4690	4.5348	0.6092
B	Mean	0.0485	0.0595	0.0547	0.2652	0.4255	4.5833	0.1865
	Minimum	0.0331	0.0538	0.0537	0.2501	0.3758	4.4101	0.0949
	Maximum	0.0534	0.0622	0.0566	0.3076	0.4752	4.6954	0.1001
	Median	0.0379	0.0619	0.0550	0.3013	0.4253	4.5693	0.1192
C	Mean	0.0169	0.0183	0.0238	0.1450	0.0297	1.9039	0.1405
	Minimum	0.0138	0.0165	0.0222	0.1075	0.0191	1.5003	0.2179
	Maximum	0.0286	0.0190	0.0252	0.1482	0.0193	2.5705	0.2035
	Median	0.0166	0.0171	0.0231	0.2284	0.0273	2.0121	0.1492
D	Mean	0.0289	0.0192	0.0172	0.0595	0.0241	0.4335	0.2205
	Minimum	0.0118	0.0164	0.0128	0.0540	0.0222	0.2687	0.1651
	Maximum	0.0330	0.0207	0.0171	0.0706	0.0251	0.4927	0.2205
	Median	0.0177	0.0188	0.0180	0.0596	0.0235	0.4361	0.2210
E	Mean	0.0171	0.0249	0.0180	0.0967	0.0165	0.6670	0.1746
	Minimum	0.0118	0.0211	0.0166	0.0736	0.0152	0.5142	0.1478
	Maximum	0.0264	0.0265	0.0186	0.1182	0.0288	0.7437	0.1765
	Median	0.0180	0.0225	0.0169	0.0951	0.0167	0.6493	0.1759
F	Mean	0.0213	0.0233	0.0233	0.0876	0.0198	1.0218	0.1665
	Minimum	0.0172	0.0208	0.0208	0.0548	0.0179	0.7639	0.1639
	Maximum	0.0546	0.0263	0.0263	0.0910	0.0272	1.9735	0.1826
	Median	0.0200	0.0224	0.0224	0.0617	0.0197	1.0532	0.1662
G	Mean	0.0324	0.0284	0.0170	0.0729	0.0163	0.6742	0.1648
	Minimum	0.0229	0.0255	0.0136	0.0571	0.0144	0.3020	0.1417
	Maximum	0.0352	0.0284	0.0216	0.0816	0.0180	0.9684	0.1870
	Median	0.0272	0.0277	0.0169	0.0711	0.0162	0.6848	0.1642

Table 2
Value of the t_{exp} parameter for Student's t -test of differences in par $\{\alpha = 0.05, t_{crit} = 2.13\}$

Couple/indicator	COD	TOC	κ
{C vs. A}	3.1	6.35	5.12
{C vs. B}	1.71	2.23	1.19
{C vs. G}	2.22	2.31	1.15
{C vs. D}	3.47	2.49	1.31
{C vs. E}	3.19	5.39	1.17
{C vs. F}	2.05	1.99	1.20

dosing method have been being published. In the presented study, the authors compared the selected modifications of the Fenton process applied for the remediation of landfill leachate originating from a selected landfill of non-neutral and non-hazardous municipal waste, located in central

Poland. The decontamination efficiency was determined by assessing the COD and TOC indicators in the leachate following the treatment process. Moreover, selected metal contents and specific conductance were determined. The study showed that the lowest efficiency of landfill leachate treatment was achieved with hydrogen peroxide only. High efficiency of landfill leachate remediation was ensured by the application of the Fenton process, and the best one – its modification using the sequential dosage method while H₂O₂ dose was added in four equal portions every 30 min. It was demonstrated that the main disadvantage of Fenton's method was a significant increase in the leachate specific conductance. A decrease in metal contents in relation to raw leachate was noted. It was statistically demonstrated that the Fenton's method using linear sequential dosing of the oxidant enabled obtaining the highest degree of total organic content elimination from landfill leachate for the selected measurement series. However, it should be stressed that in no case has it been possible to reduce the COD values below

125 mg L⁻¹, so that the wastewater treated in this way can be discharged directly into the receiver. It seems, however, that the improvement in the effectiveness of remediation in the Fenton process, obtained by sequencing the oxidant, may be insufficient in relation to potential problems related to the necessity of precise selection of doses in the set time intervals.

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