YOSR SMAOUI[1], SALMA MSEDDI[1], NAJLA AYADI[1], SAMI SAYADI[2], JALEL BOUZID[1]

EVALUATION OF INFLUENCE OF COAGULATION/FLOCCULATION AND FENTON OXIDATION WITH IRON ON LANDFILL LEACHATE TREATMENT

Landfill leachates (LFL) collected from Sfax (Tunisia) discharge area are characterized by high chemical oxygen demand (COD), ammonium and salts contents. They constitute a source of phytotoxicity and pollution for ground water and surface water resources which requires an adequate treatment process. To evaluate the efficiency of the coagulation/flocculation treatment, special attention was paid to the effect of pH, coagulant and flocculant doses. Then, effect of zero valent iron was also studied alone and in combination with coagulation/flocculation pretreatment. Our results indicate high removal efficiencies by coagulation/flocculation (46% COD and 63% turbidity) and Fenton process (48% COD and 76% turbidity). The combined application of coagulation/flocculation and Fenton revealed higher COD removal (62%) and turbidity reduction (90%). These results showed the applicability of this combined treatment method for the degradation of organic compounds and reduction of the treated leachate toxicity.

1. INTRODUCTION

Landfilling is the most common method used for the disposal of solid waste at economical costs with potentially less environmental effects [1]. The degradation of the organic fraction of waste in combination with percolating rainwater leads to the generation of leachate. It constitutes a high contaminated liquid due to the presence of toxic compounds such as organic constituents, heavy metals, ammonium and phthalates [2]. Therefore, leachate is considered as a source of pollution for ground surface water resources.

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[1]Laboratoire Génie de l'Environnement et Ecotechnologie, Ecole Nationale d'Ingénieurs de Sfax, Université de Sfax-Tunisie, PB 1173, 3038, Sfax, Tunisia, corresponding author Y. Smaoui, e-mail address: smaoui_yosr@yahoo.fr

[2]Laboratoire des Bioprocédés Environnementaux, LMI Cosys-Med, Centre de Biotechnologie de Sfax, BP 1177, 3018, Sfax, Tunisia.

Due to the high chemical oxygen demand and nitrogen concentration, the treatment of landfill leachate is a complex procedure that requires the combination of various processes. Biological treatments are usually suggested for the elimination of non-stabilized organic matter in young leachate [3]. However, the presence of toxic elements in those leachate may affect the efficiency of microorganisms. That is why it is important to reduce organic matter content for an effective application of the biological processes and preliminary physicochemical treatments [4].

Coagulation/flocculation is one of the most common physicochemical processes used for the landfill leachate treatment [5, 6]. It is a handy tool used as a pretreatment step to reduce pollutant load, remove recalcitrant compounds and improve the biodegradability of leachate [7]. Many factors such as pH and dosage of coagulant/flocculants, play an important role in this process. The determination of the best experimental conditions is required to increase the process efficiency [8].

During the last decades, the applicability of advanced oxidation processes (AOPs) to remove organic matter and improve biodegradability of leachate has gained significant interest. The Fenton reaction has been applied for the degradation of toxic organic compounds. In the Fenton process, H_2O_2 is added to wastewater in the presence of iron, generating strongly oxidative species with respect to the organic compounds present. Hydroxyl radicals generated are able to mineralize refractory organic matter into more biodegradable compounds that could be subsequently treated by using more economical biologically-based methods [9].

Elemental iron is one among many strong reducing agents that have received much attention for groundwater remediation and wastewater treatment processes. An alternative Fenton system has been studied involving the oxidation of iron metal under acidic conditions generating in situ Fe^{2+} which promotes the generation of hydroxyl radicals. The cost saving and the fast transformation of the ferric iron into ferrous species at the metal surface, present the most advantages of this process compared to the conventional Fenton processes. The Fenton oxidation has been successfully applied for the treatment of various types of wastewaters such as olive mill wastewater [10], pharmaceutical wastewater [9], and landfill leachate [11].

The combination of coagulation/flocculation and Fenton oxidation processes was previously applied to improve the treatment of landfill leachate [8, 12, 13]. However, no attempt has been made to combine both techniques for the treatment of landfill leachate in Tunisia.

This study aims to treat a young landfill leachate trying to reach the legal limits of release into natural waters. In the first stage, the leachate was subjected to a coagulation/flocculation process. Subsequently, the efficiency of Fenton oxidation with iron metal and a combination of these treatments were evaluated, investigating the optimum operational conditions for an efficient removal of organic compounds and toxicity reduction.

2. MATERIALS AND METHODS

Materials. The leachate used in this study was obtained from a landfill in the Tunisian Sfax region. Treatment of household waste and the leachate unit have been operating since 2008. The leachate was taken straight from the collection box, kept at 4 °C in the dark before being used in the experiments to avoid its decomposition. The main leachate physicochemical characteristics are given in Table 1. Metallic iron used in this study was obtained from a metal turner. It constitutes a residual product from this activity and was characterized by a spiral form. Ferric chloride, hydrochloric acid, sodium hydroxide and H_2O_2 were purchased from Merck (France).

Coagulation/flocculation. Coagulation/flocculation experiments were carried out using a Floclab Jar Test (Prolabo-France) equipped with six beakers of 500 cm^3 at room temperature. The chemical reagents used were ferric chloride ($FeCl_3 \cdot 7H_2O$) as a coagulant and polyacrylamide as a flocculant. A 500 cm^3 leachate sample was poured into each jar, and pH was adjusted to the desired value with 1 M HCl solution and 5 M NaOH solution. The experimental process consisted in three subsequent phases [14]: Flash mixing started at 150 rpm for 5 min with addition of various doses of ferric chloride (0.2–1 g/dm^3). A flocculation process was then conducted for 60 min by slow stirring at 50 rpm with simultaneous addition of polyacrylamide (10–30 mg/dm^3). The whole was then allowed to settle down for 30 min to improve the sedimentation of flocs through a coagulation/flocculation driven process. Samples were taken from the liquid level about 3 cm below the surface for chemical analyses and further treatment by the Fenton process.

Fenton process. A Floclab (Prolabo, France) jar-testing apparatus equipped with six beakers was used to conduct Fenton experiments at ambient temperature (25 °C). Metallic iron (1–4 g Fe/dm^3) in a spiral form was added to 500 dm^3 of leachate sample; pH was adjusted to 3, 4, 5 and 6. Various doses of H_2O_2 (0–4 g/dm^3) were then added under continuous stirring at 200 rpm. Spontaneous corrosion of iron metal occurred in the presence of H_2O_2 leading to the production of iron species in acidic conditions. A first reaction time of 2 h was performed to study the effect of pH and concentrations of iron and hydrogen peroxide. The Fenton reaction was then carried out during 24 h. Samples were taken every hour for the first eight hour of reaction and a final sample was taken at the 24th h of the reaction time. To stop the production of OH radicals and to remove residual H_2O_2, pH of the samples was increased above 10 using 10 M NaOH solution [15].

Combined treatment. Experiments were performed in the same Jar-test used for the coagulation/flocculation process. A 500 cm^3 leachate treated by coagulation/flocculation under optimal conditions was subsequently used for the Fenton oxidation. For the

process parameters, pH and contact time were fixed at their optimum conditions obtained when applying the Fenton alone. However, the doses of Fe and H_2O_2 were optimized again by varying their values from 1 to 4 g Fe/dm^3 and from 0 to 4 g H_2O_2 /dm^3, respectively.

Phytotoxicity study. Leachate toxicity was measured according to the Zucconi test [16]. Ten seeds of tomato (*Lycopersicon esculentum*) were placed in a Petri dish of 90 mm in diameter containing a sterile filter paper. 5 cm^3 sample for each leachate treatment was added to the Petri dish and incubated at 25±2 °C for 72 h. Distilled water was used as a control. Four different dilutions (0, 10, 30 and 50%) in distilled water were performed in order to widen the field of response to the toxicity of each sample. The germination index (*GI*) was calculated:

$$GI = \frac{Gs}{Gc} \times \frac{Ls}{Lc} \times 100\% \tag{1}$$

where: *Gs* is the number of germinated seeds in the effluent, *Gc* is the number of germinated seeds in distilled water, *Ls* is the root length in the sample and *Lc* is the root length in distilled water. A sample rule was used to measure the radical length in millimeter units.

Microtoxicity. ALUMIStox equipment (GmbH, Düsseldorf, Germany) was used to determine the microtoxicity of leachate. The test principle consisted in measuring the inhibition rate (*IB*, %) of bioluminescence of the bacterium *Vibrio fischeri*, strain DSM 2167 relative to a control (distilled water).

Analytical techniques. Chemical oxygen demand (COD) was determined using the method described by Knechtel [17]. Biochemical oxygen demand (BOD$_5$) was estimated by means of a respirometer (BSB-controlled model Oxitop (WTW)). The color of leachate was evaluated by measurement of absorbance at 400 nm wavelength as maximum absorbance of solution. The measurement of pH, turbidity, total solids (TS), total suspended solids (TSS), total dissolved solids (TDS), ammonium and total Kjeldahl nitrogen (TKN) were performed according to standard methods for the examination of water and wastewater [18].

3. RESULTS AND DISCUSSION

The characteristics of the collected landfill leachate is presented in Table 1. LFL contains a high organic matter expressed in terms of COD with a value about 45 g O$_2$/dm^3. Biodegradability was low with a BOD/COD ratio around 0.28. Ammonium was present

with a high value and represented more than 80% of the total nitrogen. In fact, the presence of ammonium ions in the leachate can inhibit biological treatment [19]. High content of suspended matter and high turbidity prove the significant load of colloidal particles present in the leachate. High value of electrical conductivity (EC) can be explained by the solubility of chloride in alkaline solution [20]. Dark color of leachate samples proved the presence of humic substances that accounted for the major organic compounds in the leachate [21].

Table 1

Physicochemical characteristics of the leachate
collected during the study period

Parameter	Values	LLD[a]
pH	8–8.2	6.5–9
EC, mS/cm	36	nd
Turbidity, NTU	365	nd
TSS, g/dm^3	0.8–0.9	0.4
TS, g/dm^3	45–46	nd
COD, g O$_2$/dm^3	45–50	1
BOD$_5$, g O$_2$/dm^3	13–14	0.4
BOD$_5$/COD	0.28	nd
TKN, g/dm^3	3–3.5	0.1
NH$_4^+$, g/dm^3	2.7–2.8	nd

[a]LLD – legal limits for discharge into urban-
ized streams (NT. 106.002), nd – not determined.

Coagulation/flocculation is a simple technique used to reduces pollutant loads and recalcitrant compounds to improves leachate biodegradability [22]. It depends on various factors such as pH, coagulant and flocculants doses. Generally, iron salts are the most appropriate coagulant/flocculant agents to reduce organic load, turbidity and color of landfill leachate. This can be explained by different hydrolyzed species of ferric ion. Leachate samples were treated by the addition of ferric chloride. Figure 1 shows that the optimum amount of coagulant was 0.8 g Fe^{3+}/dm^3 in order to obtain 45% removal of COD and 62% of turbidity. This result can be explained by the charge neutralization theory. In fact, the addition of coagulant to the leachate promotes the interaction between cations, their hydrolyzed forms and colloids, causing charges neutralization. The overdose of coagulant should be avoided. It resulted in absorption of the cations by colloids and generates a re-stabilization of particles and a decrease of organic matter removal efficiency [8].

The role of pH is significant as it determines the electrical charge of both organic and inorganic colloids. The most effective hydrolysis species are produced at optimum pH. This can be explained by the interaction between metal hydrolysis products and organic ligands or anions. It is clear in Fig. 2 that low pH values are suitable for coagulation/flocculation processes. In fact, it was found that an increase in pH resulted in

a decrease in the retention of ferric chloride particles. Indeed, under acidic conditions, the sorption mechanism dominated the removal of organic matter. Optimum pH of 4 allowed 42% removal of COD and 61% of turbidity. This is in agreement with data reported by Guerreiro et al. [23] who showed that coagulation/flocculation process using ferric chloride is more efficient at pH 3.
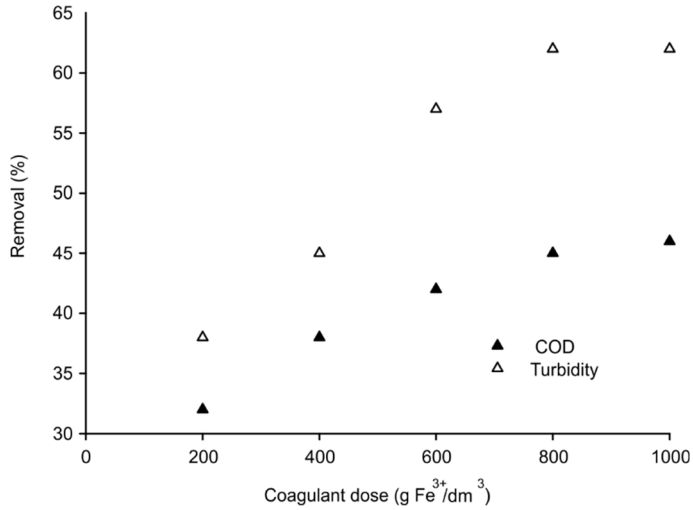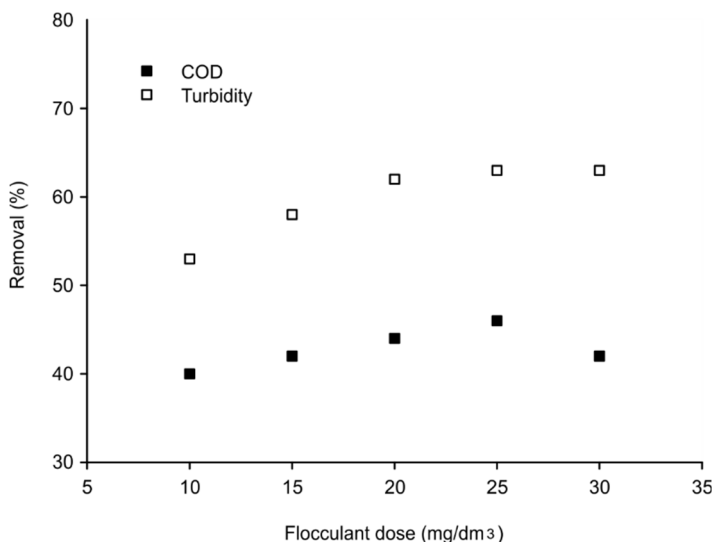

Fig. 1. Removal of COD and turbidity as a function of coagulant dose during the coagulation/flocculation (initial pH 4, flocculant dose 20 mg/dm^3)
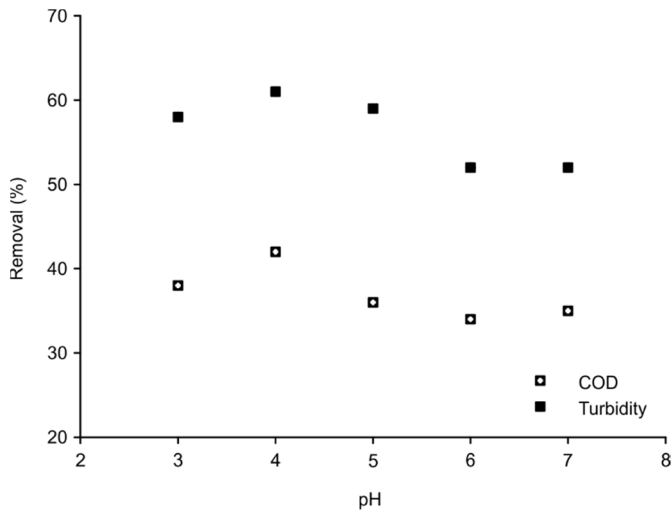
Fig. 2. Removal of COD and turbidity as a function of pH during the coagulation/flocculation (coagulant dose 0.8 g Fe^{3+}/dm^3, flocculant dose 20 mg/dm^3)

The optimization of the polyacrylamide dose was also performed. In this study, pH and dose of coagulant were fixed at 4 and 0.8 g Fe^{3+}/dm^3, respectively. The concentrations of flocculant ranged from 10 to 30 mg/dm^3 based on monitoring turbidity and COD removal. As seen in Fig. 3, a flocculant concentration of 25 mg/dm^3 induced a reduction yield of 63% for turbidity and 46% for COD.

In summary, the pre-treatment of landfill leachate by the application of coagulation/flocculation process resulted in an efficient removal of organic and pollutant load (Table 2).

Fig. 3. Removal of COD and turbidity as a function of flocculant dose
during the coagulation/flocculation (initial pH 4, coagulant dose 0.8 g Fe^{3+}/dm^3)

Table 2

Organic load removal
of landfill leachate after pretreatment
by coagulation/flocculation

Parameter	Removal [%]
COD, mg O_2/dm^3	46
NTK, mg N/dm^3	12
NH_4^+, mg N/dm^3	23
TSS, g/dm^3	50
TDS, g/dm^3	16
Turbidity, NTU	63

pH 4, coagulant dose 0.8 g Fe^{3+}/dm^3,
flocculant dose 25 mg/dm^3.

These results corroborate those reported by Bakraouy et al. [6] who demonstrated the effectiveness of coagulation/flocculation processes on the post-treatment of landfill leachate. A COD reduction around 80% was obtained at optimal concentration of 4.4 g/dm^3 of ferric chloride and 9.9 cm^3/dm^3 of cationic polymer.
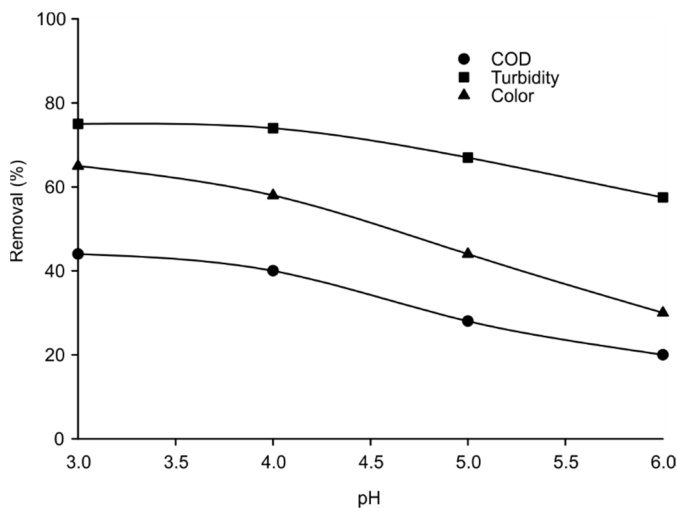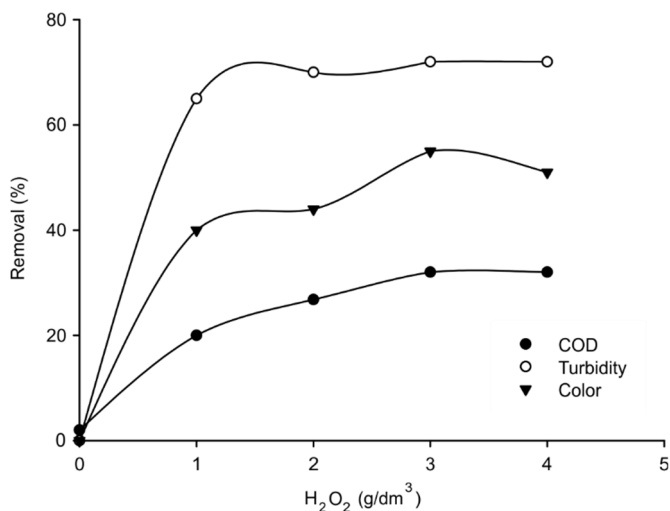

Fig. 4. Effect of pH on the COD, turbidity and color removal efficiency
during the Fenton oxidation of leachate (Fe 2 g/dm^3, H$_2$O$_2$ 3 g/dm^3, time 2 h)

The efficiency of advanced chemical process known as the Fenton process was evaluated for the treatment of raw leachate. Since the first most important parameter in the Fenton oxidation process is pH, preliminary experiments were carried out at pH between 3 and 6. Figure 4 shows the pH dependence of the degradation of organic matter, color and turbidity. The removal of COD decreased with increasing pH. The optimum pH was 3, which agrees with studies of other authors suggesting that optimum pH for the Fenton oxidation ranges between 2 and 4 [1, 7]. COD removal reached 44% with 2 g Fe/dm^3, 3 g H$_2$O$_2$/dm^3 and 2 h contact time. Under these conditions, 75% removal of turbidity and 65% of color were reached. pH affects the oxidation reaction by the decomposition of H$_2$O$_2$, reduction of OH$^\bullet$ radical production and formation of ferric hydroxo complexes [24]. Dosages of Fenton reagents determine the operating costs and efficiency of organic compounds removal. Generally, organics' removal increased with increasing concentrations of iron salts and H$_2$O$_2$. Organic matter removal is optimal when reagents are added in their optimal ratio. It was observed that [H$_2$O$_2$]/[Fe^{2+}] ratio had a significant effect on COD removal [25]. In fact, it determines the mineralization effectiveness of organic compounds via the Fenton reaction. This is linked to the variation of Fe^{2+} and H$_2$O$_2$ concentrations. However, an excess of both compounds inhibit the Fenton reaction leading to a decrease in the degradation of organic matter. The effect of H$_2$O$_2$ dosage was first investigated at fixed concentrations of metallic iron. Then the optimization of

the iron concentration at H_2O_2 dosage was further examined. It was observed that H_2O_2 effect is more critical than that of iron because it directly affects the maximum theoretical mass of $OH^\bullet$ generated. Experiments involving H_2O_2 doses within the range of 0–4 g H_2O_2/dm^3 were carried out at pH 3 using 1 g/dm^3 of Fe (Fig. 5).

Fig. 5. Effect of H_2O_2 concentration on the COD, turbidity and color removal efficiency during the Fenton oxidation of leachate (initial pH 3, Fe^0 1 g/dm^3, reaction time 2 h)
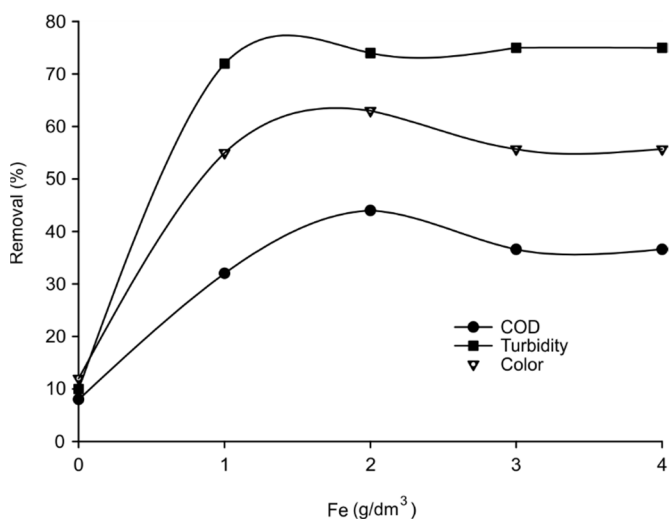
Fig. 6. Effect of Fe concentration on the COD, turbidity and color removal efficiency during the Fenton oxidation of leachate (initial pH 3, H_2O_2 3 g/dm^3, time 2 h)

As shown, COD removal increased up to 30% for 3 g H_2O_2/dm^3. The removal of color had a similar trend to COD reaching 55%. These data suggest that color was mainly produced by organic matter and some insoluble compounds. The H_2O_2 increase had no effect on COD removal that showed a maximum yield of 30%. This can be explained by the saturation of oxidation. Figure 6 shows that COD removal increases gradually with increasing of iron metal content and reaches 44% with 2 g Fe^0/dm^3 and 3 g H_2O_2/dm^3. Beyond this concentration, COD removal decreased and remained steady. The maximum removal of the color and turbidity was also observed at these conditions. After that, the concentration of iron increases, it interacts with hydroxyl radicals and causes maximum removal of COD and the dark color of the leachate becomes brown. The overdose of Fe or H_2O_2 can react with the hydroxyl radical and inhibit the oxidation reaction [10].

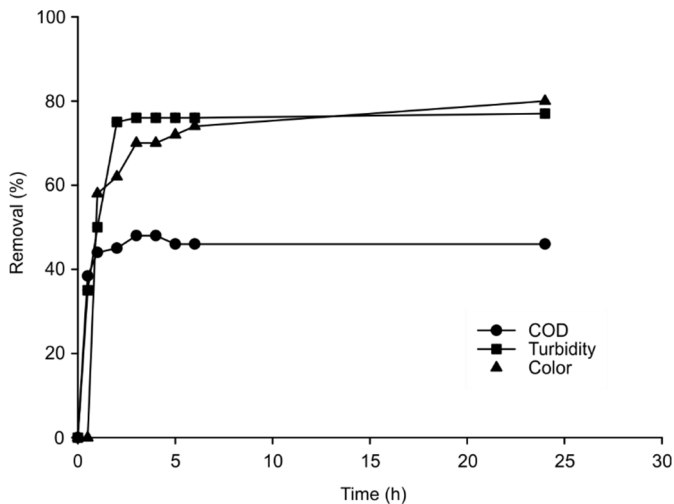
Fig. 7. Effect of reaction time on the COD, turbidity and color removal efficiency
during the Fenton oxidation of leachate (pH 3, Fe 2 g/dm³, H_2O_2 3 g/dm³)

The kinetics of organic matter removal was evaluated. Figure 7 shows a gradual increase of COD removal within the first hour that reached a maximum after 3 h with 48% removal. During this period, iron catalyzes the generation of hydroxyl radicals and then oxidizes the dissolved organic matter present in the leachate. Thereafter, the process becomes slower due to the limited availability of iron. In comparison with the results found during the application of coagulation/flocculation, it can be concluded that the Fenton process allows a significant reduction of the organic matter present in the leachate. According to Vilar et al. [11], the improvement of the leachate biodegradability by increasing the BOD/COD ratio from 0.02 to 0.33 was obtained at the optimum conditions of pH 3, contact time of 2 h, and concentration of 0.8 g Fe^{2+}/dm^3 and 3 g H_2O_2/dm^3.

Fig. 8. Effect of H_2O_2 concentration on the COD removal efficiency
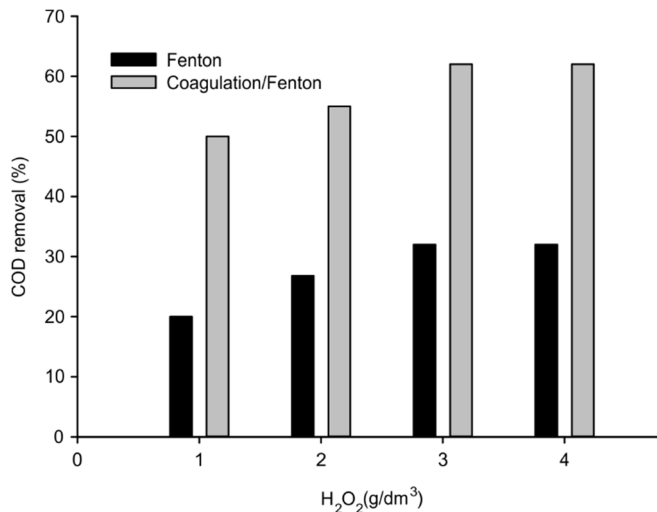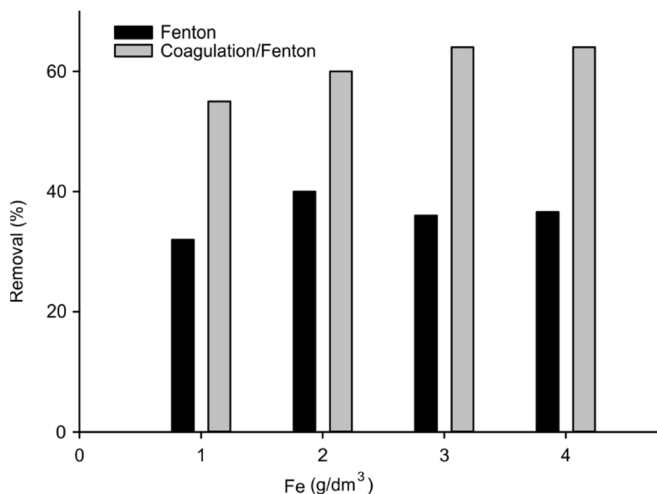during Fenton and combined process (coagulation/flocculation and Fenton oxidation)

Fig. 9. Effect of Fe concentration on the COD removal efficiency
during Fenton and combined process (coagulation/flocculation and Fenton oxidation)

Considering the insufficiency of COD removal obtained from the coagulation/flocculation or the Fenton process, the combination between these two processes has been tested. Leachate treated by coagulation/flocculation was then subjected to oxidation with Fenton's reagent. The pH and the reaction time were fixed according to the best operating conditions previously selected. Nevertheless, the reagent doses were optimized. Figure 8 shows the removal of COD during Fenton and combined processes in

dependence of the H_2O_2 dose. COD removal increased with the increase of H_2O_2 concentration reaching a maximum amount similar to that obtained by the application of the Fenton alone but with an improved performance. This can be explained by the fragmentation of organic compounds that may facilitate the reaction with H_2O_2. Regarding the iron dose, the data showed that increasing the dose to 3 g Fe/dm^3 increased the efficiency of the integrated process to 62% COD. This value increased compared to that obtained with the Fenton oxidation only (Fig. 9).This may be due to the fact that the added iron accelerated the rate of decomposition of the H_2O_2 generating hydro-peroxide radicals. This is in correlation with Amor et al. [8]. These authors showed that the combination of coagulation/flocculation with Fenton oxidation led to high COD removal rates.

In order to compare the effectiveness of the treatments performed, the removal of chemical oxygen demand, turbidity, color and ammonium after each treatment are presented in Fig. 10.
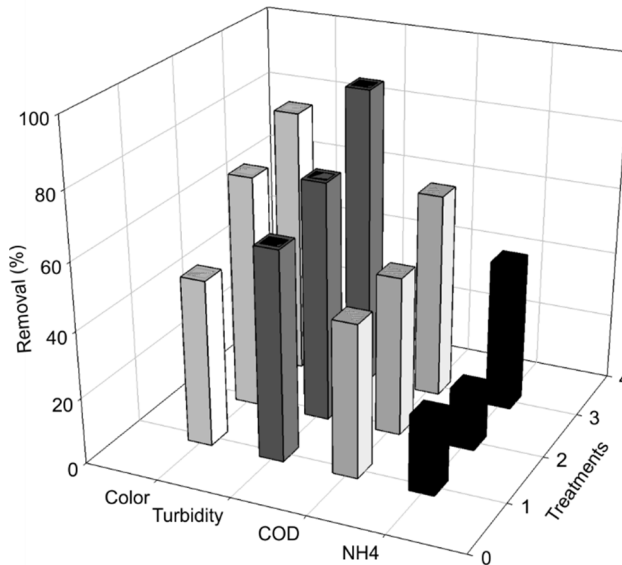

Fig. 10. Chemical oxygen demand, turbidity, color and ammonium removal efficiencies
against treatment stage (1 – coagulation/flocculation, 2 – Fenton oxidation, 3 – combined process)

Microtoxicity tests were carried out using the luminescent bacterium *V. fischeri*. The principle of the test consisted in measuring the inhibition of bioluminescence (*IB*, %). The test showed that the leachate samples exhibited high microtoxicity since they totally inhibited the bioluminescence of *V. fisheri*. Leachate toxicity was also evaluated on plants in order to assess inhibition risk of seed germination in with different concentrations of the test product. Seed germination was completely inhibited (*GI* = 0), when the

raw leachate was used suggesting a high phytotoxicity. Indeed, Zucconi et al. [16] reported that the effluent is phytotoxic if the *GI* is below 50%. The used of 50-fold diluted leachate decreased toxicity, although an inhibitory effect was still observed. This toxicity can be related to the presence of toxic compounds such as ammonium and polyphenols. The use of treated leachate led to a significant decrease of the phytotoxicity which was 90% with the leachate treated by the combined processes (Fig. 11).
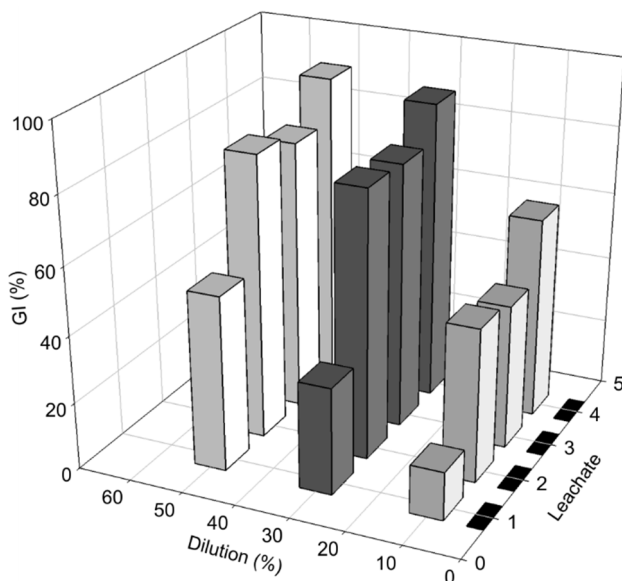

Fig. 11. Phytotoxicity improvement of raw leachate (1) and treated
by coagulation/flocculation (2), Fenton oxidation (3) and combined process (4)

These data are in agreement with the results of Moradi et al. [13] who observed an improvement of *GI* from 5.6% to about 81.9% after the application of coagulation and Fenton oxidation for the landfill leachate treatment. Moreover, Boumechhour et al. [12] proved that coagulation/flocculation followed by Fenton process can be effective in reducing organic matter since they observed a final COD removal higher than 80%.

4. CONCLUSION

Coagulation/flocculation and Fenton processes were tested as efficient treatment for young landfill leachate. The coagulation/flocculation was carried out using ferric chloride and polyacrylamide. The selected conditions were pH 4, coagulant dose of 0.8 g Fe^{3+}/dm^3 and flocculant dose of 25 mg/dm^3. The Fenton oxidation employed could remove the organic matter from the leachate. At an optimum pH of 3, H_2O_2 dosage of

3 g/dm^3, Fe of 2 g/dm^3 and the contact time of 3 h, the oxidation yielded a good COD removal (48%). The combination of coagulation/flocculation with Fenton led to high COD removal rates of 62%.

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