Inżynieria i Ochrona Środowiska **2012, t. 15, nr 2, s. 203-217**

Paulina JELONEK, Ewa NECZAJ
Czestochowa University of Technology, Faculty of Environmental Engineering
and Biotechnology
Brzeznicka 60a, 42-200 Częstochowa

The use of Advanced Oxidation Processes (AOP) for the treatment of landfill leachate

Formation of leachate poses a problem closely related to the use of landfill sites. Landfill leachate is a wastewater, which as a result of permeation elutes mineral and organic compounds from a bed. Due to its diverse composition, both physical and chemical, it is necessary to purify the leachate before its discharge into drains or a natural receiver. The following article shows that there is a variety of pollutants in municipal landfill leachate. It also presents the dependency existing between the age of a landfill site, and the concentration of pollutants in leachate, as well as how it affects biodegradation of contaminants.

There were discussed various methods to purify leachate and the physical, chemical, physico-chemical and biochemical processes were compared. Comparing these processes, many factors were taken into account: the efficiency and effectiveness of the processes, their side effects, the costs, the amount of energy that is required for a process to take place, reaction dynamics, and more. A successful purification of leachate with use of a single process unit is not possible. Therefore, there are used hybrid systems that combine biological methods of physico-chemical processes, especially the advanced oxidation processes. The most important among the chemical processes used for treatment of leachate are Advanced Oxidation Processes - AOP.

Advanced oxidation processes are divided into chemical and photochemical oxidation. The most commonly used methods include oxidation with ozone and hydrogen peroxide and Fenton's reagent oxidation. Processes using ozone are usually employed as the third stage of landfill leachate treatment. This process allows discharge of the leachate into a receiver. The largest decreases in the number of pollutants are obtained using combined processes. Some of the best effects were observed after employment of oxidation both with ozone and hydrogen peroxide, helping to additionally enhance this process photocatalytically. AOP proved to be the most effective method of treatment of waste water that contains organic products (waste water from chemical and agrochemical industries, textiles, paints, dyes). More conventional techniques cannot be used to treat such compounds because of their high chemical stability and low biodegradability. There was also performed a literature review in the field of biological, physical and chemical purification methods of landfill leachate.

Keywords: **landfill leachate, Advanced Oxidation Processes (AOP), biodegradability enhancement**

Introduction

Dynamic development in the industry, as observed over the last year, is causing a growing number of municipal waste and industrial pollution. Landfill is due to economic reasons the most common method of disposal. Exploitation of landfill sites is closely linked with the problem of leachate and the necessity of its purifying.

Landfill leachate is a waste water that penetrates a bed and elutes its organic and mineral impurities. The qualitative composition of the leachate determines the biochemical processes that occur during the landfill. Over two hundred substances which are organic leachate pollutants were characterized. Thirty-five of them belong to the so-called "priority pollutants". With the passage of time in a landfill leachate the concentration of easily degradable organic volatile acids, and other small molecules decreases, while the number of difficult biodegradable compounds - fulvic acid and humic increases [1].

The sources of leachate are: precipitation, inflow of groundwater and surface water, storage of wet material, water losses due to evaporation, transpiration, surface flow, as well as hydrolysis and biodegradation of organic compounds. Leachate is produced at the time of exceeding the maximum water absorption by the weight of the stored waste. Absorptivity for the compacted mass of waste is estimated to be 30% of volume [2].

Leachate from landfills located in Poland is characterized by high values of COD and BOD_5, including high salinity and hardness, high concentration of ammonia nitrogen and relatively low levels of heavy metals. Hardness is related to presence of chlorides and sulfates of calcium, magnesium, potassium and sodium [3].

Wastewater treatment of waste is more complicated than municipal wastewater treatment. This is due to high concentration of pollution found in the leachate. The composition of pollutants varies with age of the landfill. It was necessary to take into account the high concentration of refraction, as well as differences in volume depending on the season.

Research carried out for many years, show that it is possible to successfully purify leachate when using one process unit. The methods usually employed for this purpose are hybrid systems that connect biological methods of physico-chemical processes: advanced oxidation processes, membrane methods or adsorption on activated carbon.

More and more attention is focused on the use of advanced oxidation processes - AOP. The distinguishing feature of these processes is the presence of an oxidizing agent. Oxidizing agents are very reactive hydroxyl radicals. They have a high oxidation-reduction potential, so that they are able to oxidize organic compounds [4].

AOP processes lead to the mineralization of contaminants. It is based on the oxidation of to carbon dioxide, water, and inorganic compounds [5]. The use of AOP as a pre-treatment, supporting biological treatment, causes that these processes are effective and cost-effective from the point of view of economic development [6].

1. Landfill leachate - composition and characteristics

The volume and composition of leachate is closely associated with many factors, including:

- ground conditions,
- topography of the environment,
- the method of separating substrate of the landfill site and the bed from contact with ground and surface waters,

- the amount of atmospheric precipitation, humidity and the rate of evaporation,
- the type of collected waste and its degree of fragmentation,
- biochemical and physical changes that occur in the waste,
- storage and compression technology of waste,
- the age of the landfill site,
- vegetation which grows in the landfill site after its reclamation [7].

Over time, wastes accumulated in the landfill undergo biochemical and physical processes. Characteristic of leachate is closely associated with these processes. There are three main phases of biochemical stabilization of waste:

- aerobic,
- anaerobic acidic,
- methanogenic.

Simultaneously with these there are involved other processes: dissolution, adsorption, dilution, precipitation, and ion exchange.

The main impurities in the composition of leachate are ammonia, organic compounds, heavy metals and chlorides. It is their presence in the leachate that determines the choice of methods of its treatment and management. Rating concentrations of organic compounds is possible with indicators: COD, BOD_5, TOC. The high value of the ratio of COD (3÷60 g/dm^3), and a high ratio of BOD_5/COD (> 0.6) present in the leachate is typical for young landfill sites (< 2 years). In landfill sites the age of which exceeds 10 years, rates of leaching are much lower. COD ratio is maintained in this case at the level of 100÷500 mg/dm^3, while the ratio of BOD_5/COD is lower than 0.3.

In leachate there occurs a vast quantity and variety of chemical compounds. Therefore, their complete identification is practically impossible to carry out. It is understood that in the landfill leachate there are present two hundred types of organic compounds. Their presence is often associated with depositing waste in landfill sites, which often contain dangerous waste [8].

In Table 1 there are presented the results of research conducted by Slak et al. [9]. This research is related to the composition of the leachate, including heavy metals and organic compounds. These data come from landfills located in Europe [9].

By analyzing the distribution of molecular weights of organic compounds that are present in the leachate it has been shown that in the case of young landfill sites fraction of low molar mass (< 500 Da) represents 70% of the population. In this case, the compounds of a linear chain structure of the functional groups in the oxidized form are dominated. On the other hand, in the leachate from older landfill sites a dominant (> 77%) fraction of organic compounds has a high molecular weight (> 10,000 Da). Usually they have a cyclic structure with functional groups containing mainly nitrogen, oxygen, and sulfuric acid residue. Humic compounds are the most important organic compounds present in the leachate from old landfill sites. These compounds are anionic refraction. These include fulvic acids with lower molecular weight, and humic acid, the molecular weight of which is significantly higher. The low quotient BOD_5/COD and poor biodegradability cause high concentration of humic acids in the leachate from old landfills. Microbial contamination found in leachate is less recognizable [13].

Table 1

The composition of leachate [10-12]

Inorganic compounds	Pesticides	Pharma-ceuticals	Phthalic esters	Aromatic hydrocarbons	Aromatic hydrocarbons
Cyanides Arsenic Cadmium Chromium Copper Lead Mercury Nickel Zinc	Atrazine Dichlobenil Dichloroprop Dichlorvos Glyphosate Malathion MCPA Mecoprop Simazine	Ibuprofen Oestradiol or the like	Benzyl butyl phthalate (BBP) Di phthalate (2 ethylhexyl) (DEPH) Dibutyl phthalate (DBP) Diethyl phthalate (DEP) Folic acid	Aniline, 1,2,4-trimethylbenzene Benzene Bisphenol A Chlorobenzenes Cresols Dichlorobenzenes Ethylbenzene Hexachlorobenzene naphthalene Nonylphenol Pentachlorophenol Phenols Toluene Trichlorobenzen Xylenes Other: PAHs, PCBs Bipfenyl, MonoCB PentaCB, NonaCB	1,1,1-trichloroeatan 1,2-dichloroethane 1,4-dioxane Acetone Dichloroetyleny Dichloromethane Tert-butyl methyl ether Tetrachloroethylene Vinyl chloride Organo-tin compounds

2. AOP in landfill leachate treatment

The differences in physico-chemical composition of landfill leachate cause that prior to introduction into a natural receiver or sewage system they must be purified. There are the following methods of waste treatment:

I. discharge of leachate into the municipal sewage system and its purification at a local sewage treatment plant using activated sludge,
II. leachate collection in a tank in landfills and periodical export to municipal biological treatment,
III. purification of leachate in the landfill, the local small sewage treatment,
IV. recycling leachate through the tip,
V. evaporation of water from leachate with heat from biogas combustion.

For purification of waste water there may be employed all the unit processes, that is, biological, physical and chemical ones, as well as their combinations.

Processes of vast importance, which are used for the leachate purification are advanced oxidation processes - AOP. The oxidizing agent in advanced oxidation processes are free radicals. The most important are hydroxyl radicals (OH•), which are distinguished by a high oxidation potential of 2.8 V. Hydroxyl radicals are characterized by quick and non-selective oxidation of a variety of organic compounds to carbon dioxide and water [16].

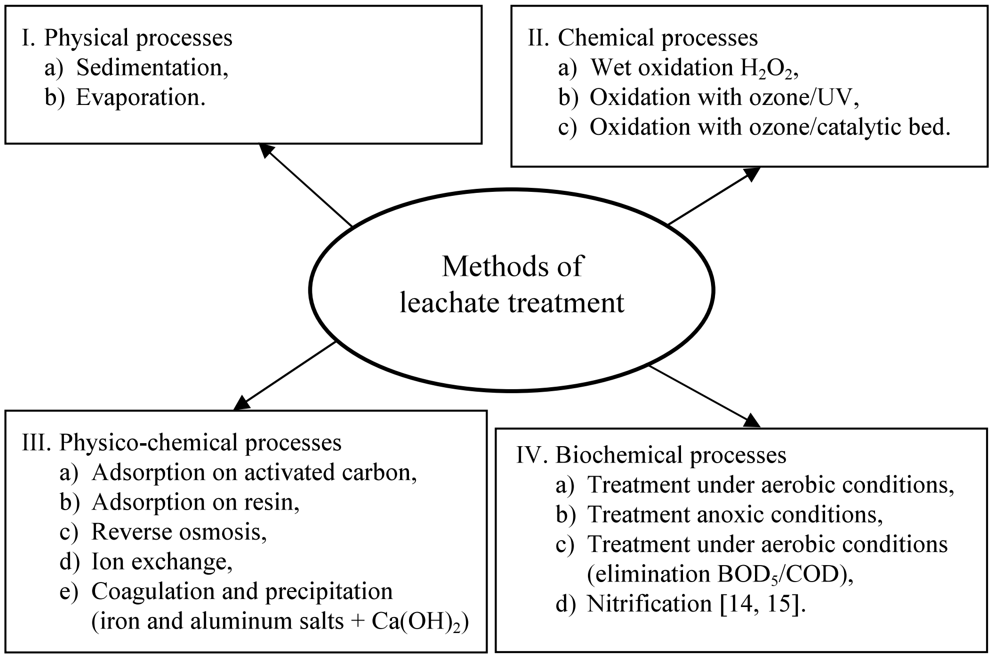

Fig. 1. The most important method of leachate treatment from municipal landfills

Table 2

Breakdown of advanced oxidation processes - AOP [21, 22]

Advanced Oxidation Processes - AOP	
Photochemical processes	*Chemical processes*
1. UV photolysis	I. Fenton reaction Fe^{2+}/H_2O_2
2. Reaction photo - Fenton $H_2O_2/Fe^{2+}/UV$	II. Oxidation with ozone and hydrogen peroxide
3. Processes using UV/H_2O_2	III. Electrochemical oxidation
4. Processes using UV/O_3	IV. Oxidation in supercritical conditions (Supercritical Water Oxidation - SCWO)
5. Processes using $UV/H_2O_2/O_3$	V. Wet Air Oxidation - WAO
6. Photocatalytic degradation in aqueous suspensions semiconductors	
7. Processes with ultrasound	

AOP are divided into photochemical and chemical processes. The most commonly used chemical methods include oxidation with ozone, hydrogen peroxide and Fenton's reagent oxidation. Ozone treatment is most often used as a tertiary treatment of landfill leachate. It is a process that allows the drain of the receiver. The decrease in content of the organic pollutants after application of ozone is at a level of 50-70% [17]. The use of combined oxidation with ozone and hydrogen peroxide with assistance of a photocatalytic process can achieve significantly better results. The increase in the ratio of BOD_5/COD from 0.1 to 0.5 was obtained in research of Wu et al. [18]. Very similar results were achieved in research by Tizaoui et al. [19]. The value of the degree of removal of the COD of 20% in the ozone was increased to 40% with addition of hydrogen peroxide. The COD after ozonation showed 20% and when hydrogen peroxide was used in addition it stated 40%. There was also observed an increase ratio of BOD_5/COD of 0.2 to 0.6 [20].

2.1. UV radiation

UV radiation is most often used in the last stage of leachate purification. It is a disinfection before pullout to the receiver. This radiation causes photolysis of organic compounds and generates ozone. Photolysis is used for the oxidation of aromatic compounds having chlorine, nitro and hydroxyl as substituents. In comparison to other photochemical methods (for example: H_2O_2/UV, H_2O_2/Fe^{2+}/UV), photolysis process is lowly efficient. However, when the method of combined: photolysis + oxidizing agents such as H_2O_2 is used, values for COD reduction can be observed.

In advanced oxidation methods oxidising systems are commonly used. The most important of these are: O_3/UV, O_3/H_2O_2, H_2O_2/UV or O_3/H_2O_2/UV, H_2O_2/Fe^{2+}/UV ingredients. After simultaneous use of several components the results of the removal of impurities are significantly better than for the individual reactants [23].

2.2. Fenton reaction

Most popular method of AOP is the Fenton reaction (Fe^{2+}/H_2O_2). Oxidation of organic compounds by Fenton's reagent results in a reduction of the COD from 45 to 75%. For additional support photocatalytic COD ratio is maintained at 70 to 78%. As a result of this process. susceptibility to biodegradation of pollutants increases, which is expressed by the ratio BOD_5/COD. This quotient is 0.5 [24].

The AOP method using the Fenton reaction can be divided into four stages of technology:

- leachate change to a suitable pH,
- the oxidation reaction of organic compounds,
- neutralization of leachate,
- sludge removal [25].

The degradation velocity of organic pollutants is significantly enhanced when UV radiation with a wavelength above 300 nm is used in addition. In the single-Fenton reaction there are often generated large quantities of iron sludge waste. UV rays diminish the amount of sludge. It is then possible to reduce the size of the reactor because the velocity of reaction in this case is very high. Unfortunately, pH (pH 2.6÷3). is to be continuously controlled Polyethylene glycol has a wide range of applications in the pharmaceutical industry. It can be found in certain industrial effluents. Hasender et al. use a method $H_2O_2/Fe^{2+}/UV$ to remove the compound [26]. The optimum conditions for this process are: a pH of 6, the concentration of hydrogen peroxide - 2.82 mmol/L, the concentration of iron hydroxide - 0.17 mol/L and UV light emitted from a 700 W lamp. Under these conditions, it was possible to remove 71% of the PEG. The same method can eliminate sulfamethoxazole (SMX) from wastewater. González et al. [27] completely removed this antibiotic from wastewater. They used hydrogen peroxide at a concentration of 300 mg/L, and ferric ions (Fe^{2+}) at a concentration of 10 mg/L. The final concentration of the antibiotic was less than 5 mg/L, when hydrogen peroxide is used at a dose of between 100÷300 mg/L. When H_2O_2 dose exceeded 300 mg/L, the concentration of antibiotic decreased to 1 mg/L. At the dose of peroxide in excess of 1000 mg/L total organic carbon was removed at 80%, while COD reduced by 92.5%. High doses of H_2O_2 resulted in the creation of readily biodegradable products with low toxicity [28].

2.3. Wet Air Oxidation

Wet Air Oxidation - WAO - involves oxidation of organic or inorganic substances in aqueous solution or suspension with the use of oxygen or air in elevated conditions of temperature and pressure. The optimum conditions for this process are 120°C and 2 MPa and 300°C and 10 MPa. The process lasts from 15 to 20 minutes. The COD reduction is from 75 to 90%. Insoluble organic compounds turn into simpler soluble compounds. On the other hand, they are oxidised and converted to CO_2 and H_2O, NO, SO_2, HCl, dioxins, furans, fly ash, etc. [29].

2.4. Oxidation of water in the supercritical state

Oxidation of water in the supercritical state is carried out above the critical point of water (> 22 MPa and 374°C). Oxidation in supercritical conditions differs greatly from other AOP processes. In the reaction mixture there is a single-phase process, and thus the kinetics of the process is only in the field of chemical kinetics. Supercritical water changes its properties as a solvent. The supercritical point of water volume is 3-fold higher than in normal conditions. As a result, under the conditions of the oxidation process at about 400°C, and at a pressure of between 23÷26 MPa, the water is present in the form of a dense gas. Organic substances including hydrocarbons and molecular oxygen are mutually soluble with water. Inorganic salts are precipitated from the solution. These unique properties allow water to contact oxygen and organic compounds in one phase, in which rapid and complete oxidation of the organic substances follows at temperatures 550÷650°C. Under these conditions, the conversion rate can be greater than 99.99% for one-minute stop-time in the machine. This is particularly important for substances known to be extremely dangerous or harmful to the environment because of their toxicity, if they are resistant to oxidation (nitrophenols, halogenated aliphatic and aromatic hydrocarbons, PCBs and dioxins). For the construction of reactors there are needed materials with a high corrosion resistance and strength [30].

2.5. Electrochemical oxidation

Another method that belongs to the advanced oxidation methods is electrochemical oxidation. Its unquestionable advantage is that on the surface of electrodes only electrons are produced and consumed. Thanks to this, oxidation does not contribute a further increase in the amount and number of compounds in the environment, which often happens in other processes. The disadvantages of the electrolytic purification of leachate include the need to dilute leachate, high costs of the process and great complexity of the mechanism of electrochemical oxidation in aqueous solution.

There are three possible mechanisms of the process:

- electrocoagulation,
- electroflotation,
- electrooxidation.

Many researchers attempted to remove ammonia from wastewater using electrochemical oxidation. Chen et al. used titanium electrodes coated with ruthenium and iridium [31]. When added to a solution of chloride ions at a concentration of 400 mg/L, there was a significant reduction in ammonia concentration. Within three hours the electrochemical oxidation of ammonia was reduced from 38.6 mg/L to 3.1 mg/L. When the current density was 6 mA/cm^2 48.6% of the ammonia was removed in one hour [32].

2.6. Oxidation with ozone

Quite often, ozone is also used in oxidation process. It is a selective oxidant. Its activity is used for oxidation of non-biodegradable substances and therefore the use of ozone is employed after the biological treatment. Non-biodegradable components are oxidized with ozone, which makes them more sensitive to further biological purification. The ratio of COD (chemical oxygen demand) to BOD_5 (biological oxygen demand) is called the measure of plant susceptibility for degradation. The lower the ratio is, the easier biological wastewater treatment occurs. The ratio COD/BOD_5 for wastewater plant cellulose coming from the first purification stage is reduced from 8 to 3. In this way the efficiency of purification (for COD) for the whole system is greatly increased (from 45% to over 80%). On the other hand, in textile industry, ozone is used to decolorize wastewater in the post-treatment step. In the pharmaceutical industry ozone is used for disinfection or inactivation of pathogenic organisms. Wastewater is usually a complex mixture of the wide range of different chemical compounds at various concentrations. Processing of these compounds with ozonation, or other methods should lead to disposal of toxic compounds, to partial oxidation of not biodegradable substances to biodegradable forms or to elimination of color. The use of photolysis ozone, which combines the effect of photolysis and ozonation, increases the number of hydroxyl radicals produced. Photolysis of ozone causes formation of H_2O_2. Therefore, the combination of UV with ozonation is more effective than the sum of the two individual processes. This method is used for the same compounds that are resistant to ozone [33]. By using an O_3/UV process, Chen et al. obtained a very effective mineralization of the total organic carbon (TOC) with a UV radiation of 96 W and an ozone dosage of 3.8 g/h. This method permits the degradation of dinitrotoluene (DNT) and trinitrotoluene (TNT) [31]. Dimethylsulfoxide (DMSO) is another waste water pollutant. Its toxicity is fairly low, but DMSO significantly hinders biological wastewater treatment. When a combination of ozone and UV radiation was used, there were obtained a degradation by 76% of the DMSO after 30 min and a TOC removal by 64.6% after 300 min of treatment at pH 10 at a temperature of 25°C. When this combined method was compared to a simple ozonation method, it was found that the removal of the DMSO runs more efficiently if a combined method is employed [34]. Bactericidal properties of this method were shown by Sharrer and Summerfelt [35]. They used ozone in combination with UV radiation to inactivate bacteria in the water from fish culture tanks. After such treatment the number of heterotrophic bacteria was reduced to 0-4 colony forming units (CFU). The total coliform bacteria were reduced to 0-3 cfu/100 mL. In this way an ozone dosage of only 0.1÷0.2 (min mg)/L and a UV radiation dosage of 50 mJ/cm^2 reduced bacteria counts to nearly zero.

Japanese experience on the use of ozone for municipal wastewater treatment is described in Takahara et al. [36]. A dose of ozone per unit volume of water constitutes the most important parameter in the design and operation of such treatment The typical dose is 10÷15 mg O_3/L and the research shows the effectiveness of ozone and its potential applications. Unfortunately, the research conducted by Ried et al. [37] shows that ozone waste water treatment generates considerably high costs.

2.7. Oxidation with H_2O_2

The advanced oxidation methods include use of hydrogen peroxide in combination with UV radiation. This process entails formation of hydroxyl radicals generated by photolysis of H_2O_2 and the corresponding propagation reactions. An H_2O_2/UV system can totally mineralize any organic compound, reducing it to CO_2

and water. This method have been also employed for the mineralization of NMP. Muruganandhami et al. [38] used hydrogen peroxide at a concentration of 500 mg/L, a pH of 10, at 25°C and a UV intensity of 5.5 mW/cm^2 for water treatment of NMP at a concentration of 1 g/l. They observed that the degradation of the compound had considerably longer reaction time than when the water was treated with the O_3/UV method. The hydrogen peroxide used in the process results in a more rapid decay of O_3/UV ozone and increases the generation of OH radicals. The disadvantage of this process are extremely high costs. When the process is used for wastewater decontamination, and the products to be removed only weakly absorb UV radiation, it is more cost-effective to externally add hydrogen peroxide with a reduced flow of UV. This method allows a significant reduction in TOC. The oxidation velocity in these three processes can be very high. But unfortunately so is the cost to generate the UV radiation [39, 40].

2.8. Ultrasonic technology

Ultrasonic technology has been used successfully in the treatment of landfill leachate. The range of application possibilities of ultrasonic field is very wide. It is closely associated with various phenomena taking place in the area of impact. The most important reactions are sonochemical reactions that occur in an ultrasonic field. They are especially significant for difficultly biodegradable compounds. These reactions occur in the interior surface and in immediate surroundings of cavitation vesicles. Free radicals, which are produced, react with different compounds contained in the liquid, oxidize them and cause them to disintegrate or destabilize. Ultrasound is usually used to support the biological treatment of landfill leachate in the SBR and UASB reactors [41, 42].

Unfortunately, advanced oxidation processes are relatively expensive, because they are not widely used. Often there are required large doses of oxidants and the cost of equipment such as: ozone generators, ultrasound emitters, UV lamps is very high [43].

3. Discussion

Advanced Oxidation Processes is an effective method of treatment of leachate from the landfill. Oxidizing factor for these processes are free radicals. It is a common feature of AOP. Among these processes, the most commonly used are: oxidation with ozone, hydrogen peroxide and Fenton's reagent oxidation. Ozonation is usually used as a third stage of landfill leachate treatment. When using trioxygen loss of organic pollutants ranks from 50 to 70%. Oxidation of organic compounds by Fenton's reagent results in a reduction of the COD from 45 to 75%. Wet Air Oxidation causes a reduction in the COD from 75% to 90%. In advanced oxidation processes there are commonly used oxidising systems. The most important of these are: O_3/UV, O_3/H_2O_2, H_2O_2/UV or O_3/H_2O_2/UV, H_2O_2/Fe^{2+}/UV. When several components are employed at the same time, it results in the removal of impurities are significantly better than for the individual reactants. Advanced oxidation processes are effective in wastewater treatment, unfortunately, they are also expensive.

4. Conclusions

AOP is an alternative to conventional methods, which often do not work well for substances resistant to degradation. The advantages of using the aforementioned processes are primarily: effective degradation of organic pollutants, hardly biodegradable compounds and toxins, significant reduction of COD and BOD_5 in the leachate and increased susceptibility to biodegradation of pollutants.

Table 3

Comparison of AOP

Type of treatment	Type of wastewater	Effect on the rate of COD	Remarks
O_3/H_2O_2	Mature landfill leachate	O_3/H_2O_2 removal COD efficiency was 72%	The hydrogen peroxide used in the process O_3/UV causes rapid decomposition of ozone generation and increases the radical • OH.
Fenton process	Landfill leachate	COD removal efficiency from 60 to 86%	the most popular method of AOP, uses additional UV radiation in order to avoid formation of ferric sludge waste
Wet air oxidation	Municipal landfill leachate	COD reduction of 78%	The most optimum conditions for this process are 120°C and 2 MPa and 300° C and 10 MPa. The duration of the process is from 15 to 20 min.
UV/H_2O_2	Landfill leachate	Achieved 72 and 65% of color and COD removal efficiencies	This method allows the mineralization of NMP
Electrochemical oxidation using an oxide-coated titanium anode	Municipal landfill leachate	Higher COD (92÷80%) and ammonia nitrogen (67÷75%) removal efficiency was achieved in SBR process operated with ultrasound conditioned leachate	The disadvantage is that first of all effluents need to be diluted. This process is also expensive
O_3	Landfill leachate	Higher COD (80%)	Ozone applying stage is placed after the biological treatment step

Summary

Landfill leachate vary widely in chemical composition. This composition is dependent on numerous factors and undergoes changes during the exploitation of the landfill site. In young landfill sites there dominate acidic phase products that are easily biodegradable compounds. When a landfill site is more older, the leachate contains more degradable biochemical substances. These substances are mainly humic acids. Due to the differences in chemical composition of leachate for its purification there are used a variety of methods with both biological and physico-chemical properties. For the purification of landfill leachate from young landfill sites there are generally used biological methods, as the leachates usually contain biodegradable compounds. For the hardly decomposable impurities, contained in the leachate from stabilized landfill sites there apply any physico-chemical methods. To choose the appropriate purification method of municipal landfill leachate an in-depth analysis should be carried out, considering waste storage technologies, landfill types, quality and quantity of leachate that arise and the size of the landfill site. We must also take into account the expected life of the landfill, as well as legal requirements allowing prior drainage of purified leachate to the receiver. Advanced oxidation processes are effective, but relatively expensive, so they are not widely used. Advanced oxidation methods can be divided into homogeneous and heterogeneous processes. Homogeneous processes can be carried out with or without power. However, it is the combined processes that are definitely more efficient. These methods can effectively remove or reduce the number of pollutants that could not be removed by conventional methods. Advanced oxidation processes have the ability to break down hardly biodegradable compounds and they are regarded as an effective tool for the treatment of water from the persistent residue.

Acknowledgements

This work was financially supported by the statutory research fund No. BS/PB 401-303/11 of the Institute of Environmental Engineering, Częstochowa University of Technology.

References

[1] Żygadło M., Strategia gospodarki odpadami komunalnymi, praca zbiorowa, Wydawca Polskie Zrzeszenie Inżynierów i Techników Sanitarnych, Poznań 2001.

[2] Girczys J., Procesy utylizacji odpadów stałych, Seria Monografie nr 100, Wyd. Politechniki Częstochowskiej, Częstochowa 2004.

[3] Szpadt R., Usuwanie i oczyszczanie odcieków ze składowisk odpadów komunalnych, Przegląd Komunalny 2006, 12 (184).

[4] Hoigne J., Intercalibration of OH radical sources and water quality parameters, International Conference, Oxidation Technologies for Water and Wastewater Treatment, Goslar, May 12-15 1996.

[5] Rosik-Dulewska C., Podstawy gospodarki odpadami, Wydawnictwo Naukowe PWN, Warszawa 2005.

[6] Cañizares P., Paz R., Sáez C., Rodrigo M.A., Costs of the electrochemical oxidation of wastewaters: a comparison with ozonation and Fenton oxidation processes, Journal of Environmental Management 2009, 90, 410-420.

[7] Oller I., Malato S., Sánchez-Pérez J.A., Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination-A review., Science of the Total Environment 2011, 409, 4141-4166.

[8] Renou S., Givaudan J.G., Poulain S., Dirassouyan F., Moulin P., Landfill leachate treatment: Review and opportunity, Journal of Hazardous Materials 2008, 150, 468-493l.

[9] Slak R.J., Gronow J.R., Hall D.H., Voulvoulis N., Household hazardous waste disposal to landfill, Environmental Pollution 2007, 146, 501-509.

[10] Surmacz-Górska J., Groźne odcieki z wysypisk, Przegląd Eureka 2001, 4.

[11] Bilitewski B. i inni, Podręcznik gospodarki odpadami - Teoria i praktyka, Wydawnictwo „Seidel-Przywecki", Warszawa, 2006.

[12] Prousek J., Advanced oxidation process for water treatment. Chemical process, Chem. Listy 1996, 90, 229-237.

[13] Szyc J., Odcieki ze składowisk odpadów komunalnych, Monografie, Instytut Ochrony Środowiska, Warszawa 2003.

[14] Anielak A.M., Chemiczne i fizykochemiczne oczyszczanie ścieków, Wydawnictwo Naukowe PWN, Warszawa 2000.

[15] Surmacz-Górska J., Degradacja związków organicznych zawartych w odciekach z wysypisk, Monografie nr 5, Polska Akademia Nauk, Komitet Inżynierii Środowiska, Lublin 2001.

[16] Lee Y., Gunten U., Oxidative transformation of micropollutants during municipal wastewater treatment: Comparison of kinetic aspects of selective and non-selective oxidants, 2010, 44, 555-566.

[17] Haapea P., Korhonen S., Tuhkanen T., Treatment of industrial landfill leachates by chemical and biological methods: ozonation, ozonation + hydrogen peroxide, hydrogen peroxide and biological posttreatment for ozonated water, Ozone Science Engineering 24(5), 369-378.

[18] Wu J.J., Wu C.-C., Ma H.-W., Chang C.-C., Treatment of landfill leachate by ozone-based advanced oxidation processes, Chemosphere 2004, 54, 997-1003.

[19] Tizaoui C., Bouselmi L., Mansouri L., Gharbi A., Landfill leachate treatment with ozone and ozone/hydrogen peroxide system, Journal of Hazardous Materials 2007, 140, 316-324.

[20] Prousek J., Advanced Oxidation Process for water treatment. Photochemical process, Chem. Listy 1996, 90, 307-315.

[21] www.chem.univ.gda.pl

[22] Lopez A., Pagano M., Volpe A., Di Pinto A., Fenton`s pre-treatment of mature landfill leachate, Chemosphere 2004, 54, 1005-1010.

[23] Biń A.K., Zastosowanie procesów pogłębionego utleniania do uzdatniania wody, Ochrona Środowiska 1998, 1(68), 3-6.

[24] Deng Y., Englehardt J.D., Treatment of landfill leachate by the Fenton process, Water Research 2006, 3683-3694.

[25] Dabek L., Ozimina E., Oxidation of organic contaminants adsorbed on active ted carbons, Ochrona Środowiska i Zasobów Naturalnych 2009, 41, 427-436.

[26] Hasender R., Fdez-Navamuel B., Hartel G., Degradation of polyethylene glycol by Fenton reaction: a comparative study, Water Science and Technology 2007, 55(12), 83-87.

[27] González O., Sans C., Espulgas S., Sulfamethoxazole abatement by photo-Fenton. Toxicity, inhibition and biodegradability assessment of intermediates, Journal of Hazardous Materials 2007, 146, 459-464.

[28] Zarzycki R., Imbierowicz M., Rogacki G., Filipiak T., Nowoczesne metody unieszkodliwiania odpadów, Mat. seminarium naukowego nt. Ochrona środowiska w przemyśle - techniki i technologie, Łódź 1996.

[29] Wąsowski J., Piotrowska A., Rozkład organicznych zanieczyszczeń wody w procesach pogłębionego utleniania, 2002, 85, 27-32.

[30] Kim S.M., Geissen S.U., Vogelpohl A., Landfill leachate treatment by a photoassisted Fenton reaction, Water Science and Technology 1997, 35(4), 239-248.

[31] Chen W., Juan C., Wei K., Decomposition of dinitrotoluene isomers and 2,4,6-trinitrotoluene in spent acid from toluene nitration process by ozonation and photo-ozonation, Journal of Hazardous Materials 2007, 147, 97-104.

[32] Neczaj E., Ultradźwiękowe wspomaganie biologicznego oczyszczania odcieków wysypiskowych, Wydawnictwo Politechniki Częstochowskiej, Częstochowa 2010.

[33] Roche P., Volk C., Carbonnier F., Paillard H., Water oxidation by ozone/hydrogen peroxide using the 'Ozotest' or 'Peroxotest' methods, Ozone Science & Engineering 1994, 16, 135-55.

[34] Zaleska A., Janczarek N., Nowoczesne procesy utleniania, Politechnika Gdańska, Wydział Chemiczny, Gdańsk.

[35] Skarrer M., Summerfelt S., Ozonation followed by ultraviolet irradiation provides effective bacteria inactivation in a freshwater recirculating system, Aquacultural Engineering 2007, 37, 180-191.

[36] Takahara H., Nakayama Sh., Tsuno H., Application of ozone to municipal sewage treatment, International Conference Ozone and UV Proceedings, 17-23.

[37] Ried A., Mielcke J., Wieland A., The potential use of ozone in municipal wastewater, Ozone: Science & Engineering 2009, 31, 415-421.

[38] Muruganandham M., Chen S., Wu J., Mineralization of N-methyl-2-purolidone by advanced oxidation process, Separation and Purification Technology 2007, 55, 360-367.

[39] Schwarzenbeck N., Leonhard K., Wilderer P.A., Treatment of landfill leachate-high tech or low tech, Water Science and Technology 2003, 48, 277-284.

[40] Ceçen F., Aktas O., Aerobic co-treatment of landfill leachate with domestic wastewater, Environmental Engineering Science 2004, 2, 303-312.

[41] Rokhina E.V., Lens P., Virkutyte J., Low-frequency ultrasound in biotechnology: state of art, Trends in Biotechnology 2009, 27, 5, 298-306.

[42] Neis U., Ultrasound in water, wastewater and sludge treatment, Water 2000, 2, 36-39.

[43] Poyatos J.M., Muñio M.M., Almecija M.C., Torres J.C., Hontoria E., Osorio F., Advanced Oxidation Processes for wastewater treatment: state of the art, Water Air Soil Pollut. 2010, 205, 187-204.

Wykorzystanie zaawansowanych metod utleniania (AOP) do oczyszczania odcieków składowiskowych

Problemem ściśle związanym z użytkowaniem składowiska odpadów komunalnych jest powstawanie odcieków oraz konieczność ich oczyszczania. Odcieki składowiskowe są wodami odpadowymi, które w wyniku przenikania przez złoże wymywają z niego związki mineralne i organiczne. Ze względu na różnorodny skład zarówno fizyczny, jak i chemiczny istnieje konieczność ich oczyszczenia przed odprowadzeniem do odbiornika naturalnego bądź kanalizacji. Liczba i różnorodność związków chemicznych, jakie występują w odciekach, jest ogromna, a ich pełna identyfikacja praktycznie niemożliwa. W artykule omówiono zależność, jaka występuje między wiekiem składowiska a stężeniem zanieczyszczeń w odciekach, a także, jak powyższa zależność wpływa na biodegradację zanieczyszczeń. Do oczyszczania odcieków z młodych składowisk można stosować metody biologiczne z uwagi na znaczne stężenie zanie-

czyszczeń podatnych na biodegradację. Do usuwania zanieczyszczeń trudno rozkładalnych, znajdujących się w odciekach ze składowisk ustabilizowanych, zastosowanie znajdują różnorodne metody fizyczne i chemiczne.

Przy doborze odpowiedniej metody oczyszczania odcieków ze składowisk odpadów komunalnych należy przeprowadzić wnikliwą analizę ich właściwości fizycznych i chemicznych. Należy ponadto rozpatrzyć technologie składowania odpadów, rodzaje składowanych odpadów, jakość i ilość odcieków, jakie powstają, oraz wielkość składowiska. Trzeba również uwzględnić przewidywany czas eksploatacji składowiska, jak również wymogi prawne, pozwalające na odprowadzenie uprzednio oczyszczonych odcieków do odbiornika.

Prowadzone od wielu lat badania ukazują, iż niemożliwe jest dobre oczyszczenie odcieków, kiedy stosuje się jeden proces jednostkowy. Zwykle wykorzystuje się do tego celu układy hybrydowe, które łączą metody biologiczne z procesami fizyczno-chemicznymi: procesy zaawansowanego utleniania, metody membranowe bądź procesy sorpcji na węglu aktywnym.

Coraz większą uwagę skupia się na wykorzystaniu zaawansowanych procesów utleniania - AOP (Advanced Oxidation Processes) do oczyszczania ścieków o niewielkiej podatności na biodegradację. Cechą, która wyróżnia te procesy, jest czynnik utleniający. Czynnikami utleniającymi są bardzo reaktywne rodniki hydroksylowe. Posiadają one wysoki potencjał utleniająco-redukcyjny, dzięki czemu są zdolne do utleniania związków organicznych. Procesy AOP prowadzą do mineralizacji zanieczyszczeń, polegającej na utlenieniu zanieczyszczenia do dwutlenku węgla, wody i nieorganicznych związków. Zastosowanie AOP jako obróbki wstępnej, wspomagającej oczyszczanie biologiczne, powoduje, że procesy te są efektywne i opłacalne z punktu widzenia ekonomicznego. Do najczęściej stosowanych metod chemicznych zaliczamy utlenianie ozonem, nadtlenkiem wodoru oraz utlenianie odczynnikiem Fentona. Ozonowanie stosuje się najczęściej jako trzeci stopień oczyszczania odcieków wysypiskowych. Metody zaawansowanego utleniania wydają się obiecującą alternatywą dla konwencjonalnych sposobów postępowania z odciekami ze składowisk odpadów komunalnych. Niemniej jednak wysoki koszt technologii AOP oraz nie do końca poznany mechanizm reakcji chemicznych i fizycznych wymaga wciąż prowadzenia dodatkowych badań naukowych.

Słowa kluczowe: **odcieki składowiskowe, zaawansowane metody utleniania, AOP, zwiększenie biodegradowalności**