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Research Article

THE EFFICIENCY OF LANDFILL LEACHATE TREATMENT USING THE FENTON'S REAGENT

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ABSTRACT
In this studies the influence of the dose and ratio of chemical reagents (Fe^{2+} and H_2O_2) on the efficiency of COD removal and changes of BOD_5/COD ratio in landfill leachate was analysed. The molar Fe^{2+}/H_2O_2 ratio was lower than 1 and amounted to: 1:10, 1:5, 1:3, three research series with 1; 2.5 and 5 g/L Fe^{2+} concentration. A higher efficiency in removing BOD than COD, and therefore the decrease of BOD_5/COD ratio in effluent was stated. The efficiency of COD removal from leachate was from 58.34% (Fe^{2+} 0.5 g/L, Fe^{2+}/H_2O_2 1:5) to 8.33% (Fe^{2+} = 0.1 g/L, Fe^{2+}/H_2O_2 = 1:10), while the efficiency of BOD removal ranged from 62 to 77%. With the molar ratio Fe^{2+}/H_2O_2 equal 1:5 the BOD_5/COD ratio was the largest for each of the analysed Fe^{2+} doses. The lowest BOD_5/COD ratio was observed for the Fe^{2+} dose 0.1 g/L and molar ratio of reagents 1:3.

Keywords: wastewater treatment, landfill leachate, Fenton's reagent.

INTRODUCTION

Landfilling is the most common method of municipal waste management, due to both technological and economic reasons. One of the drawbacks of this method of dealing with waste is the formation of leachate. Leachate result from the physical and chemical as well as biological changes, occurring in the bed and rainwater percolating through layers of waste [Hermosilla et al. 2009].

Characteristics of leachate depend on the composition and amount of deposited waste, construction and operational conditions of landfill, and most of all on the age of the landfill. Leachate from young landfills, being in the acidic phase, are characterised by low pH, average concentrations of ammonium nitrogen (500 – 2000 mg/L), high concentrations of organic substances expressed as BOD (4000 – 13 000 mg/L) and COD (30 000 – 60 000 mg/L) so as a result the value of BOD/COD coefficient is high and ranges from 0.4 to 0.7. During the methanogenic phase in leachate appear non-biodegradable organic substances, the degradation of volatile fatty acid (VFA) occurs, and pH increases to approximately 7. Along with the time of landfilling and increased advantage of anaerobic processes taking place in the bed, ammonium nitrogen appears in leachate in high concentrations (3000 – 5000 mg/L), the value of COD is 5000 – 20,000 mg/L, and BOD/COD ratio is lower than 0.1 [Foo, Hameed, 2009, Guo et al. 2010, Ahmed, Lan 2012].

Leachate treatment with biological methods is widely used, most of all due to low operating costs. However, these methods do not provide sufficient efficiency of the removal of organic substances resistant to biological degradation, whose amount increases in later phases of biochemical changes of the landfill. Therefore, for treatment leachate from old landfills, more expensive physicochemical processes, such as: coagulation and flocculation [Amokrane et al. 1997, Aziz et al. 2007], adsorption on activated carbon [Foo, Hameed 2009], membrane filtration [Tabet et al. 2002, Li et al. 2010] or advanced oxidation [Rivas et al. 2004, Singh, Tank 2013] are used.

Although the process of advanced oxidation using Fenton's reagent was discovered and described over 100 years ago, this method was adapted to remove refractory substances from leachate only in the 90s (Huang et al., 1993). In this process there is used H_2O_2 as oxidiser and Fe^{2+} as a catalyst, in order to create hydroxyl radicals ($OH^{\bullet}$) (equations 1 – 5) [Singh, Tang 2013].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\bullet} \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow HO_2^{\bullet} + H^+ \quad (2)$$

$$RH + OH^{\bullet} \rightarrow H_2O + R^{\bullet} \quad (3)$$

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (4)$$

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^- \quad (5)$$

Hydroxyl radicals efficiently mineralise or convert indecomposable organic compounds to biodegradable forms, which are then removed in biological processes. During reactions between substances dissolved in landfill leachate and Fenton's reagent, compounds with high molecular mass are converted into compounds with low mass, and complex aromatic and aliphatic hydrophobic chains are transformed to substances with the hydrophilic structure [Zhao et al. 2013, Koc-Jurczyk 2014]. The effectiveness of the process depends on the pH, doses and molar ratio of reactants (Fe^{2+} and H_2O_2) and ratios H_2O_2/COD as well as Fe^{2+}/COD.

The aim of the study was the assessment of effectiveness of organic substances removal with the method of advanced oxidation with Fenton's reagent. In the study the influence of varied doses of Fenton's reagent (Fe^{2+} and H_2O_2) and molar ratio of reagents to such parameters like effectiveness of removing organic substances expressed as COD and BOD_5, as well as the change of the relation BOD_5/COD were determined.

METHODOLOGY

Materials

For research raw leachate derived from 22 year old municipal landfill in Kozodrza (Poland) were used, which is the main landfill in the Sub-Carpathian region, where non-hazardous municipal wastes are received in the average amount of 55.8 thousand Mg/y. Leachates were characterised by the concentration of organic substances expressed as COD on the level of 4785 mg/L, and BOD_5 – 636 mg/L. Accordingly, the ratio of BOD_5/COD was 0.13. Mixed leachates were collected from the retention reservoir to 25 L plastic tanks and immediately transported to the laboratory, where they were stored for further analyses in 4 °C in the dark.

Experimental procedure

Studies on the leachate treatment with the Fenton's reagent were conducted in static conditions, in laboratory reactors with the capacity of 1 L, at a temperature 20 °C using 100 rpm stirring. Chemical reagents were dosed once at the beginning of the cycle, in the mixing phase, directly to the reactor. As the first one, $FeSO_4 \times 7H_2O$ was injected to the reactor, and directly after H_2O_2 (30%). Due to the application character of studies in the course of the experiment, the pH was not adjusted. The pH raw leachate was 8.57.

Three research series with different concentration Fe^{2+} (1; 2.5 and 5 g/L) were conducted. While for each Fe^{2+} concentration increasing doses of H_2O_2, were added obtaining as a result molar ratios of Fe^{2+}/H_2O_2 lower than 1, equal: 1:10, 1:5, 1:3. The proportions, H_2O_2/COD in raw leachate was from 0.125 to 1.8 (Figure 1), while the proportion Fe^{2+}/COD ranged from 0.02 to 0.1 (Figure 2).

In order to determine the effectiveness of the leachate treatment process by Fenton's reagent,

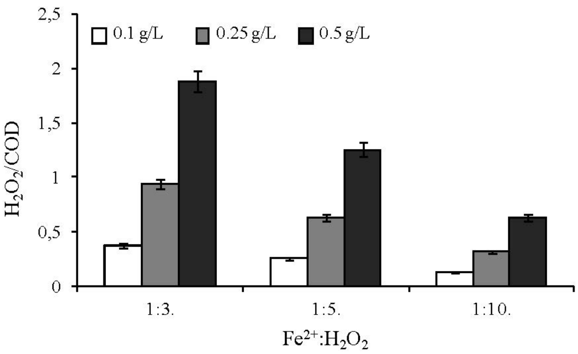

Figure 1. Doses of hydrogen peroxide expressed as a ratio to COD concentration in raw leachate

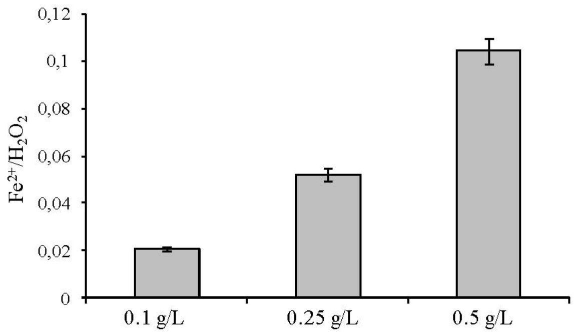

Figure 2. Doses of iron(II) sulfate expressed as a ratio to COD concentration in raw leachate

the concentrations of organic substances as COD were analysed, according to the standard PN-ISO 6060:2006P, concentration of organic substance as BOD_5 (DIN EN1899-1/EN 1899-2) and pH value (Elmetron CPC-401). Samples for organic matter measurement were collected after 1 h of mixing and 0.5 h of sedimentation after addition of reagents.

RESULTS AND DISCUSSION

In raw leachate concentration of organic substances expressed as COD and BOD_5 was respectively 4785 mg/L and 636 mg/L. After the treatment with the method of advanced oxidation using Fenton's reagent, regardless of the dose and ratio of the used reagents, both COD, and BOD_5 was lowered (Figure 3).

It was stated that regardless of the molar Fe^{2+}/H_2O_2 ratio, the lowest concentration of organic substances expressed as COD in the treated leachate was observed in the Fe^{2+} dose equal 0.5 g/L. For the ratio of reagents 1:3, 1:5 and 1:10 this value was, respectively, 2051, 1993 and 3930 mg/L. The smallest effectiveness of removing organic substances was stated for the dose Fe^{2+} 0.1 g/L (respectively; 3191, 2734 and 4386 mg/L).

Numerous literature data report the increase of concentration of biodegradable organic matter expressed as BOD_5 after the application of the advanced oxidation for the treatment of wastewater [Renou et al. 2008, Umar et al. 2010]. In this study, a decrease of BOD_5 concentration in each of the proposed technological variants was observed. In case of using Fe^{2+}/H_2O_2 1:10 ratio, the BOD_5 concentration in the outflow was 240 mg/L, regardless of the used Fe^{2+} dose. The lowest concentration of biodegradable forms of organic carbon was obtained after using the molar ratio of reagents 1:3 and Fe^{2+} doses 0.1 or 0.5 g/L (respectively 145 and 150 mg/L).

The efficiency of removing organic compounds expressed as COD from leachate was highest with the molar ratio of reagents 1:3 and 1:5 and for the dose Fe^{2+} 0.5 g/L, and was respectively 57.13 and 58.34%. The lowest removal efficiency of organic compounds expressed as COD occurred for the ratio of 1:10, and for doses Fe^{2+} 0.1, 0.25 and 0.5 g/L and equals respectively 8.33; 13.1 and 17.8%. With the increase of the Fe^{2+} dose, the efficiency of removing organic carbon (COD) grows, regardless on the molar ratio of reagents.

Considering the concentration of biodegradable organic substances (BOD_5) its decrease was also observed and so the efficiency of removing BOD_5 was also calculated. The efficiency of treatment was higher than in case of COD (Figure 4) and was within the range from 62 to 77%. The highest efficiency of BOD_5 removal was stated in case of using the 1:3 molar ratio of reagents, regardless of the dose Fe^{2+}.

Highly reactive forms of oxygen formed during Fenton's reaction lead to the simplification of the structure of complex organic compounds so the authors observe the decrease of COD, at the expense of simultaneous increase of BOD_5. Zhao et al. [2013] and Singh, Tang [2013] report that macromolecular organic substances can be effec-

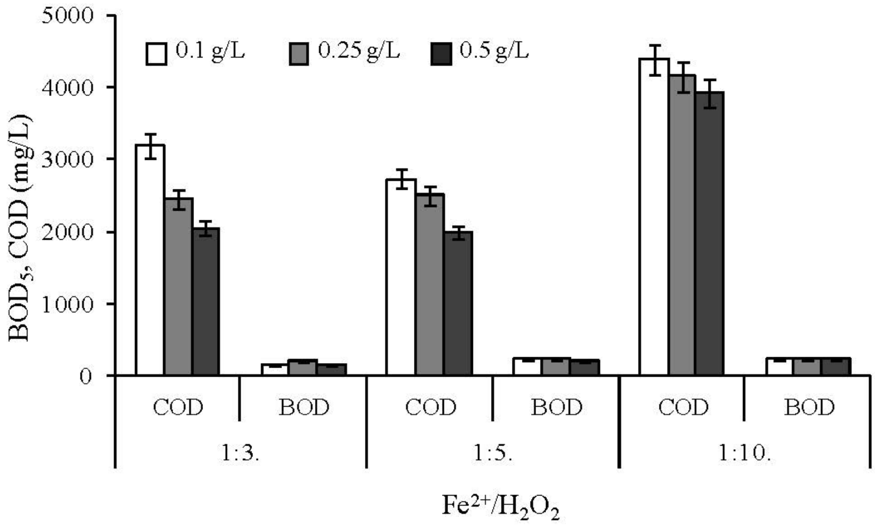

Figure 3. Concentration of organic compounds, expressed as COD and BOD, in leachates after Fenton's reagent treatment in different proportions

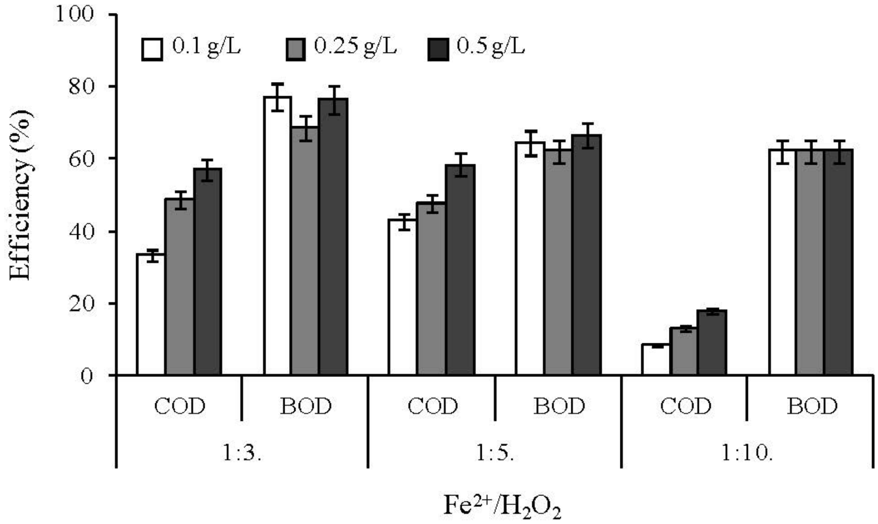

Figure 4. COD and BOD removal efficiency during the leachate treatment using Fenton's oxidation

tively oxidised using Fenton's reagent. While in this paper there was stated rather modest reduction of the COD value, with significant decrease of BOD_5 and lowering pH value to the approximately 6. Probably, under conditions which were proposed in this experiment, much more biodegradable organic compounds underwent fully mineralisation to carbon dioxide, than non-biodegradable forms transformed into biodegradable.

Zhao et al. [2013] report that efficiency of removing COD during landfill leachate AOP treatment increased with the increase of the proportion Fe^{2+}/H_2O_2 and achieved the highest value 86 and 73.4% respectively, with the Fe^{2+} dose 2.24 and 0.56 g/L. The increase of the proportion of reagents to 1:10 caused the decrease of efficiency of treatment, regardless of the iron dose.

According to Singh, Tang [2013] the optimal $Fe^{2+}:H_2O_2$ molar ratio ranges from 2:5 to 1:100 (average 1:3) and effectiveness of leachate treatment ranges from 31 to 95%. In case of treatment of raw leachate the proportion Fe^{2+}/H_2O_2 ranges from 2:5 to 1:60 (effectiveness of the treatment 31–86%).

Effectiveness of treating leachate in Fenton's process depends on the concentration of both applied reagents. Although, as it is stated by Sing, Tang [2013] H_2O_2 is the main oxidiser to refraction substances.

The theoretical H_2O_2/COD ratio with chemical oxidation with Fenton's reagent is approx. 2.1. High efficiency of removing COD from leachate was obtained after the application of the H_2O_2/COD proportion equal 3.3 [Primo et al. 2008]. In studies the proportion H_2O_2/COD was from 0.125 to 1.8 (Figure 1). Effectiveness of removing the chemical oxygen demand grew with the increase of proportion H_2O_2/COD; with the proportion of 0.125 it was the lowest and reached 8.33%, but after increasing the amount of Fe^{2+}, and thus the increase of concentration of H_2O_2, the proportion H_2O_2/COD increased to 1.8 and 1.2 and the effectiveness of COD removing was the highest and was respectively 57 and 58.3%. It was also stated that with the same proportion of H_2O_2/COD equal 0.62, the effectiveness of removing COD was different, depending on the dose and molar ratio of reagents. With the dose Fe^{2+} 0.25 g/L and ratio Fe^{2+}/H_2O_2 1:5 effectiveness of removing COD was 47.6%. After increasing the dose of Fe to 0.5 g/L and increasing the share of H_2O_2 in the reacting mixture (Fe^{2+}/H_2O_2 = 1:10) effectiveness decreased to 17.8%. As it is reported by scientific papers, the optimal H_2O_2/COD ratio for raw leachate treating is higher in comparison to optimal dose for preliminary-treated leachate. For the H_2O_2/COD ratio lower than 10, effectiveness of COD removal is between 31 – 95%. Increasing the dose of H_2O_2 does not influence the increase of effectiveness of cleaning. The greatest effectiveness of treatment (31 to 85%) was obtained using the ratio H_2O_2/COD of 0.7–1.2. [Singh, Tang 2013]. Hermosilla et al. [2009] used the ratio H_2O_2/COD of 0.42 and obtained 80% of efficiency for treating raw leachate derived from young landfill. However, the same technological conditions in case of leachate from average and old landfills resulted in the lowering of effectiveness to less than 70%.

As it follows from the above mentioned data, the ratio of H_2O_2/COD used in the studies was correct, and the lower effectiveness of treatment than the one given in literature may result from the lack of regulation of the pH. Due to the application character of this study, the pH equilibration step was abandoned, because of technological problems and additional costs that may occur in technical scale on the treatment plant.

The initial oxidation of organic compounds depends also on the concentration of Fe^{2+}. In this studies the ratio of Fe^{2+}/COD in the range from 0.02 to 0.1 was used (Figure 2). An increase of effectiveness of COD removal with the increase of Fe^{2+}/COD was observed regardless of the Fe^{2+}/H_2O_2 ratio. The influence of the amount of H_2O_2 on leachate treatment efficiency was also observed - in low concentrations of H_2O_2 (Fe^{2+}/H_2O_2 = 1:3) effectiveness of treatment was 33 to 57% but after increasing Fe^{2+}/H_2O_2 ratio to 1:10 the effectiveness lowered significantly to values from 8.33 to 17.8%. As it is reported by Sing, Tang [2013] with the increase of Fe^{2+} amount in reagent mix, the rate of organic compound oxidation grows. However, if the amount of Fe^{2+} will be exceeded, the iron ions (II) compete with organic substances for $OH^{\bullet}$ radicals. In this case the process of coagulation starts to dominate, producing the additional chemical sludge [Neyens, Baeyens 2003]. Sing, Tang [2013] report that the optimal Fe^{2+}/COD ratio ranges between 0.01 and 14.9 (on average 0.8). Just like in case of H_2O_2/COD ratio, increasing the Fe^{2+}/COD proportions does not result in the increase of the effectiveness of treatment.

When Fe^{2+} or H_2O_2 are in the excess, they are consuming $OH^{\bullet}$ radicals, what inhibits COD removal (Eq. 6 and 7) [Sign, Tang 2013, Zhao et al. 2013].

$$H_2O_2 + OH^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \quad (6)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+ \quad (7)$$

The excess of H_2O_2 may also cause flotation of the sludge due to the presence of O_2 in the gaseous form [Singh, Tang 2013].

As a measure of the biodegradability potential of organic compounds in leachate, the ratio of organic carbon measured as BOD to organic carbon measured as COD is widely accepted. Thus, this ratio is the uppermost indicator from the technological point of view, when designing biological treatment of leachate is planned for a given object. In this case, raw leachate was characterised with the ratio BOD_5/COD at the level of 0.13.

Due to a slight reduction of COD concentration and quite large BOD_5 decrease, the ratio between both indicators after treatment became lower than before, regardless of the applied research variant (Figure 5).

The lowest BOD_5/COD ratio was observed for the dose of Fe^{2+} 0.1 g/L with the molar ratio of reagents 1:3 (0.04). At the ratio 1:10 the obtained results were comparable and were 0.05 and 0.06 for doses of Fe^{2+} respectively 0.1, 0.25 and 0.5 g/L. When molar ratio Fe^{2+}/H_2O_2 was 1:5 the BOD_5/COD ratio was the highest for each of the analysed Fe^{2+} doses; in the concentration of 0.5 g/L reaches 0.106, and with higher Fe^{2+} concentrations, 0.1 and 0.25 g/L, this values were respectively 0.08 and 0.09.

In the experiment there was used 1h of reaction and 0.5h sedimentation, which corresponds to the requirements of further technical scale application. However similar conditions of the process were used by Lopez et al. [2004], Mohajeri et al. [2011] and Singh, Tang [2013] in laboratory scale too. Zhang et al. [2006] report that the rapid degradation of macromolecular organic compounds occurs during first 30 minutes of mixing. In turn,

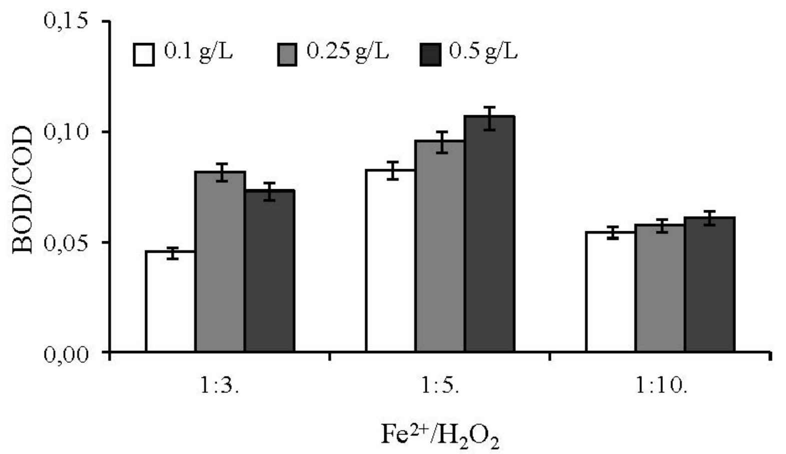

Figure 5. Changes of BOD_5/COD ratio in leachate after Fenton's reagent treatment in different proportions

Goi et al. [2010] report that the best effectiveness of removing macromolecular substances is provided only after 24 hour reaction. The increase of time of reaction does not always correspond to the higher effectiveness of COD removal. Gotvajn et al. [2009] obtained 86% of COD removing during the time of 10 minutes, and Kim, Huh [1997] 67% effectiveness of COD removing in the time of 2 days.

CONCLUSIONS

The study analysed the influence of Fe^{2+} dose and molar ratio of Fe^{2+}/H_2O_2 on the effectiveness of removing leachate organic compounds expressed as COD and BOD_5 and the changes of BOD_5/COD ratio from a landfill. It was stated that the effectiveness of removing organic substances (COD) ranged from 8.33 to 58.34%. The most effective was the dose of Fe^{2+} equal 0.5 g/L in ratio 1:5.

Also the influence of H_2O_2/COD was analysed ratio; the lowest effectiveness of treatment was obtained with the ratio equal 0.125, the highest one with 1.2. It was observed that with such small ratio H_2O_2/COD (0.62) effectiveness of treatment of leachate depended on the concentration and molar ratio of reagents. With the increase of Fe^{2+}concentration from 0.25 to 0.5 g/L and increase of proportion of H_2O_2 in the reacting mixture from 1:5 to 1:10 effectiveness of treatment decreased from 47.6 to 17.78%. Analyzing the influence of the Fe^{2+}/COD ratio on the effectiveness of treatment, there was stated the negative influence of the increase of H_2O_2 proportion in the reacting mixture.

In the studies higher effectiveness of BOD_5 removal than COD was also stated, what caused the decrease of proportion BOD_5/COD in leachate after treatment. Presumably, in proposed technological conditions the biodegradable organic compounds were more susceptible to convert to mineral forms, than refractory macromolecular compounds to biodegradable forms.

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