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The comparison of efficiency of Fenton and photo-Fenton treatment of stabilised landfill leachate[1]

Porównanie efektywności oczyszczania odcieków z ustabilizowanego składowiska odpadów komunalnych w procesie Fentona i foto-Fentona

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Słowa kluczowe: odcieki składowiskowe, foto-Fenton, proces fentona, biodegradowalność

Abstract
The goal of this article was to compare the efficiency of Fenton and photo-Fenton reaction used for stabilised landfill leachate treatment. The mass ratio of COD:H_2O_2 was fixed to 1:2 for every stages. The dose of reagents (ferrous sulphate/hydrogen peroxide) was different and ranged from 0.1 to 0.5. To determine the efficiency of treatment, the BOD (biochemical oxygen demand COD (chemical oxygen demand), TOC (total organic carbon) , ammonia nitrogen and BOD/COD ratio was measured. The experiment was carried out under the following conditions: temperature was 25ºC, the initial pH was adjusted to 3.0. Every processes were lasting 60 minutes. The most appropriate dose of reagents was 0.25 (Fe^{2+}/H_2O_2). It was found that the application of UV contributed to increase of COD, TOC and ammonia removal efficiencies by an average of 14%.

Streszczenie
W pracy porównano efektywność oczyszczania odcieków pochodzących ze „starego" składowiska odpadów komunalnych w procesie Fentona i foto-Fentona. Podczas wszystkich etapów badań stosunek masowy ChZT:H_2O_2 był stały (1:2). Dawki reagentów (stosunek siarczan żelaza/nadtlenek wodoru) zmieniano w zakresie od 0.1 do 0.5. Efektywność obu procesów oceniano w oparciu o stopień obniżenia BZT_5 (biochemicznego zaporzebowania tlenu) ChZT (chemicznego zapotrzebowania tlenu), OWO (ogólnego węgla organicznego), azotu amonowego i zmiany wskaźnika BZT_5/ChZT. Podczas oczyszczania odcieków z odczynnikiem Fentona wyznaczono najkorzystniejsze parametry prowadzenia procesu tj. temperatura (25ºC), początkowy odczyn odcieków (pH=3.0) . Czas trwania reakcji ustalono na 60 min. Stwierdzono, że dla tego rodzaju wód odpadowych najkorzystniejsza dawka reagentów to 0.25. Zauważono, że obecność dodatkowego czynnika (UV) przy każdej przebadanej dawce reagentów skutkowało średnio 14% wyższym stopniem usunięcia ChZT i OWO z badanych odcieków.

1. INTRODUCTION

The term 'leachate' means water generated from rainwater percolated through landfill. The mineral and organic compounds achieved as a result of biological and chemical transformation are washed out from the layers of landfills [Huang-Jung, Hung-Yee 2006, Rodriguez at al. 2004]. The leachate is characterised by different composition due to the different composition of wastes and technologies of landfilling [Jeong-Hoon, Hae-Jin 2001, Surmacz-Górska 2000]. As a result of biochemical conversion of wastes the leachate's composition is connected with the degree of degradation of organic matter [Jeong-Hoon, Hae-Jin 2001, Surmacz-Górska 2000]. The major components of young leachate (below 5 years) are high biodegradable products of acidic phase of fermentation such as volatile fatty acids, alcohols and ketones. This leachate is characterised by the high value of BOD_5 and COD. The BOD_5/COD ratio is usually above 0.7 [Bohdziewicz, Kwarciak 2008]. The older the landfill is, the lower the concentration of organic matter: the BOD_5/COD ratio decreases to 0.05 [Dąbrowska et al. 1999, Kwarciak, Bohdziewicz 2007, Bohdziewicz, Kwarciak 2008, Kurniwan et al. 2006]. It was found that the main compound of mature leachate is humic acid which is characterised by stable structure and low biodegradability. This is the reason that the treatment of mature leachate with the activated sludge is not effective [Surmacz-Górska 2000, Szyc 2003, Bohdziewicz, Kwarciak 2008]. The leachate is specific wastewater in the case of which are not general treatment method. The research for effective treatment is widely conducted all over the world. The advanced oxidation processes (e.g. methods involving Fenton reagent, UV/H_2O_2, UV/O_3 or Fenton process modification) are promising physico-chemical method of treatment. Advanced oxidation processes (AOP) has many advantages over conventional physical and chemical leachate treatment techniques. AOP are the most attractive because they are suitable for degrading concentrated leachate from any type of source . The main advantage of Fenton's process is that oxidation and flocculation occur simultaneously which results in greater organic matter removal without producing any toxic

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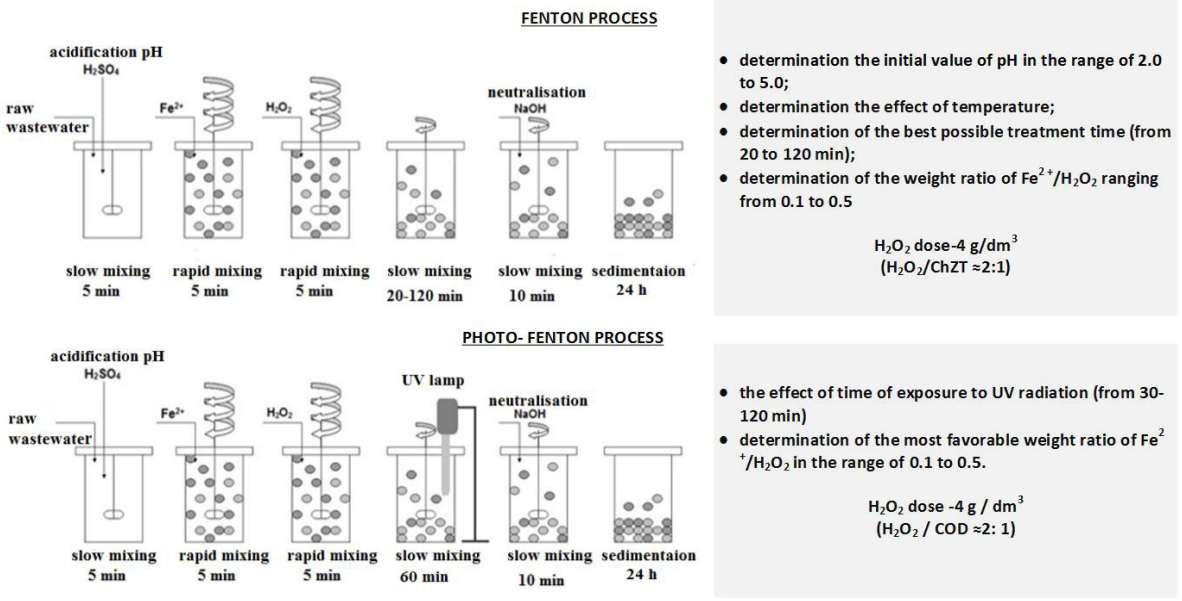

Fig. 1. Steps of wastewater testing by the use of jar test- Fenton and photo- Fenton processes

byproducts. Non-biodegradable organic components can be removed and the toxicity of wastewater can be lowered by free radical-mediated oxidation [Yu et al 2015]. The process does not require any form of energy as catalyst and is relatively simple to perform. The Fenton's reagent reaction depends on a number of parameters such as reaction time, pH, H_2O_2 to Fe (II) molar ratio, Fenton's reagent dosage, initial COD and temperature [Gupta et al. 2014, He et al. 2015]. Hydroxyl radicals are generated as a result of reduction of hydrogen peroxide by ferrous ion in Fenton and photo-Fenton processes. Both hydroxyl radical and ferrous ions are involved in the oxidation of organic matter in leachate [Zmudziński 2012, Zhangi et al. 2005]. The regeneration of Fe^{2+} and increased production of hydroxyl radicals is the result of Fenton reagent associated with ultraviolet radiation [Barbusiński 2013]. Hydrogen peroxide does not create harmful byproducts (decomposes to water and oxide) and therefore it is called ecological oxidant [Barbusiński 2001].

2. METHODS AND MATERIALS

2.1. Research material

The leachate was characterised by pH 8.66 and light brown colour. The COD value was 2070 mg/dm^3 on average and BOD_5 was under 130 mg·dm^{-3}. The BOD_5/COD ratio was at a low level – 0.06– that indicated low biodegradability. The amount of total nitrogen and TOC was 1820 mg·dm^{-3} and 570 mg·dm^{-3}, respectively. The total number of mesophilic bacteria was on average 5.4x10^{3}ctu·cm^{-3}.

2.2. Methodology

The advanced oxidation treatment of leachate was divided into two main steps: Fenton and photo-Fenton process. Both of these processes were conducted under static conditions (jar test). The volume of reactors was 1 dm^3. The photo-Fenton reactor was equipped with UV lamp emitting wavelength of 254 nm. The goal of Fenton process was to determine the most appropriate conditions necessary for the process: temperature, initial pH value, reaction time. For photo-Fenton process the time of irradiation by UV was determined. The Fe^{2+}/H_2O_2 ratio was constant and equal to 0.25 in every cases. Ferrous ions were dosed as $FeSO_4x7H_2O$ and hydrogen peroxide was indicated as 30% solution. The COD/H_2O_2 weight ratio was 1:2 for every stages (Fig.1).

2.3. Analyses

The effectiveness of each processes were determined based on COD, BOD_5, TOC and TN measurements. The COD was determined using dichromate method according to PN-85/C-04578/02. The BOD_5 was determined with respirometric method using OXI Top WTW kit. The Kiper TOC 10C analyser PX-120 with autosampler AS40-Dione3.11 was used to determine the TOC and TN value. The total number of mesophilic bacteria was determined by Koch method [ALPHA 1999, Wójcik-Szwedzińska et al. 2000].

3. RESULTS

3.1. Determination of the most favourable conditions for Fenton and photo-Fenton processes

The first step was to determine the influence of temperature for organic compounds (TOC) reduction in treated leachate. The TOC was the most appropriate indicator of pollution index due to the fact that it is not depending of residual hydrogen peroxide [Janiga, Michniewicz 2007]. The temperature of reaction was varied from 25ºC to 45ºC. The Fe^{2+}/H_2O_2 ratio was constant (0.25)

and pH was 3.5. The highest removal efficiency was achieved for 25ºC (50%) and 30ºC (48%). Increasing the temperature to 40ºC and 45ºC has resulted in a slight decrease of TOC reduction to 43%. Zhang et al. [2005] and Barbusiński [2001, 2013] provide that increasing the temperature of Fenton reaction above 40ºC leads to the degradation of hydrogen peroxide to water and oxide. It was found that the effectiveness of reaction is decreasing at this temperature [Zhang et al. 2005, Barbusiński 2013]. The temperature of reaction in the next stages was fixed to 25ºC.

Seven experiments were conducted to establish the best pH of raw wastewater. Each of the Fenton processes was carried out at a different pH (from 2 to 5). The reaction time was 60 minutes. The Fe^{2+}/H_2O_2 ratio was 0.25. It was found that the lowest removal efficiencies was obtained at pH=2.0 (27%) and pH=5.0 (30%). The effectiveness of Fenton reaction was decreasing at pH above 4.0. The highest TOC removal efficiency (48%) was obtained at pH=3.0.

During the establishment of the best reaction time (slow mixing phase) the time was changing from 20 to 120 minutes. It was found that extending the reaction time of Fenton process over 60 minutes did not impress the effectiveness of treatment. The TOC removal efficiency was 50% on average at 60 minutes time of reaction.

The chemicals included in leachate might be converted into another ones. The absorption of photon of energy can lead to breaking the bonds in molecule chemical or entirely degrading them [Zmudziński 201]. The impact of photolysis time on TOC reduction was determined in this research. It was found, that reaction times over 60 minutes do not increase the TOC removal efficiency. The result for 60, 90 and 120 minutes were 19.5%, 22% and 23.2%, respectively.

3.2. Fenton and photo-Fenton reaction – comparison of effectiveness

The COD determination in wastewater treated with advanced oxidation process based on the action of hydrogen peroxide is depending of the amount of residual hydrogen peroxide. This is due to the influence of hydrogen peroxide on COD's measurement. The residual hydrogen peroxide might increase the COD value in treated wastewater [Janiga, Michniewicz 2007].

The use of the highest Fe^{2+}/H_2O_2 ratio (0.1) in Fenton reaction has resulted in the lowest effectiveness and COD removal efficiency was about 26.8%. The addition of UV radiation to Fenton process has created a possibility to increase the removal of pollutants by next 24%. After application of Fenton and photo-Fenton processes at that dose of reagents the COD in treated wastewater was 1513 mg·dm^{-3} and 1016 mg·dm^{-3}, respectively. It was found that the lower the oxidiser to catalyst weight ratio was, the higher COD removal efficiency was. The highest COD removal efficiency (64.7%) was obtained at 0.5 weight ratio of reagents for Fenton process. The same result was found (64%) after use of photo-Fenton reaction with 0.25 weight ratio of reagents (Fig. 2a).

It was also found that Fenton process involving UV radiation has led to a higher reduction of COD value, 14% on average. Ultraviolet radiation has contributed to hydrogen peroxide destruction to hydroxyl radicals. It means that all hydrogen peroxide has reacted.

The TOC value was 570 mg·dm^{-3} in raw leachate. The lowest value was observed after treatment in photo-Fenton process. The most suitable dose of reagents was 0.5. The TOC removal efficiency was 76.5%. Comparing the removal efficiencies with that resulted from the Fenton process without additional UV radiation and the same dose of reagents it was found that removal efficiency was lower by 11.8%. The measurement has shown that TOC value was 201 mg·dm^{-3} in treated leachate. The highest TOC level (417 mg·dm^{-3}) was after the application of 0.1 reagent's ratio without UV radiation. The use of UV radiation has resulted in the increase of effectiveness of advanced oxidation from 26.8% to 50.7% (Fig. 2b).

The main goal of pretreatment by advanced oxidation processes like Fenton and photo-Fenton was to achieve the highest BOD_5/COD ratio. The raw leachate is characterised by low biodegradability. The use of advanced oxidation processes will have led to improve the effectiveness of biological treatment using SBR. It was found that during the Fenton and modified with UV Fenton processes the BOD_5/COD ratio has been increasing apart from the reagent's dose. The highest BOD_5/COD ratio increasing (from 0.06 to 0.091) was observed at 0.25 dose of reagents. The use of UV radiation has contributed to increasing the BOD_5/COD ratio at lower dose of reagents (0.12). Under these conditions the

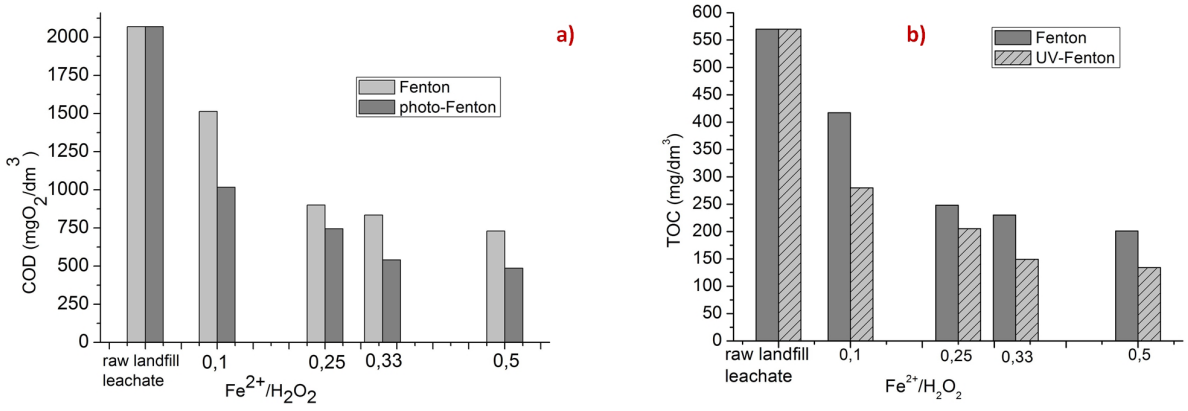

Fig. 2. Comparison of COD (a) and TOC (b) value the raw and treated leachate in the Fenton and photo-Fenton processes

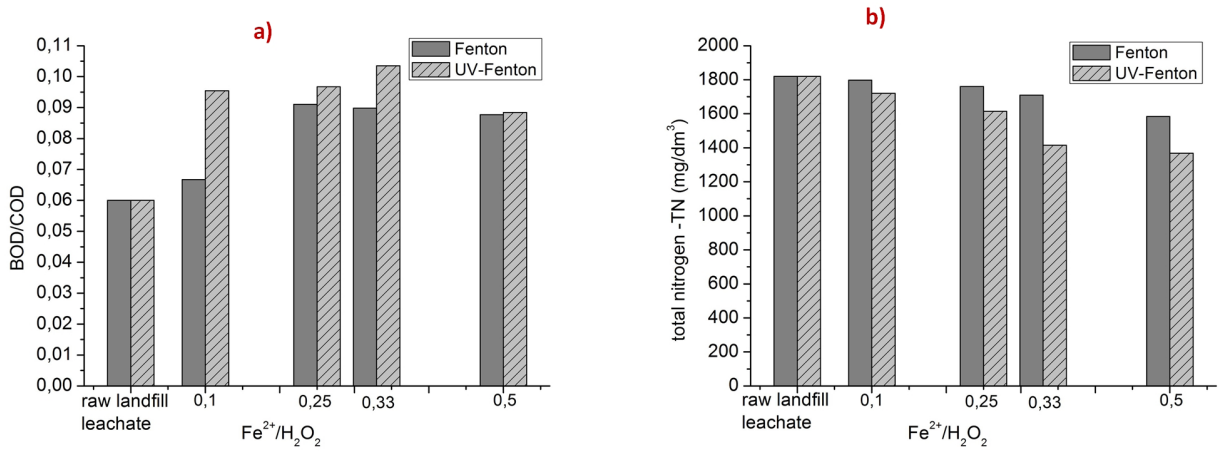

Fig.3. Comparison of BOD/COD (a) and TN (b) value the raw and treated leachate in the Fenton and photo-Fenton processes

Table 1. Landfill leachate treatment efficiency in the Fenton and photo-Fenton processes (with most favourable doses of Fe^{2+}/H_2O_2)

Pollution indices	Concentration of pollution in landfill leachate	Landfill leachate after Fenton process (Fe^{2+}/H_2O_2- 0.25)		Landfill leachate after photo-Fenton (Fe^{2+}/H_2O_2- 0.33)		Permissible standards-natural receiver*
		Concentration	R (%)	Concentration	R (%)	
pH	8.66	8.0	-	8.0	-	6.5-9
COD (mg·dm^{-3})	2070	900	56.5	540	75.3	125
BOD (mg·dm^{-3})	130	82	37	65	50	25
BOD/COD	0,06	0,091	-	0,12	-	-
TN (mg·dm^{-3})	1820	1760	3.3	1415	22.2	10
TOC (mg·dm^{-3})	570	232	59.2	149	73.8	30

*Regulation of the Ministry of Environmental Protection, Natural Resources and Forestry dated 28 January 2009 on the classification , (J. Law, No. 09.27, item 169)., R-retention

value of BOD_5/COD was 0.095. It was assumed that the most proper dose of Fenton's reagents was 0.33 for combined process (UV and Fenton). The highest value of BOD_5/COD was 0.1 for this conditions (Fig. 3a).

There was a high value of total nitrogen (1820 mg·dm^{-3}) in raw wastewater. Both of the advanced oxidation processes did not affect the removal of it. The lower was the oxidiser/catalyst weight ratio, the higher was the removal efficiency of total nitrogen in both processes. The highest removal efficiencies were obtained at highest doses of reagents (0.33 and 0.5). The TN removal efficiency was 12% and 24% for Fenton and photo-Fenton process, respectively (Fig. 3b).

The amount of mesophilic bacteria was determined both in raw and treated leachate. The raw wastewater was characterised by 5.4x10^{3}ctu·cm^{-3} of bacteria. It was found that use both of these advanced oxidation processes result in total reduction of mesophilic bacteria.

The Table 1 compares landfill leachate treatment efficiency in the Fenton and UV-Fenton processes (at most favourable parameters).

4. CONCLUSIONS

1. The best parameters of Fenton and photo-Fenton process are: temperature (25ºC), pH=3.0, reaction time (60 minutes).
2. The best dose of reagents (Fe^{2+}/H_2O_2) for Fenton reaction was 0.25. It results in the increase of BOD_5/COD ratio from 0.06 to 0.091. The COD, TOC and TN removal efficiencies are 57.4%, 56.5% and 8%, respectively.
3. The best dose of reagents for combined method (UV-Fenton) is 0.33. The BOD_5/COD ratio was 0.1.
4. It was found that the presence of UV radiation for every dose of reagents has resulted in on average 14% higher TOC and COD removal efficiencies.

5. Due to the poor quality treated wastewater is planned to conduct a series of studies associating Fenton process (or photo-Fenton) with the ultrafiltration process or the SBR system.

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