COD REMOVAL FROM LANDFILL LEACHATE USING FENTON OXIDATION AND COAGULATION

Krzysztof BARBUSIŃSKI a*, Barbara PIECZYKOLAN b

a Prof.; Faculty of Energy and Environmental Engineering, Silesian University of Technology, Konarskiego 18A, 44-100 Gliwice, Poland
E-mail address: krzysztof.barbusinski@polsl.pl

b Dr.; Faculty of Energy and Environmental Engineering, Silesian University of Technology, Konarskiego 18A, 44-100 Gliwice, Poland

Received: 13.09.2010; Revised: 29.11.2010; Accepted: 29.11.2010

Abstract
The treatment of old municipal landfill leachate by Fenton oxidation, coagulation as well as coagulation combined with the Fenton oxidation was carried out on a laboratory scale. It has been found that organic pollutants in leachate could be successfully removed by Fenton oxidation. The most advantageous dose of \( \text{H}_2\text{O}_2 \) and \( \text{Fe}^{2+}/\text{H}_2\text{O}_2 \) ratio were 1350 mg/L and 0.2, respectively at pH 3 and reaction time of 45 minutes. In these operating conditions, the COD removal efficiency reached 61%. However, a 73.1% removal of COD was attained after 26 hours of Fenton oxidation. In coagulation process, the efficiency was within the range of 39-45.8% using PIX as a coagulant at dose of 500 mg/L (pH 5 and 30 min of reaction time). The best result of COD removal (65.3%) was obtained in the combined treatment system including a coagulation process, followed by a Fenton oxidation. In this case, COD removal by coagulation was 45.8% while by Fenton oxidation only 19.5%. Therefore more experiments need to be done towards optimisation of such combined system. It concerns particularly the second treatment stage by Fenton oxidation. It was concluded that the Fenton oxidation or combined coagulation-Fenton oxidation system are very efficient and promising methods for treatment of non-biodegradable landfill leachate.

Keywords: Landfill leachate; Fenton reagent; Coagulation; Advanced oxidation.
Coagulation and flocculation is a relatively simple technique that may be employed successfully in treating old landfill leachates [7, 9, 16]. However, this treatment only leads to moderate removals of COD and TOC, and it has its drawbacks: sludge is produced, and in some cases, when traditional chemical coagulants are used, an increase on the concentration of aluminium or iron, in the liquid phase, may be observed [5]. Therefore, coagulation/precipitation is not appropriate for a full treatment of leachate, due to its limited efficiency for removal of organic content. However, coagulation/precipitation can be an efficient pretreatment prior to biological or membrane treatment, or an effective post-treatment for the leachate [4, 7], as well as can be used as one of the elements of a technological setup for the purification of leachates from municipal solid waste landfills [13].

One available technology widely used to treat landfill leachate in recent years is Fenton’s oxidation process \( (\text{H}_2\text{O}_2 + \text{Fe}^{2+}) \) [17], which has the advantages of both oxidation and coagulation processes [9, 18]. Among the different technologies reported in literature for the treatment of highly contaminated effluents, Fenton’s reagent is characterized by its cost effectiveness, simplicity and suitability to treat aqueous wastes showing a variable composition [19, 20]. The Fenton reagent has been found to be effective in degradation of various industrial wastewater components [21-28].

The Fenton reaction can be effectively exploited to treat landfill leachate, and may be particularly appropriate for mature leachate. Fenton processes are applicable to the treatment of highly toxic leachate and exhibit noticeably faster kinetics as compared with biological treatment processes. Fenton treatment also achieves considerably higher efficiency of removal of organic compounds from leachate, compared with other physical/chemical technologies including coagulation and activated carbon adsorption. In particular, Fenton treatment effects chemical destruction rather than pollutant transfer from one phase to another, in contrast with membrane filtration and with other separation processes. Importantly, capital costs and energy requirements of Fenton treatment can be expected to be very low compared with other advanced oxidation processes [29].

In the Fenton process, coagulation and oxidation both contribute to the removal of pollutants from leachate, and their relative importance depends on leachate characteristics and reaction conditions. The relative importance of oxidation and coagulation depends primarily on the \( \text{H}_2\text{O}_2/\text{Fe}^{2+} \) ratio. Chemical coagulation predominates at a lower \( \text{H}_2\text{O}_2/\text{Fe}^{2+} \) ratio, whereas chemical oxidation is dominant at higher \( \text{H}_2\text{O}_2/\text{Fe}^{2+} \) ratios [30]. Generally, an initial pH between 2.0 and 4.5 favours the Fenton reaction [29].

Fenton treatment can be implemented alone or in tandem with other technologies for leachate treatment. Several flow sheets reported for Fenton-based leachate treatment schemes are shown in Figure 1 [29]. These flow sheets can be roughly grouped into four categories: direct Fenton treatment of raw leachate, Fenton pretreatment prior to biological treatment, Fenton treatment preceded by physical/chemical treatment, occasionally followed by bio-
logical treatment, and Fenton treatment preceded by biological treatment, occasionally followed by physical/chemical or biological treatment.

In this paper, COD removal efficiency from old municipal landfill leachate has been examined using Fenton oxidation as well as coagulation process. In the Fenton oxidation, the effects of several process conditions such as dosage of H₂O₂, Fe²⁺/H₂O₂ ratio, pH and reaction time were investigated. Moreover, the effect of different dosages of PIX (FeCl₃SO₄) in coagulation process was studied. Additionally, a coagulation process combined with the Fenton oxidation was also used.

2. MATERIALS AND METHODS

Landfill leachate: Leachate was collected from the municipal solid waste landfill in southern Poland. Its characteristics were: dark brown colour, poor clarity, COD in the range from 932 to 1325 mg/L, BOD₅/COD = 0.2 and pH 6.7-7.3 (average pH = 7.0). Taking into account the low value of the BOD₅/COD
ratio, this leachate was classified as “old” and non-biodegradable.

**Experimental procedure:** The Fenton oxidation experiments were performed in ambient temperature in glass reactors with a magnetic stirrer. The following parameters were examined and optimized: \( \text{H}_2\text{O}_2 \) concentration, \( \text{Fe}^{2+}/\text{H}_2\text{O}_2 \) weight ratio, pH and time. The procedure was as follows: 0.5 L of leachate was put into reactors of 1-litre volume, and then acidified with \( \text{H}_2\text{SO}_4 \) to the selected value, since a Fenton reagent is effective in acidic pH range. After that, various doses of 30\% \( \text{H}_2\text{O}_2 \) and solid \( \text{FeSO}_4\cdot7\text{H}_2\text{O} \) were added. After appropriate time the leachate was neutralized with 5\% solution of \( \text{NaOH} \) up to about pH 8.5. Then, the samples were centrifuged at 3000 rpm (2.5 min) and analysed.

Coagulation studies were performed in a conventional jar-test apparatus (Flocculator SW1) equipped with 6 beakers of 1 L volume. The experimental procedure consisted of three subsequent stages: the initial rapid mixing lasted 2 min at 120 rpm, the following slow mixing for 30 min at 30 rpm, while the final settling step lasted for another 1 hour. Chemical reagent used as coagulant was PIX 110 (\( \text{FeClSO}_4 \)) at pH 5. After the settling period, the supernatants were withdrawn from the beaker and analysed.

In the combined method, experiments were performed using a coagulation process, followed by a Fenton oxidation. The optimal operating parameters, that were determined earlier, were used for each process.

**Analytical methods:** COD\(_{\text{Cr}}\) in leachate was determined in accordance with Polish Standard [31], while pH was measured by pH-meter (pH 196, Poland). In the samples of leachates treated by Fenton oxidation, concentration of residual \( \text{H}_2\text{O}_2 \) was analysed by iodicometric method before the COD measurement. The presence of \( \text{H}_2\text{O}_2 \) increase the COD value since it acts as a reductant, especially in the chromate based analysis of COD [32, 33]. The initial dark brown colour of raw leachate was not an obstacle in determination of \( \text{H}_2\text{O}_2 \) because, after Fenton process, the leachate was discolouring. However, in no case the presence of residual \( \text{H}_2\text{O}_2 \) was found in leachate after Fenton oxidation and neutralization. Therefore, there was no need to calculate COD as difference between the total COD measured and the COD due to residual \( \text{H}_2\text{O}_2 \).

### 3. RESULTS AND DISCUSSION

#### 3.1. Fenton oxidation

Preliminary batch tests were conducted to determine the optimum dose of \( \text{H}_2\text{O}_2 \) (Fig. 2). The COD values were determined after 90 minutes of the Fenton oxidation. The experiments were performed in the wide range of 200-1600 mg \( \text{H}_2\text{O}_2/L \). As the dosage of \( \text{H}_2\text{O}_2 \) changed from 200 to 1350 mg/L, COD removal efficiency increased from 39.8 to 69.7\% (COD value 631 and 282 mg \( \text{O}_2/L \) respectively). However, above the dose of 1350 mg \( \text{H}_2\text{O}_2/L \) a slight decrease in COD removal was observed. These phenomena could be explained by the excess of hydrogen peroxide concentration, behaving as a hydroxyl radical's scavenger in the Fenton reaction, according to the following reaction [34]:

\[ \text{OH}^* + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^* \]

Therefore, further experiments concerning the optimisation of pH and \( \text{Fe}^{2+}/\text{H}_2\text{O}_2 \) ratio were continued at \( \text{H}_2\text{O}_2 \) dose of 1350 mg/L.
In order to investigate the optimum FeSO₄ dosage, five different Fe²⁺/H₂O₂ ratios were tested using constant H₂O₂ concentration of 1350 mg/L (Fig. 3). The reaction time was extended to 120 min. These results show that with an increase in Fe²⁺/H₂O₂ ratio in the range of 0.1–0.2 COD removal efficiency significantly increases from 42% to 61%. However, above Fe²⁺/H₂O₂ ratio of 0.2, only slight changes in COD removal were observed and COD value kept almost the same level about 457-506.2 mg/L. Therefore, Fe²⁺/H₂O₂ ratio of 0.2 was chosen for further experiments.

Hydrogen peroxide was most stable in the range of pH 3-4, but the decomposition rate was rapidly increased with increasing pH above 5. In a pH reaction higher than 5, the COD removal efficiency by oxidation was rapidly decreased, not only by decomposition of hydrogen peroxide but also by deactivation of a ferrous catalyst with the formation of ferric hydroxocomplexes [9, 35]. Therefore, in order to estimate the pH effect on COD removal, the experiments were conducted at pH values varying between 1 and 5. As presented in Figure 4, COD removal efficiency was shown to be maximum (60.1%) around a reaction of pH 3, and it rapidly decreased with decreasing pH below 2. This inhibitory effect could be explained by an observation that excessive hydrogen ions are the dominant OH• radical scavenger according to the following reaction [22, 34, 36]:

\[
\text{OH}^* + H^+ + e^- \rightarrow H_2O
\]

As the pH changed from 3 to 5, the COD removal efficiency was only slightly decreased from 60.1% to 57.3%.

A very important factor was also the reaction time. Figure 5 shows the changes of COD as a function of reaction time during 26 hours of the Fenton oxidation. The results demonstrated that COD removal efficiency was rapidly increasing within the first 45 minutes of reaction time. Maximum efficiency of COD removal (62.9%) was observed after 60 min. After this time, COD removal was diminished to 61.4% and 52.3% after 90 and 120 min. respectively. These phenomena could be explained by the formation of by-products more resistant to oxidation. Degradation by-products of Fenton’s reaction were not identified in this study. When the reaction time was extended up to 26 hours, COD removal efficiency was reached 73.1%, probably as a result of oxidation of these by-products. This supposition is based on the other observations that high efficiency of COD removal from leachates and industrial wastewater (using Fenton reagent or coagulation) was not always followed by significant reduction of their toxicity to an acceptable level [13, 22, 32]. Prolongation of reaction time caused distinct toxicity reduction to low level [32]. However, because between 45 and 60 min., the change of COD became insignificant, 45 minutes’ reaction time was chosen as economically accepted in this study.

3.2. Coagulation process

The aim of the coagulation process was to determine possible efficiency of COD removal from landfill leachate. As a coagulant, the PIX 110 (FeClSO₄) was used at pH 5, because optimum pH range for PIX is 4.5-5.5. Several coagulant doses were tested without adding any polymers to improve flocculation quality. The results are presented in Figure 6.
With increasing PIX dose, the COD removal efficiency increased gradually, giving a maximum (39%) at 500 mg/L and next decreased beyond this dose. This COD removal decrease (above dose of 500 mg/L) can be explained by the acidic character of PIX. When the dose of PIX was increased, pH decreased continually (pH was not adjusted during coagulation) and thus optimum pH range for coagulant was not maintained. This remains in agreement with the observations by Amokrane et al. [7] and Kang and Hwang [9]. According to Amokrane et al. [7], also with increasing PIX dose, the dark brown colour of raw leachate turned, after sludge separation, to a clear brown, then to yellow and became clear yellow for the coagulant dose near the optimal value.

On the basis of insufficient efficiency of the COD removal in coagulation process performed alone, it can be stated that for more effective treatment of leachate, the coagulation should be integrated with a Fenton oxidation.

### 3.3. Fenton oxidation combined with a coagulation process

The combined tests were performed using a coagulation process, followed by a Fenton oxidation. In the coagulation process (1st stage), the PIX dose of 500 mg/L was added at pH 5. These optimal parameters were determined earlier, when coagulation process was carried out alone. In the Fenton oxidation (2nd stage), also earlier determined parameters were used: \( \text{H}_2\text{O}_2 \) dose = 1350 mg/L, \( \text{Fe}^{2+}/\text{H}_2\text{O}_2 \) ratio = 0.2, pH 3 and 45 minutes’ reaction time.

As presented in Figure 6, COD removal efficiency 45.8% and 19.5% was observed after coagulation and Fenton oxidation process respectively. The overall COD removal efficiency in combined process reached 65.3%. This efficiency was higher than after coagulation and Fenton oxidation performed alone. This relatively little increase in COD removal, observed by Fenton oxidation in the combined treatment system (19.5%) in relation to Fenton oxidation performed alone (61%) was probably because of effective COD removal by the coagulation process. In the presented experiments, the combined methods were performed using the optimal operating parameters that were determined earlier for each process alone. In such combined method, the effectiveness of the first stage is an important parameter that influences the second one and consequently the efficiency of the total process.

### 4. CONCLUSIONS

The application of coagulation and Fenton oxidation for non-biodegradable, old leachate collected from a sanitary landfill were examined in this study. The optimal operation conditions and results received for particular treatment systems are presented in Table 1. It has been found that organic pollutants in leachate could be successfully removed by Fenton oxidation. The COD removal efficiency reached 61%, using the following optimum operational conditions: \( \text{H}_2\text{O}_2 = 1350 \text{ mg/L, Fe}^{2+}/\text{H}_2\text{O}_2 \) ratio = 0.2, initial pH = 3.0 and reaction time = 45 min. When the reaction time was extended up to 26 hours, COD removal efficiency reached 73.1%.

In coagulation process, the addition of PIX coagulant (500 mg/L at pH = 5.0 and reaction time = 30 min.) to landfill leachate resulted only in 39% reduction of COD. Further improvement of the coagulation efficiency could be probably obtained by adding polymers to improve flocculation quality. Applying other coagulants should also be taken into consideration to this effect.

The best results of COD removal (65.3%) were obtained in the combined treatment system including a coagulation process, followed by a Fenton oxidation. In this case, COD removal by coagulation was 45.8% while by Fenton oxidation only 19.5%. Therefore more experiments need to be done towards optimisation of such combined system. It concerns particularly the second treatment stage by Fenton oxidation. In such optimisation process the changes of toxicity should be also taken into consideration.
On the basis of the above results it can be stated that the Fenton oxidation or combined coagulation-Fenton oxidation system are very promising methods for treatment of non-biodegradable landfill leachate. Moreover, the effectiveness of Fenton oxidation and combined coagulation-Fenton system can be probably improved by the stepwise addition of both hydrogen peroxide and ferrous iron.

REFERENCES


[31] Polish Standard PN-74/C-04578


