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COD REMOVAL FROM LANDFILL LEACHATE USING H_2O_2 , UV RADIATION AND COMBINATION THESE PROCESSES

Experiments for removal of organic compounds (expressed as COD) from “young” municipal landfill leachate, using oxidation by H_2O_2 , UV photooxidation and UV/ H_2O_2 process, were carried out on a laboratory scale. Studies have shown that the most effective method was UV/ H_2O_2 process. When oxidation was conducted under the most suitable conditions (parameters found during experiments), maximum value of COD removal equaled 74.6%, 19.6% and 19.3% when the treatment was realized by use of H_2O_2 /UV, H_2O_2 and UV radiation, respectively. These results demonstrate that in order to attain high efficiency of COD removal, use of advanced oxidation process (H_2O_2 /UV) is necessary.

1. INTRODUCTION

Landfill leachate is called the rainfall water, which penetrated through the bed of waste [1]. Leachate may also be a surface and underground waters, which have been in contact with the deposited waste [1]. Moreover, these are also the water generated in the process of physicochemical and biochemical changes of organic compounds content in deposited waste [1, 2]. Landfill leachates are industrial wastewaters which, according to Polish law, should be collected and treated. Degradation of pollutants in the leachate is so complex that their physicochemical composition is very diverse and depends on many factors, both internal (i.e. type of deposited waste, or waste compaction process) and external (i.e. intensity and frequency of rainfall weather). No universal method exists for purification of this type of industrial wastewater, ensuring the required efficiency [1, 2].

Many various methods are known for industrial wastewater treatment, one of them being oxidation processes exploiting various oxidative agents or their combinations including hydrogen peroxide, UV irradiation and H_2O_2 /UV irradiation.

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Hydrogen peroxide is a multipurpose oxidant applied in many treatment systems [3]. It is one of the cheapest oxidizers normally used in residual waters, with high oxidizing power, easy to handle and water-soluble. Hydrogen peroxide does not produce toxins or colour in byproducts. Among others, H_2O_2 can be used to eliminate cyanides, for removing chromium(VI), for oxidation of sulfur compounds, and elimination of some inorganic nitrogen compounds [4]. Hydrogen peroxide can be applied directly or with a catalyst. As catalysts, the following metals can be used: Fe^{2+} (so called Fenton reagent [5–7]), Al^{3+} and Cu^{2+} [3].

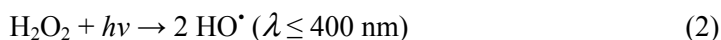
Photochemical oxidation with ultraviolet light is also a method which can be used for wastewater treatment. Many organic contaminants absorb UV energy being degraded due to direct photolysis or becoming excited and more reactive with chemical oxidants. However, there are some limitations for use of this kind of oxidation. One restriction is that organic compound to be eliminated must absorb light competitively to other compounds present in treated wastewater. The other one is that the organic compounds generate a wide variety of photochemical reactions which may produce products more complex for degradation. Moreover, not all emitted radiation is fully exploited, only the radiation absorbed. That is why only a part of radiation produces chemical changes [3, 8].

In photochemical reactions, hydroxyl radicals may be generated by water photolysis (Eq. (1)) [3]. This reaction is a poor source of radicals and in the oxidation process intermediates absorbing part of the radiation are generated, which causes a decrease of the photooxidation kinetics of the contaminants. For this reason, the method finds application only for effluents with low concentration of pollutants. The process of photochemical oxidation, for example, can be used for tomato wastewaters treatment [9, 10] or for removal pharmaceuticals such as ketoprofen, diclofenac and antipyrine from wastewater [11]:



To improve efficiency of UV oxidation other reagents (like hydrogen peroxide and/or ozone, metallic salts or semiconductors like TiO_2) can be used together with UV radiation. These combined methods are so-called advanced oxidation processes (AOPs) [3]. That kind of oxidation methods can be used in wastewater treatment for removal of organic compounds, specific pollutants destruction, increasing the biodegradability of wastewater and even for sludge treatment [9].

The $\text{H}_2\text{O}_2/\text{UV}$ process generates hydroxyl radicals by hydrogen peroxide photolysis and subsequent propagation reactions. The mechanism most commonly accepted for the photolysis of H_2O_2 is [3, 8]:



The method provides a cheap and reliable source of hydroxyl radicals and its efficiency is comparable when UV radiation is applied together with ozone. It is really

effective oxidation process for aromatic compounds removal. However major drawback of this process is that cloudy wastewaters or those containing compounds which may compete with hydrogen peroxide in absorption of UV radiation can present problems being treated by this method. The $\text{H}_2\text{O}_2/\text{UV}$ process can be used for wastewater from tannery treatment [12, 13], for decolorisation [14–18] or even for degradation of wastewaters from cork manufacturing [19].

Organic compounds, except nitrogen compounds, belong to main pollutants found in landfill leachate. Moreover, concentration of organic matter in leachate is limited when it is discharged into sewerage or natural environment. In the paper, application of the oxidation methods for removal of organic compounds from municipal landfill leachate has been examined. The efficiencies of applied methods were measured as decrease of COD value.

2. EXPERIMENTAL

Leachate from “young” municipal landfill was used in the research. Age of deposited wastes on that landfill was not larger than 5 years. Values of COD in leachate ranged from 1900 to 2700 $\text{mg O}_2/\text{dm}^3$. The ratio of BOD_5/COD in the treated leachate was very low (0.16).

During the study, three various processes were applied such as: oxidation by hydrogen peroxide, photooxidation by UV radiation and oxidation by $\text{H}_2\text{O}_2/\text{UV}$ process.

In the first series of experiments, the most appropriate parameters of oxidation with H_2O_2 were determined. They were: pH (4.0; 6.0 and 8.5), dose of oxidant (from 1 to 5 g/dm^3) and reaction time (from 1 to 3 h). Experiments were conducted in 1 dm^3 reactors equipped with a magnetic stirrer. In the second series of experiments, photochemical oxidation by means of UV radiation (15 W UV lamp, minimum radiation dose of 400 J/m^2 , irradiation time from 0.5 to 1.5 h) was investigated. H_2SO_4 or NaOH (both 50%) were added into treated leachate to reach desired initial pH (3.0; 4.0; 5.0; 6.0; 7.5; 8.5 and 10.0). Then leachate was placed in a continuous flow UV reactor with recirculation. During the third series of experiments, the following parameters for $\text{H}_2\text{O}_2/\text{UV}$ process were chosen: pH (2.0; 4.0; 5.0; 7.5; 8.5), dose of H_2O_2 (from 1 to 5 g/dm^3) and radiation time (from 0.5 to 1.5 h). The same reactor as in second series was used. First, pH of the treated leachate was adjusted (by adding alkali or acid), then hydrogen peroxide was added into leachate and the leachate was placed in a continuous flow UV reactor with recirculation.

Efficiency of oxidation processes was estimated by measuring the COD values. They were determined in accordance with the Polish Standard by the chromate-based method [20]. pH was measured with a pH-meter (pH-196, Poland).

In the samples of leachates treated with H_2O_2 and $\text{H}_2\text{O}_2/\text{UV}$ irradiation, concentration of residual H_2O_2 was analysed by the iodometric method before the COD meas-

urement. The presence of H_2O_2 increased the COD value since it acted as a reductant, especially in the chromate-based analysis of COD [21]. Both in the first and third series, residual H_2O_2 in leachate after oxidation was present. Therefore to calculate the COD as a difference between the total COD measured and the COD due to residual H_2O_2 following formula was applied [22]:

$$\text{COD} = \text{COD}_m - f[\text{H}_2\text{O}_2] \quad (3)$$

$$f = 0.4706 [\text{H}_2\text{O}_2] - 4,06 \cdot 10^{-5} [\text{H}_2\text{O}_2] \quad (4)$$

where: COD_m is the value of COD obtained during titration of the treated leachate sample, f – the correction coefficient.

3. RESULTS AND DISCUSSION

3.1. H_2O_2 OXIDATION

Five various doses of H_2O_2 (from 1 to 5 g cm^3) were applied at 3 different pH values (4.0; 6.0 and 8.5). In every case, the influence of reaction time (from 1 to 3 h) on the efficiency of COD removal was checked. The best efficiency was obtained at low values of initial pH (4 and 6). The maximum efficiency of COD removal (20.9%) was observed at initial pH = 4, $[\text{H}_2\text{O}_2] = 1 \text{ g/dm}^3$ and reaction time of 3 h (Fig. 1a). A little lower efficiency (19.6%) was noted at pH 6, and the same values of H_2O_2 dose and reaction time (Fig. 1b). However when initial pH equalled 8.5 (Fig. 1c) maximum COD removal was only 17.0%. Such a value was obtained for the dose of H_2O_2 4 g/dm^3 after 2 h of reaction time and for the dose of H_2O_2 was 5 g/dm^3 after 3 h.

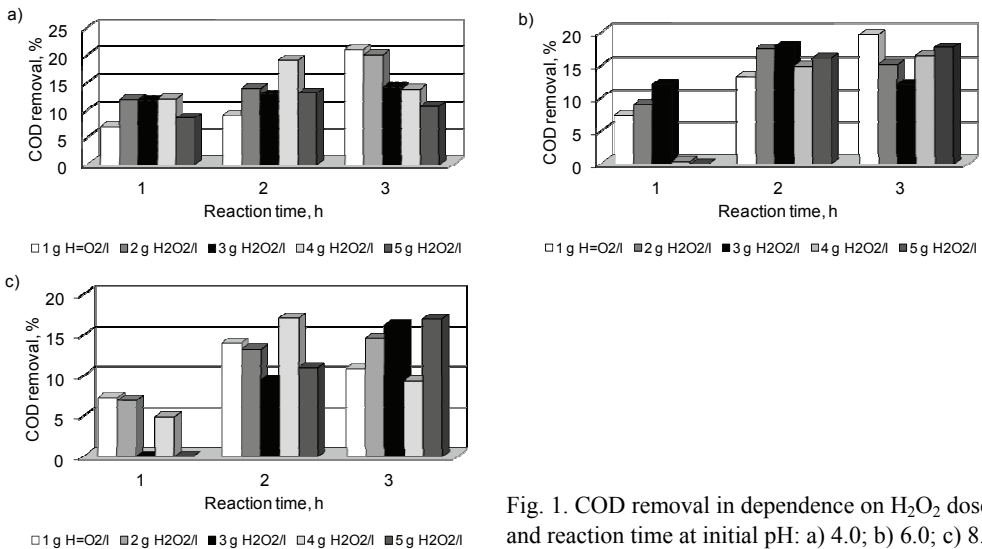


Fig. 1. COD removal in dependence on H_2O_2 dose and reaction time at initial pH: a) 4.0; b) 6.0; c) 8.5

In almost every case, the efficiency of COD removal increased upon increasing reaction time. However in some cases, increase in reaction time from 2 to 3 h caused decrease of COD removal efficiency (Figs. 1a–c). This phenomenon may be due to the formation of specific by-products which were characterized by higher values of COD in comparison with raw leachate.

3.2. UV PHOTOOXIDATION

In the second series of experiments, the most appropriate parameters of photochemical oxidation by UV irradiation were chosen. The influence of radiation time and initial pH value on removal of organic compounds was examined. Seven different initial pH values (3.0; 4.0; 5.0; 6.0; 7.5; 8.5 and 10.0) were applied and radiation time was increased from 0.5 to 1.5 h.

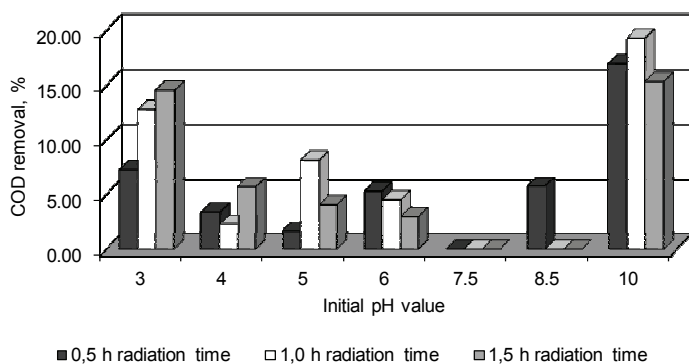


Fig. 2. COD value in dependence on initial pH and radiation time in UV oxidation process

After UV irradiation, the highest COD removal (from 15 to 19.3%) was observed at initial pH = 10.0. Maximum efficiency of photooxidation (19.3%) was reached at pH = 10.0 and 1 h reaction time. A little lower efficiency (14.6%) was noted when the oxidation process occurred at pH = 3 and 1 h radiation time. When initial pH ranged from 4.0 to 8.5 (except pH 7.5), the COD value was reduced for about 200 mg O₂/dm³, and the highest obtained efficiency ranged from 5.3 to 8.1%. However the worse effects of oxidation were observed when initial pH was 7.5. In this case, an increase of the COD value in leachate after oxidation in comparison with raw leachate was obtained. It may be due to by-products of oxidation characterized by higher values of COD in comparison with raw leachate. Moreover, experiments showed that at most of initial pH (3.0; 4.0; 5.0 and 10.0) efficiency of treatment process increased upon increasing radiation time. However in general, a small maximum efficiency (only 19.3%) of COD removal during photochemical oxidation by UV radiation was ob-

tained. This could be caused by dark-brown colour of the leachate which caused dissipation of UV radiation and made effective treatment impossible.

3.3. PHOTOOXIDATION WITH H₂O₂/UV IRRADIATION

During photooxidation with H₂O₂/UV irradiation the results showed that the maximum efficiency (74.6%) was reached at initial pH of 4.0, H₂O₂ dose of 3 g/dm³ and 1.5 h radiation time (Fig. 3b).

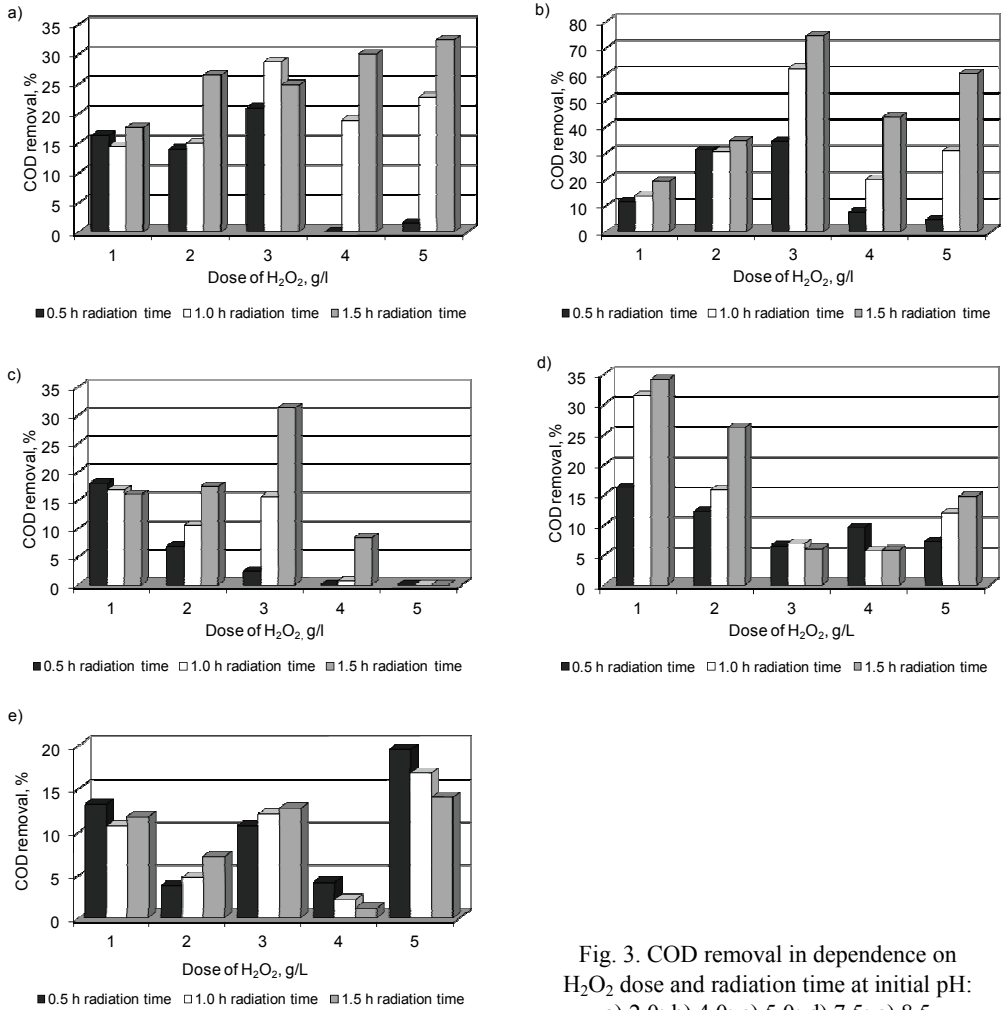


Fig. 3. COD removal in dependence on H₂O₂ dose and radiation time at initial pH: a) 2.0; b) 4.0; c) 5.0; d) 7.5; e) 8.5

In almost every case (both initial pH values and H₂O₂ doses) COD removal efficiency increased upon increasing irradiation time. The highest increase in the COD

removal efficiency was observed at doses of hydrogen peroxide ranging from 3 to 5 g/dm³ at initial pH of 2, 4 and 5 (Figs. 3a–c). However, lower doses of hydrogen peroxide (1 and 2 g/dm³) resulted in smaller enhancement of efficiency in comparison with higher doses added into leachate. Such changes of efficiency of organic compounds removal with time in dependence on H₂O₂ doses could be caused by hydroxyl radicals generated. When small doses of oxidant were added, the smaller number of OH[•] were generated; thus the oxidation process was most intensive during first 30 min of irradiation. However, when doses of H₂O₂ increased to 3–5 g/dm³, number of hydroxyl radicals was high enough for oxidation to occur during the whole process up to 90 min of irradiation.

On the other hand, when the oxidation process was carried on at initial pH = 7, the highest increase of efficiency upon increasing radiation time was observed for H₂O₂ doses 1 and 2 g/dm³ (Fig. 3d). In this case, the highest efficiency of COD removal (34.1%) was obtained at 1 g of H₂O₂/dm³ and 1.5 h radiation time. Yet, the lowest efficiency was obtained when initial pH was 8.5 (Fig. 3e). The maximum efficiency of COD removal in this case was only 19.5% at 5 g H₂O₂/dm³ and 0.5 h radiation time.

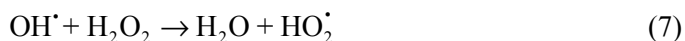
The results of the experiments showed also that the most appropriate initial pH for oxidation the leachate with H₂O₂/UV irradiation was 4.0. Lower initial pH resulted in decrease of the COD removal efficiency, probably due to reaction of OH[•] radicals with hydrogen ions acting as hydroxyl radicals “scavengers” [22]:



Similarly as in previous processes, initial pH > 4 also caused a decrease of COD removal efficiency by fast decomposition of hydrogen peroxide due to H₂O₂ dissociation:



Moreover, when larger amounts of H₂O₂ (4 and 5 g/dm³) were applied at initial pH 5.0 and 7.5, a decrease of COD removal efficiency in comparison with smaller doses of oxidant was observed. Hydrogen peroxide probably reacts (as a scavenger radicals) with generated OH[•] radicals (Eq. (7)) forming HO₂[•] radicals with much lower oxidation potential in comparison with hydroxyl radicals [22]:



4. CONCLUSIONS

Three different oxidation processes were examined for landfill leachate treatment: with H₂O₂, UV and H₂O₂/UV irradiation. The results showed that the most efficient was the latter process. When oxidation was conducted exploiting the most appropriate parameters (determined during the experiments), the maximum value of COD removal

equalled 74.6%, 20.9% and 19.3% for use of H₂O₂/UV irradiation, H₂O₂ and UV irradiation, respectively. These results showed that in order to attain high efficiency of COD removal, it was necessary to use advanced oxidation process (H₂O₂/UV) in which strong oxidative agents (hydroxyl radicals) are generated for effective treatment of contaminants in leachate.

Small efficiency obtained during UV photooxidation could be caused by a dark-brown colour of leachate what might disperse the UV radiation. The next problem was insufficient power of the low-pressure lamp used as the radiation source in the experiments.

The results showed also that to obtain high efficiency of the H₂O₂/UV irradiation process, suitable conditions of oxidation should be fulfilled. Too low initial pH could strongly deteriorate treatment effects. On the other hand, too high initial pH contributes to dissolution of hydrogen peroxide into oxygen and water. Moreover, too large dose of hydrogen peroxide could lead to reaction between H₂O₂ and OH[•] radicals and decrease the amount of hydroxyl radicals. H₂O₂/UV irradiation method enabled one to obtain high efficiencies of removal of organic compounds. In addition, the method can be easily implemented and used to pre-treatment of leachate within the landfill before discharge it to sewerage.

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