



Removal of organic compounds from landfill leachate by Fenton process in combination with acidification, precipitation, and lime coagulation

Jacek Leszczyński

Białystok University of Technology, 45E Wiejska Str., 15-351 Białystok, Poland, email: j.leszczyński@pb.edu.pl (J. Leszczyński)

Received 28 September 2019; Accepted 16 February 2020

ABSTRACT

This paper presents research aimed at comparing the efficiency of organic compound removal from landfill leachates using acidification and precipitation, lime coagulation, and FeSO_4 in combination with highly efficient Fenton oxidation. The tested leachate originated from a stabilized solid waste landfill characterized by high salinity and a significant content of organic pollutants expressed as the chemical oxygen demand (COD) indicator. The research was carried out using variable dose reagents in the coagulation process as well as hydrogen peroxide and iron in the Fenton method. The precipitation process was carried out in leachate samples in the pH range of 1.6–2. Basic analytical tests included the measurements of color, COD, total organic carbon (TOC), $\text{UV}_{254\text{nm}}$ absorbance, 16 PAH (polycyclic aromatic hydrocarbons), and selected heavy metals in raw waste. The obtained results indicate the possibility of the effective removal of impurities using CaO , FeSO_4 coagulation, and the Fenton method. Relatively high efficiency of removing organic compounds from the effluents that was obtained after the acidification process, where there is intensive precipitation of the suspension at a pH below 2. After removing the precipitate, decreases in color, COD and TOC, and $\text{UV}_{254\text{nm}}$ absorbance were obtained by 55.1%, 32.3%, 27.4%, and 41.9%, respectively. In addition, in such treated effluents, an increase in the efficiency of Fenton impurities removal has been recorded. In this case the COD reduction was 82%, TOC 77%, and $\text{UV}_{254\text{nm}}$ 89.6%. Slightly higher removal efficiency of color 98.8% and COD 82.7% was observed only in the Fenton process after lime coagulation.

Keywords: Landfill leachate; Fenton process; Acidification and precipitation; Humic acids, Coagulation; Combined treatment

1. Introduction

Storage of municipal waste leads to the production of leachates that arise during the migration of rainwater and snowmelt by a waste layer. The dissolved and suspended fractions of wastes from both mineral and organic origin get into the effluent [1,2]. Some of these admixtures are, among others, pesticides, phthalates, phenols, heavy metals, aromatic hydrocarbons, and aliphatic hydrocarbons. An important group of pollutants considered dangerous are the so-called xenobiotic substances, which include, among others, polycyclic aromatic hydrocarbons (PAHs), benzene, toluene, ethylbenzene, and xylene, chlorinated aliphatic and

aromatic compounds as well as polychlorinated biphenyls. Therefore, landfill leachate should be considered a heavily polluted wastewater that may pose a direct or indirect threat to water systems [3,4].

The quality of the leachate is influenced by many factors such as; the type of waste and its composition, the age of the landfill, and seasonal weather changes. Leachates from young landfills, for which their operating time usually does not exceed 5 y, are characterized by a high content of organic pollutants. Biochemical oxygen demand (BOD) values of such leachates are most often range from 3 to 24 g/L and COD 3 to 60 g/L. The organic compounds presented

in this type of leachate, due to the BOD/COD ratio in the range of 0.4–0.7, show fairly good biodegradability [5]. As the landfill gets older, the transformation of biodegradable organic compounds occurs, which leads to the stabilization of leachate composition. Therefore, in these types of leachate, organic substances with a higher molecular weight resistant to biodegradation prevail. Humus type components constitute an important group of these substances. The leachates from the stabilized storage site are characterized by a BOD/COD ratio below 0.1 [3,6,7]. In leachate from old landfills, the concentration of heavy metals is relatively low, while they are usually heavily contaminated with ammonia resulting from the hydrolysis and fermentation of nitrogen-containing waste fractions [8].

Characterization of the landfill leachate is the fundamental step leading to the selection of efficient treatment techniques. The relationship between the age of the landfill and the composition of organic matter can be a useful criterion for choosing the appropriate treatment process. For the treatment of leachate, physical, and chemical processes are used for purification, mainly coagulation/flocculation, adsorption, chemical oxidation, precipitation, biological, and membrane methods [9–11]. Iron salts, mainly iron(III) chloride, iron(III) sulfate, and less often aluminum sulfate or aluminum polychloride, are used most often as coagulants [12–14]. Biological processes are mainly intended for the purification of leachates characterized by higher BOD/COD ratios, that is, those originating from young landfills [15,16].

Advanced oxidation processes (AOPs) for landfill leachate treatment have received a great deal of attention in recent decades. These methods rely on the formation of highly reactive free radicals. The basic methods of generating free radicals are based on chemical and photochemical processes. The main chemical processes are the combination of ozone with hydrogen peroxide and the Fenton reaction. In most photochemical methods, UV radiation is used in combination with ozone, hydrogen peroxide, Fenton reaction, and mutual combinations of these methods. In addition, persulfates and catalysts with semiconductor properties, mainly TiO_2 , are used to generate free radicals. The HO^\bullet and $\text{SO}_4^{\bullet-}$ radicals are characterized by a high oxidation–reduction potential; they act non-selectively and quickly react with many organic compounds, including those resistant to biodegradation and toxic refractive compounds. In addition, AOPs are effective methods for purifying leachate from landfills, the purpose of which is to degrade organic matter [2,10,13,17].

Fenton reaction is one of the most popular oxidation processes, in which Fe^{2+} ions react with hydrogen peroxide forming the HO^\bullet radical according to the reactions (Eqs. (1) and (2)) [18,19].



The resulting Fe^{3+} can be re-converted to Fe^{2+} , while the HO^\bullet can react with Fe^{2+} (Eqs. (3) and (4)).



This process does not require specialized equipment and is characterized by high efficiency of degradation of organic pollutants. As a result of oxidation, some organic compounds are converted into more readily biodegradable forms which allow their further purification using biological methods [6]. Degradation of organic compounds in the Fenton process depends mainly on the dose, iron, and hydrogen peroxide as well as pH and reaction time. The most significant effect on COD removal in the Fenton process is pH, an iron dose, and $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ratio [20–22].

The paper presents research results aimed at comparing the effectiveness of organic compounds removal from landfill leachates using the acidification and precipitation process at pH below two, the lime coagulation, and FeSO_4 coagulation in combination with Fenton's reaction. The phenomenon of pollutant precipitation below pH 2 was applied as a method of pre-treatment of leachate, in which the humic acid fraction, insoluble in this range of pH, is removed.

2. Materials and methods

2.1. Experimental sample

The leachates used for technological research originated from a solid waste landfill located in the north-eastern part of Poland. The effluents were collected from the retention tank into a 30 L plastic container and stored at 4°C.

2.2. Reagents

In technological studies, H_2O_2 at the concentration of 30% (w/w), $\text{FeSO}_4 \times 7\text{H}_2\text{O}$, Na_2SO_3 , H_2SO_4 95%–97% (w/w), NaOH, and lime in the form of CaO were used.

2.3. Processes and methods

Experimental studies included the following processes: acidification and precipitation at pH below two, FeSO_4 coagulation, CaO coagulation, Fenton reaction, and the combination of the Fenton method with individual processes. Preliminary studies, including the acidification and precipitation process, coagulation of FeSO_4 and CaO, and Fenton reaction, were carried out in order to determine the parameters of individual processes, mainly doses of reagents which were then used for research on the combination of individual processes. The block diagram of the experimental setup is shown in Fig. 1. All experiments were carried out using a batch reactor, as shown in Fig. 2.

Acidification and precipitation were carried out with concentrated H_2SO_4 . Sulfuric acid was dispensed into a 3 L leachate sample until flocs appeared (pH < 2), then the leachate was allowed to settle. The sample prepared after separation of the precipitate was subjected to physicochemical analysis and was assigned to subsequent technological tests. The precipitate separated after acidification and sedimentation was first dried to a constant weight, then dissolved with 0.1 mol NaOH according to the International Humic Substances Society and then the TOC was determined.

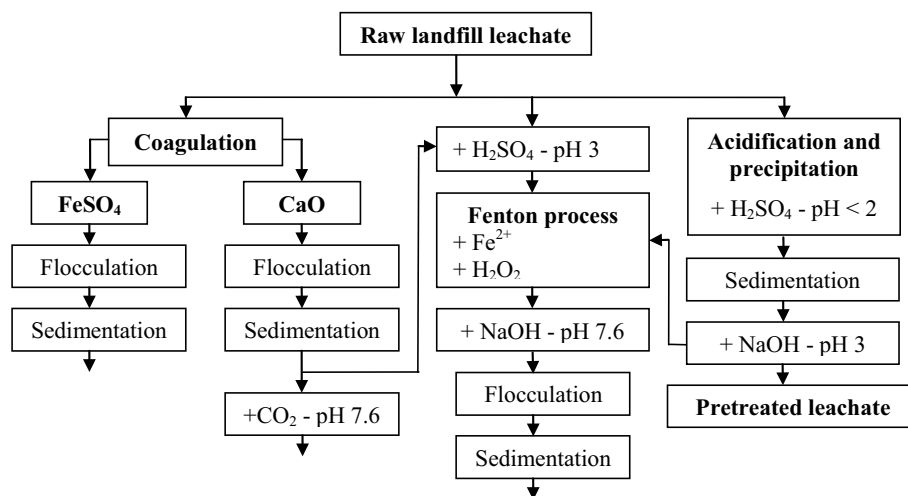


Fig. 1. Schematic view of the experimental setup.

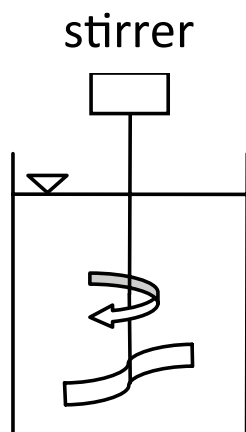


Fig. 2. Schematic diagram of batch reactor.

Coagulation with lime and FeSO_4 was carried out in cylindrical reactors with a volume of 1 L. The process included a step of fast and slow mixing, sedimentation, and filtration. In the first phase of the process, the effluents, together with the reagent, were mixed for 2 min with an intensity of about 120 rpm followed by 25 min at about 30 rpm. Thereafter, the flocs were allowed to settle for a specified time (90 min). The clarified liquid layer was then separated from the sediments. The lime dose was determined experimentally based on the assumed pH value of 11.5, that is, the pH of the reaction, at which $\text{Mg}(\text{OH})_2$ precipitates. The CaO dose was 5.6 g/L to reach the required pH. Samples after lime coagulation intended for analytical determinations were neutralized with gaseous CO_2 to a pH of approximately 7.6. In the iron salt coagulation, FeSO_4 at a dose of 0.1–0.6 gFe/L was used at pH 7.6. The samples after CaO coagulation were used for experimental studies using the Fenton reaction.

In the Fenton reaction, the effectiveness of the process was tested depending on the doses of iron and hydrogen peroxide. In individual series of experiments, Fe^{2+} doses were

0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 gFe/L, three doses of hydrogen peroxide were used for each iron dose: 1.5, 3.0, and 4.5 g/L. The process was carried out in samples of 0.5 L of leachate. In the first stage of testing, H_2SO_4 or NaOH were dosed to adjust the pH to 3, then the FeSO_4 and H_2O_2 were dosed in predetermined ranges. NaOH was added to the samples after acidification and precipitation. The reaction time was 60 min. During the process, the contents of the chamber were continuously mixed with an intensity of about 30 rpm. Na_2SO_3 was dosed into the sample intended for the TOC determination to quench the reaction and remove the remaining H_2O_2 . The remainder of the leachate sample was adjusted with NaOH to pH 7.6, again stirred for 25 min to coagulate and flocculate the resulting suspension and allowed to settle for 90 min.

Analytical tests were carried out according to the standard APHA 1998 procedure [23]. BOD was determined with the OxiTop kit. The pH-meter Hach session 4 was used to determine the pH and conductivity. The turbidity was determined by the nephelometric method with the WTW 550 IR device. UV absorbance was measured with a Prove 300 spectrophotometer in a 1 cm cuvette at 254 nm. The color was determined on a platinum-cobalt scale using a Hach DR 4000 spectrophotometer. The Thermo Scientific ICS 5000+ ion chromatography was used to determine the content of inorganic ions in the crude effluents. The following ions were tested: F^- , Cl^- , NO_2^- , Br^- , SO_4^{2-} , NO_3^- , PO_4^{3-} , Na^+ , NH_4^+ , Mg^{2+} , K^+ , and Ca^{2+} . The selected heavy metals were determined in the raw leachate samples, the measurements included measurements of Pb, Cd, Cu, Zn, Ni, and Cr. Determinations of heavy metals were made using the atomic absorption spectrometry method with the Thermo ICE 300 Series apparatus in mineralized samples. The TOC was measured using the TOC multi NC3100 Analytik Jena (Germany). PAHs were determined to apply the GC–MS system Triple Quad 7890B. The study included 16 specific PAHs. The content of organic compounds is expressed by COD and TOC. The presented COD values take into account the correction due to the presence of hydrogen peroxide [24]. Hydrogen peroxide in samples of leachates after the

process was determined by the iodometric method [25]. The presented research results also include a correction due to the dilution of samples with reagents.

Basic statistical analysis included the calculation of mean value and standard deviation. The presented test results represent an average of at least three repetitions and the standard deviation of the measured values did not exceed 5%.

3. Results and discussion

3.1. Leachate characteristics

Physicochemical characteristics of tested leachate are shown in Table 1. The leachates were characterized by high color 3,650 mg Pt-Co/L and high UV absorbance of 0.552 cm^{-1} , which indicates a significant proportion of aromatic groups in organic compounds. The content of organic compounds expressed in the COD index was 2,010 mg/L, TOC 464 mg/L, and BOD 95 mg/L. Therefore, according to the parameters proposed by Kang et al. [6], it was assessed that the leachate contained organic matter with low biodegradability. The BOD/COD indicator, in this case, was 0.047, which indicates the type of stabilized leachate. In this type of leachate, humic compounds which are the most difficult to decompose predominate [6]. Biodegradability of organic compounds may further reduce other impurities that have toxic effects on microorganisms. Among the pollutants studied, such properties are exhibited by PAH and heavy metals. The total PAH content in the tested effluents was $94.8 \mu\text{g/L}$ (Table 2), with the highest shares being phenanthrene $24.677 \mu\text{g/L}$, fluoranthene $14.633 \mu\text{g/L}$, pyrene $12.849 \mu\text{g/L}$, acenaphthylene $8.013 \mu\text{g/L}$, fluorene $5.324 \mu\text{g/L}$, anthracene $5.270 \mu\text{g/L}$; values of other PAH did not exceed $5 \mu\text{g/L}$. At the same time, in the tested leachate samples, there were no particularly high values of heavy metals. Among the samples, the highest share was Zn $596.1 \mu\text{g/L}$, then Cr $144.2 \mu\text{g/L}$, and Ni $79.65 \mu\text{g/L}$. The low content of heavy metals is characteristic of leachates from stabilized landfills [8,26]. Inorganic

parameters of the tested effluents indicate high contents of sodium (678.31 mg/L) and potassium (719.01 mg/L). The high values of chloride $1,013.93 \text{ mg/L}$ and ammonium ion 594.85 mg/L also deserve attention. The total content of mineral substances expressed by electrolytic conductivity was 8.9 mS/cm .

3.2. Acidification, precipitation, and coagulation using FeSO_4 and CaO

In the conducted tests, it was observed that after lowering the pH to below 2 in the sample of crude effluents, a dark brown suspension appeared, which easily sedimented. This property is exhibited by humic acids, which in acidic solutions with pH below 2 are insoluble in water and precipitate in the form of sludge. Humic acids are a fraction of humic substances of dark brown to black color. It is assumed that humic acids are macromolecular aromatic compounds [6]. The results of leachate tests after acidification and removal of the precipitated suspension are shown in Table 3. The effluents after this process were clear and in relation to the crude effluents, they were characterized by a clearly lower color of $1,639 \text{ mg Pt-Co/L}$. The obtained reduction in relation to the examined indicators was, respectively, COD 32.3%, color 55.1%, UV absorbance 41.85%, and TOC 27.4%, which indicates that along with the suspension, a significant part of organic compounds present in the leachate is removed. At the same time, in the process leachates, no significant decrease in BOD values was observed, which resulted in an increase in the BOD/COD ratio to 0.07. In addition, a significant reduction in UV absorbance indicates that aromatic organic fractions and low susceptibility to biochemical degradation are removed.

The dry mass of the precipitate separated after acidification and leachate sedimentation was 0.95 g/L . The TOC value determined in the precipitate dissolved in 0.1 mol NaOH was 135 mg/L . According to Silva et al. [27], the TOC value in the isolated fraction of humic acids from the stabilized landfill was 131 mg/L , while Fan et al. [28] recorded TOC values 72 and 101 mg/L .

The results obtained after coagulation and flocculation with FeSO_4 are shown in Fig. 3 and Table 3. Due to the adopted doses of Fe^{2+} and the COD value in the crude effluents, the Fe/COD ratio was in the range from 0.05 to 0.3. According to Primo et al. [29], the most preferred Fe/COD mass ratio is 0.33. In the experiments conducted with a dose of 0.1 g/L iron, the COD removal effect was 16.1%, 34.3% color, UV absorbance 25.7%, and TOC 11.1%. The highest process efficiency was obtained with the highest applied 0.6 g/L iron dose. In this case, the reduction of individual indicators was: COD 41.7%, color 66.9%, UV absorbance 56.3%, and TOC 36.5%. Amokrane et al. [12], with an initial COD value of $4,100 \text{ mg/L}$ and a coagulant dose (1.95 gFe/L), obtained a reduction of COD by 55%, while according to studies by Diamadopoulos [30], with an initial COD of $5,690 \text{ mg/L}$ and a 0.84 gFe/L iron dose, the COD removal efficiency was 56%.

After coagulation with lime at a dose of 5.6 gCaO/L , the COD removal effect was 52%, color 71.5%, UV absorbance 46.1%, and TOC 39.5%. In comparison to FeSO_4 coagulation, a reduction of 48% Kjeldahl total nitrogen was obtained using

Table 1
Landfill leachate characteristics

Parameter	Value	Parameter	Value
pH	7.95	Zn ($\mu\text{g/L}$)	596.1
Turbidity (NTU)	18	Pb ($\mu\text{g/L}$)	22.5
Color (Pt-Co units)	3,650	Co ($\mu\text{g/L}$)	5.1
TOC (mg/L)	464	Na^+ (mg/L)	678.31
BOD (mg/L)	95	K^+ (mg/L)	719.01
COD (mg/L)	2,010	NH_4^+ (mg/L)	594.85
UV _{254nm} absorbance (cm^{-1})	0.552	Ca^{2+} (mg/L)	215.79
TKN (mg/L)	628.4	Mg^{2+} (mg/L)	91.825
Alkalinity (mg CaCO_3/L)	3,320	Cl^- (mg/L)	1,013.93
Conductivity (mS/cm)	8.9	SO_4^{2-} (mg/L)	114.02
Fe (mg/L)	2.29	NO_3^- (mg/L)	35.58
Mn (mg/L)	0.57	NO_2^- (mg/L)	0.903
Cu ($\mu\text{g/L}$)	33.7	Br (mg/L)	17.99
Ni ($\mu\text{g/L}$)	79.65	F (mg/L)	2.97
Cr ($\mu\text{g/L}$)	144.2	PO_4^{3-} (mg/L)	22.85

Table 2
Concentration of 16 PAH for leachate

Parameter	Value ($\mu\text{g/L}$)	Parameter	Value ($\mu\text{g/L}$)
Naphthalene	2.443	Benzo[a]anthracene	3.734
Acenaphthalene	8.013	Chrysene	4.009
Acenaphthene	0.655	Benzo[b]fluoranthene	3.372
Fluorene	5.324	Benzo[k]fluoranthene	3.979
Phenanthrene	24.677	Benzo[a]pyrene	3.670
Anthracene	5.270	Indeno[1,2,3-cd]pyrene	3.036
Fluoranthene	14.633	Dibenzo[a,h]anthracene	0.238
Pyrene	12.849	Benzo[ghi]perylene	2.489

Table 3
Parameters for the leachate pre-treatment using acidification and precipitation, as well as ferrous and lime coagulation

Parameter	Acidification, precipitation and sedimentation	FeSO ₄ coagulation 0.6 gFe/L	Lime coagulation 5.6 gCaO/L
COD (mg/L)	1,361	1,091	965
Color (Pt-Co units)	1,639	1,208	1,040
UV _{254nm} (cm ⁻¹)	0.321	0.241	0.298
TOC (mg/L)	336.9	293.7	280.7

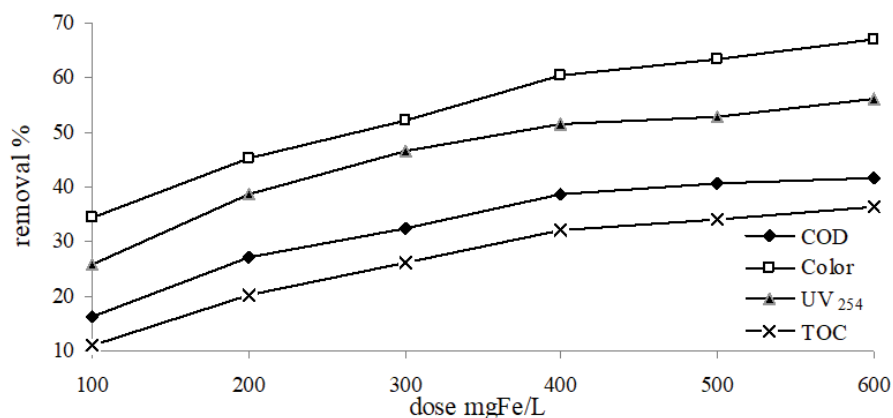


Fig. 3. Effect of Fe²⁺ concentration on the COD, color, UV_{254nm} and TOC removal efficiency during the coagulation of leachate.

lime. In this case, the NH₄⁺ ions after alkalization to pH 11.5 may undergo partial conversion to the NH₃ gas form. The results of investigations of CaO coagulation leaks are shown in Table 3. According to Amokrane et al. [12], chemical precipitation with lime removes 70%–90% of color. In addition, lime coagulation leads to the removal of carbonate hardness. The process also removes high molecular weight organic compounds, such as humic and fulvic acids.

3.3. Fenton process

The effect of removing impurities expressed as COD and TOC depending on the iron(II) and hydrogen peroxide dose is shown in Figs. 4 and 5. After the Fenton process, the COD and TOC values decrease with the increase in the doses of

hydrogen peroxide and iron. According to studies, the largest effect of hydrogen peroxide on the increase in COD and TOC reduction was recorded at a dose of H₂O₂ of 3 g/L. At a hydrogen peroxide dose of 4.5 g/L and Fe dose above 0.3 g/L, the COD and TOC removal efficiency was lower.

The decrease in the values of the tested indicators at the lowest dose of iron 0.1 g/L depending on the dose of hydrogen peroxide was within the limits of COD (24.2%–36.4%) and TOC (16.2%–26.5%) at a dose of H₂O₂ 1.5 and 4.5 g/L. The lowest COD 764 mg/L value was obtained at a dose of Fe²⁺ 0.6 g/L and a dose of hydrogen peroxide 3.0 g/L. In this case, the COD removal effect was 62%, while at the lowest dose of H₂O₂ 1.5 g/L, the COD removal efficiency was 54.9%. The TOC removal value under these conditions was 60.1% and 48.6%, respectively. Due to the COD value in the

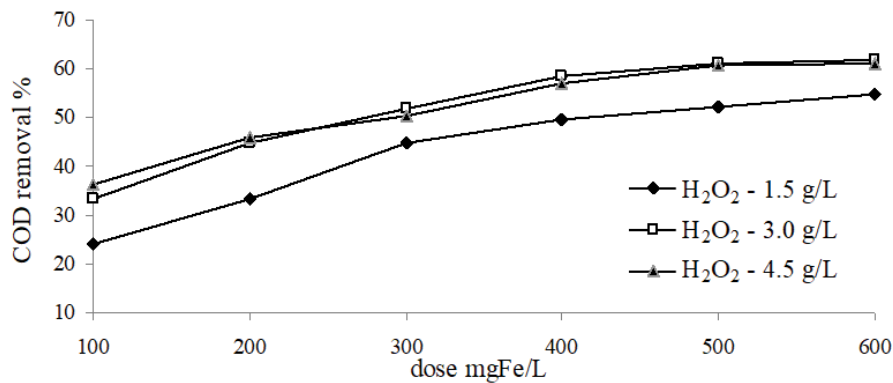


Fig. 4. Effect of Fe concentration on the COD removal efficiency during the Fenton oxidation of leachate.

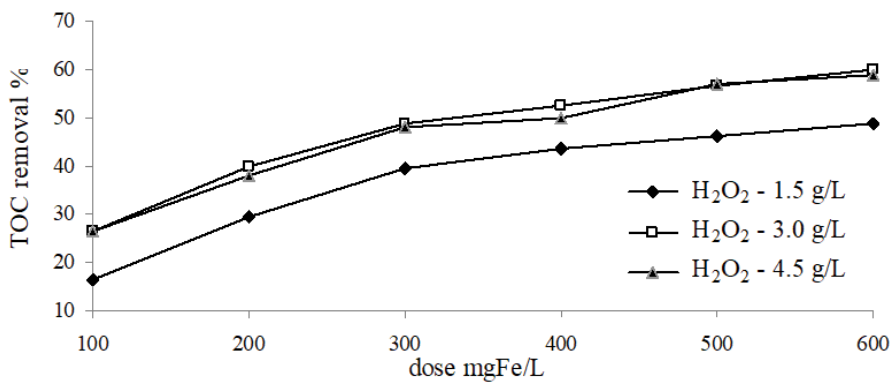


Fig. 5. Effect of Fe concentration on the TOC removal efficiency during the Fenton oxidation of leachate.

leaching prior to the process (2,010 mg/L) and the H₂O₂ dose adopted for the study, the H₂O₂/COD ratio was 0.75, 1.5, and 2.24, respectively.

Deng et al. [20] stated that in the Fenton process the dose of hydrogen peroxide turns out to be decisive. According to Barbusiński et al. [31], the most preferred dose of H₂O₂ was 1,350 mg/L at a Fe²⁺/H₂O₂ ratio of 0.2 at pH 3 and a reaction time of 45 min. Under these conditions, the removal efficiency of COD was 61%. Singh et al. [32], in the case of leachate treatment, given the median optimal relative dose of H₂O₂/Fe²⁺ 1.8 (w/w). The biologically purified effluent showed a relatively lower optimal dose ratio of H₂O₂/Fe²⁺ (median: 0.9 w/w) compared to raw (median: 2.4 w/w). According to Vilar et al. [33], reaction times longer than 2 h did not improve the removal of organic matter nor the biodegradability of organic matter, with no further significant increase in COD removal after 60 min.

The effectiveness of color removal and UV_{254nm} absorbance obtained during the tests is shown in Figs. 6 and 7. Residual hydrogen peroxide concentrations in the Fenton process are illustrated in Fig. 8. In the process, leachate at the lowest iron dose of 0.1 and 1.5 g/L hydrogen peroxide, the color reduction was 43.7% and the UV_{254nm} absorbance was 33%. The use of higher doses of H₂O₂ 3 g/L increased the efficiency of the process, and so with the highest iron dose of 0.6 g/L, the effect of color removal and UV absorbance was 96.7% and 74%, respectively. In the case of color, the dose of hydrogen peroxide 4.5 g/L did not affect the increase in the efficiency

of removing this indicator. The efficiency of removing UV absorbance did not increase significantly above an iron dose of 0.5 g/L and an H₂O₂ dose of 3 g/L. According to Mohajeri et al. [34], the highest removals of 58.1% and 78.3% were observed for COD and color, respectively. The best operating conditions were pH = 3, Fe = 560 mg/L, H₂O₂ = 1,020 mg/L, and reaction time = 120 min.

3.4. Combined treatment using acidification, precipitation, coagulation, and Fenton process

Studies applying the Fenton reaction in combination with the acidification and sedimentation process as well as with lime coagulation were carried out using doses of iron 0.3 and 0.6 g/L and a dose of hydrogen peroxide 3 g/L. The values of COD, color, UV absorbance, and TOC are presented in Table 4. Fig. 9 shows the effectiveness of removing individual indicators in combined processes compared to the independent coagulation process, acidification and sedimentation methods, and Fenton reaction.

According to the conducted tests, the initial leachate treatment using the acidification and sedimentation method significantly increased the efficiency of removing impurities in the Fenton process. At 0.3 g/L iron and 3 g/L H₂O₂ doses, the effect of COD removal was 75.4%, color 92%, and TOC 72.5%. However, the combination of initial acidification and sedimentation with Fenton's reaction at a 0.6 g/L iron and 3 g/L H₂O₂ doses increased the color removal effect to 95%

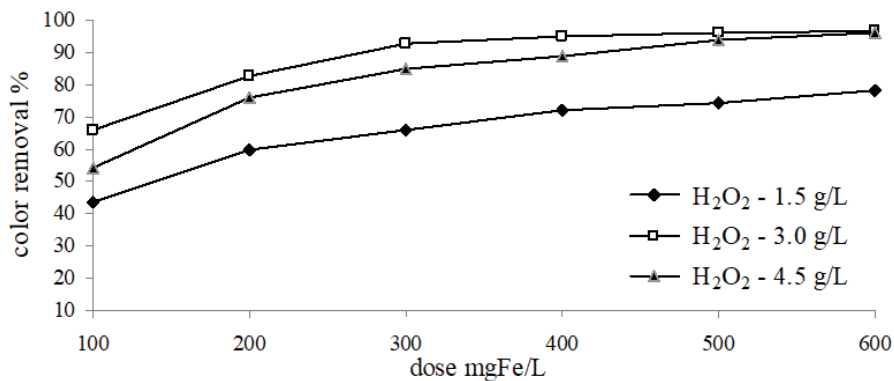


Fig. 6. Effect of Fe concentration on the color removal efficiency during the Fenton oxidation of leachate.

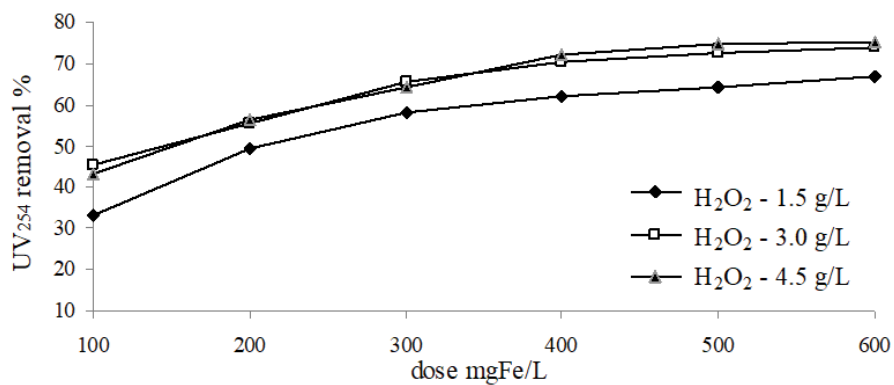


Fig. 7. Effect of Fe concentration on the UV_{254nm} absorbance removal efficiency during the Fenton oxidation of leachate.

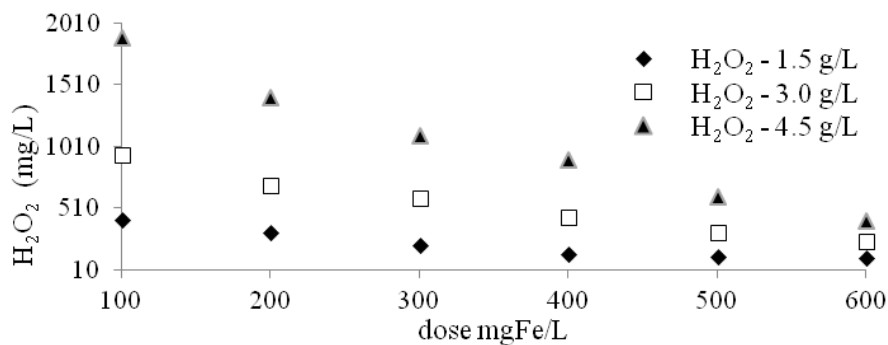


Fig. 8. Residual H₂O₂ concentration during Fenton process.

and COD to 82%. However, the decrease in UV and TOC absorbance was 89.6% and 77%, respectively. The increase in the efficiency of the Fenton process, in this case, may be associated with the removal of humic acids after acidification and sedimentation. According to Kang et al. [6], the presence of humic substances significantly affects the efficiency of the coagulation-flocculation process due to specific interactions that may occur between humic substances and dissolved forms of iron. In addition, humic substances are classified as so-called free radical scavengers [35]. However, the highest color and COD lowering efficacy was obtained using Fenton's reaction after lime coagulation. In this case, at 0.3 g/L iron and 3 g/L H₂O₂ doses, the removal effect of

these indicators was 98.8% and 82.7%, respectively. The high efficiency of Fenton's reaction after coagulation with lime can also be associated with the removal of humic substances that are adsorbed on the surface of precipitated flocs of magnesium hydroxide. In addition, in the coagulation process with lime, HCO₃⁻ ions are removed, which are also classified as free radical scavengers [30,36,37].

4. Conclusions

- In the FeSO₄ coagulation process, a satisfactory effect of removing impurities was observed when iron dosing above 0.3 g/L. At the highest dose of Fe²⁺ 0.6 g/L,

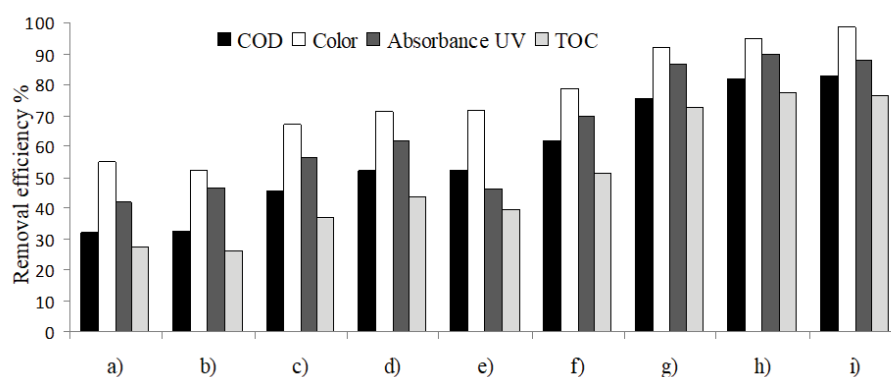


Fig. 9. Removal efficiency of COD, color, UV_{254nm}, and TOC for (a) acidification and precipitation pH < 2, (b) coagulation = 0.3 gFe/L, (c) coagulation = 0.6 gFe/L, (d) Fenton process = 0.3 gFe/L + 3 gH₂O₂/L, (e) lime coagulation = 5.6 gCaO/L, (f) Fenton process = 0.6 gFe/L + 3 gH₂O₂/L, (g) acidification and sedimentation + Fenton process = 0.3 gFe/L + 3 gH₂O₂/L, (h) acidification and sedimentation + Fenton process = 0.6 gFe/L + 3 gH₂O₂/L, and (i) lime coagulation = 5.6 gCaO/L + Fenton process = 0.3 gFe/L + 3 gH₂O₂/L.

Table 4

Parameters of treated leachate by the Fenton method in combination with acidification, precipitation, and lime coagulation

Parameter	Acidification and sedimentation + Fenton process (0.3 gFe/L + 3 gH ₂ O ₂ /L)	Acidification and sedimentation + Fenton process (0.6 gFe/L + 3 gH ₂ O ₂ /L)	Lime coagulation (5.6 gCaO/L) + Fenton process (0.3 gFe/L + 3 gH ₂ O ₂ /L)
COD (mg/L)	494	362	348
Color (Pt-Co units)	292	183	44
UV _{254nm} (cm ⁻¹)	0.073	0.057	0.066
TOC (mg/L)	127.7	106.7	110.2

the reduction of COD and TOC were 41.7% and 36.5%, respectively. Relatively high reduction effects of the tested indicators were obtained during lime coagulation. In this case, at a dose of CaO 5.6 g/L, the removal efficiencies of COD and TOC were 52% and 39.5%, respectively. In comparison to FeSO₄ coagulation, the use of CaO resulted in a higher color reduction and a slightly lower reduction in UV absorbance. Furthermore, comparing the results of coagulation experiments, it can be observed that lime was more efficient for the removal of ammonia nitrogen.

- In studies applying the Fenton reaction, it was demonstrated that the effective removal of organic compounds occurred, with the highest removal efficiencies of 62% COD and TOC 60.1% obtained with iron(II) 0.6 g/L and hydrogen peroxide H₂O₂ 3 g/L.
- Acidification of landfill leachates to pH below 2 is a simple process that allows the removal of organic compounds, mainly humic acids, which precipitate in this pH range. Humic acids are part of high molecular weight humic substances that are difficult to biodegrade. Removal of these fractions from the effluent increased the BOD/COD ratio to 0.07. According to research, the independent acidification and sedimentation processes at pH below 2 proved to be a more effective method of removing impurities than FeSO₄ coagulation at a 0.3 g/L iron dose.
- After the removal of humic acids from leachate by acidification and sedimentation, an increase in the efficiency of removing impurities in the Fenton process was observed. In a combination of these processes at a

dose of iron 0.6 g/L and H₂O₂ 3 g/L, the COD, and TOC removal effect was 82% and 77%, respectively. The high efficiency of Fenton reaction after lime coagulation is also noteworthy. In this case, the maximum reduction of COD was 82.7% and TOC 76.3%. In addition, lime coagulation increased the efficiency of removing ammonium nitrogen. However, such a combination of processes involves a significant demand for reagents for lime coagulation and acidification after this process.

References

- [1] S. Mukherjee, S. Mukhopadhyay, M.A. Hashim, B.S. Gupta, Contemporary environmental issues of landfill leachate: assessment and remedies, *Crit. Rev. Env. Sci. Technol.*, 45 (2014) 472–590.
- [2] J. Wiszniewski, D. Robert, J. Surmacz-Górska, K. Miksch, J.V. Weber, Landfill leachate treatment methods: a review, *Environ. Chem. Lett.*, 4 (2006) 51–61.
- [3] D. Kulikowska, E. Klimiuk, The effect of landfill age on municipal leachate composition, *Bioresour. Technol.*, 99 (2008) 5981–5985.
- [4] T.H. Christensen, P. Kjeldsen, P.L. Bjerg, D.L. Jensen, B.J. Christensen, A. Baun, H. Albrechtsen, G. Heron, Biogeochemistry of landfill leachate plumes, *Appl. Geochem.*, 16 (2001) 659–718.
- [5] K.Y. Foo, B.H. Hameed, An overview of landfill leachate treatment via activated carbon adsorption process, *J. Hazard. Mater.*, 171 (2009) 54–60.
- [6] K.H. Kang, H.S. Shin, H. Park, Characterization of humic substances present in landfill leachates with landfill ages and its implications, *Water Res.*, 36 (2002) 4023–4032.

- [7] H. Alvarez-Vazquez, B. Jefferson, S.J. Judd, Membrane bioreactors vs conventional biological treatment of landfill leachate: a brief review, *J. Chem. Technol. Biotechnol.*, 79 (2004) 1043–1049.
- [8] A. Shehzad, M.J.K. Bashir, S. Sethupathi, J.W. Lim, An overview of heavily polluted landfill leachate treatment using food waste as an alternative and renewable source of activated carbon, *Process Saf. Environ. Prot.*, 98 (2015) 309–318.
- [9] S.Q. Aziz, H.A. Aziz, M.J.K. Bashir, A. Mojiri, Assessment of various tropical municipal landfill leachate characteristics and treatment opportunities, *Global Nest J.*, 17 (2015) 439–450.
- [10] W. Li, Q. Zhou, T. Hua, Removal of organic matter from landfill leachate by advanced oxidation processes: a review, *Int. J. Chem. Eng.*, 2010 (2010) 46–55.
- [11] M. Smol, M. Włodarczyk-Makula, K. Mielczarek, J. Bohdziewicz, Comparison of the retention of selected PAHs from municipal landfill leachate by RO and UF processes, *Desal. Water Treat.*, 52 (2014) 3889–3897.
- [12] A. Amokrane, C. Comel, J. Veron, Landfill leachates pretreatment by coagulation-flocculation, *Water Res.*, 31 (1997) 2775–2782.
- [13] S. Renou, J.G. Givaudan, S. Poulain, F. Dirassouyan, P. Moulin, Landfill leachate treatment: review and opportunity, *J. Hazard. Mater.*, 150 (2008) 468–493.
- [14] A.A. Tatsi, A.I. Zouboulis, K.A. Matis, P. Samara, Coagulation-flocculation pretreatment of sanitary landfill leachates, *Chemosphere*, 53 (2003) 737–744.
- [15] P. Biedka, Effectiveness of coagulation in contaminants removal from biologically treated landfill leachate, *Ann. Set Environ. Prot.*, 20 (2018) 857–872.
- [16] J. Bohdziewicz, E. Neczaj, A. Kwarcia, Landfill leachate treatment by means of anaerobic membrane bioreactor, *Desal. Water Treat.*, 221 (2008) 559–565.
- [17] Z.P. Wang, Z. Zhang, Y.J. Lin, N.S. Deng, T. Tao, K. Zhuo, Landfill leachate treatment by a coagulation-photooxidation process, *J. Hazard. Mater.*, 95 (2002) 153–159.
- [18] T.A. Kurniawan, W.H. Lo, G.Y.S. Chan, Radicals-catalyzed oxidation reactions for degradation of recalcitrant compounds from landfill leachate, *Chem. Eng. J.*, 125 (2006) 35–57.
- [19] E. Neyens, J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique, *J. Hazard. Mater.*, 98 (2003) 33–50.
- [20] Y. Deng, J.D. Englehardt, Treatment of landfill leachate by Fenton process, *Water Res.*, 40 (2006) 3683–3694.
- [21] I.W.C. Lau, P. Wang, H.H.P. Fang, Organic removal of anaerobically treated leachate by Fenton coagulation, *J. Environ. Eng.*, 127 (2001) 666–669.
- [22] K. Barbusinski, S. Fajkis, Optimization of the Fenton oxidation of wastewater generated by rape oil soapstock splitting, *Environ. Prog. Sustainable Energy*, 30 (2011) 620–631.
- [23] APHA, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, Washington, DC, 1998.
- [24] Y.W. Kang, M.J. Cho, K.Y. Hwang, Correction of hydrogen peroxide interference on standard chemical oxygen demand test, *Water Res.*, 33 (1999) 1247–1251.
- [25] N.V. Klassen, D. Marchington, H.C.H. McGowan, H₂O₂ determination by the I₃⁻ method and by KMnO₄ titration, *Anal. Chem.*, 66 (1994) 2921–2925.
- [26] H.H. Liu, S.X. Sang, Study on the law of heavy metal leaching in municipal solid waste landfill, *Environ. Monit. Assess.*, 165 (2010) 349–363.
- [27] M.E. Silva, M. Santos, I. Brás, Characterization of wastewater from landfills – amount and type of humic substances extracted from leachate, E3S Web Conf., 80 (2019) 03002.
- [28] H.J. Fan, H.Y. Shu, H.S. Yang, W.C. Chen, Characteristics of landfill leachates in central Taiwan, *Sci. Total Environ.*, 361 (2006) 25–37.
- [29] O. Primo, M.J. Rivero, I. Ortiz, Photo-Fenton process as an efficient alternative to the treatment of landfill leachates, *J. Hazard. Mater.*, 153 (2008) 834–842.
- [30] E. Diamadopoulos, Characterization and treatment of recirculation stabilized leachate, *Water Res.*, 28 (1994) 2439–2445.
- [31] K. Barbusiński, B. Pieczykolan, COD removal from landfill leachate using Fenton oxidation and coagulation, *Arch. Civ. Eng. Environ.*, 1 (2010) 93–100.
- [32] S.K. Singh, W.Z. Tang, Statistical analysis of optimum Fenton oxidation conditions for landfill leachate treatment, *Waste Manage.*, 33 (2013) 81–88.
- [33] A. Vilar, M. Eiroa, C. Kennes, M.C. Veiga, Optimization of the landfill leachate treatment by the Fenton process, *Water Environ. J.*, 27 (2013) 120–126.
- [34] S. Mohajeri, H.A. Aziz, M.H. Isa, M.J.K. Bashir, L. Mohajeri, M.N. Adlan, Influence of Fenton reagent oxidation on mineralization and decolorization of municipal landfill leachate, *J. Environ. Sci. Health., Part A*, 45 (2010) 692–698.
- [35] J. Farkas, M. Náfrádi, T. Hlogyik, B.C. Pravda, K. Schrantz, K. Hernádi, T. Alapi, Comparison of advanced oxidation processes in the decomposition of diuron and monuron – efficiency, intermediates, electrical energy per order and the effect of various matrices, *Environ. Sci. Water Res. Technol.*, 4 (2018) 1345–1360.
- [36] R.G. Zepp, B.C. Faust, J. Hoigne, Hydroxyl radical formation in aqueous reactions (pH 3–8) of iron (II) with hydrogen peroxide: the photo-Fenton reaction, *Environ. Sci. Technol.*, 26 (1992) 313–319.
- [37] T. Jasemizad, M.T. Ghaneian, M.H. Ehrampoush, I. Rezapour, A. Jebali, F. Sahlabadi, Effects of radical scavengers on humic acid removal by electron beam irradiation, *Desal. Water Treat.*, 57 (2016) 29036–29043.