

Study of Different Integrated Physical-Chemical + Adsorption Processes for Landfill Leachate Remediation

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Some integrated processes to deal with landfill leachates have been investigated and their efficiencies expressed in terms of chemical oxygen demand (COD) removal. The systems tested were the result of different combinations of the following single stages: acidic pH shift (elimination of humic substances), ozonation (O₃), coagulation-flocculation with Fe(III) salts, Fenton's oxidation (Fe(III) + H₂O₂), wet air oxidation (with or without radical promoters), and adsorption onto activated carbon (commercial Norit 0.8 powdered activated carbon). COD removals obtained ranged in the interval of 80-96% for initial COD values close to 11000 mg L⁻¹. None of the processes tested reduced the COD levels sufficiently to allow direct discharge; however, the ratio biochemical oxygen demand (BOD)/COD was significantly increased (up to 1000% in some cases, i.e., from 0.1 to values above 1.0). Total carbon reduction achieved ranged from 60 to 94%, while complete decolorization (measured as the absorbance at 410 nm) was obtained in practically all the combinations investigated.

1. Introduction

Although the European Union Landfill Directive (1999/31/EC) has been built on the concept of landfill ban (progressive banning of municipal biodegradable wastes from landfill to achieve 35% of 1995 levels by 2020), landfilling is often regarded as the last resort waste management option. Moreover, according to the European Environment Agency, waste production is outstripping economic growth rates. Until the moment of the feasible development of complementary forms of downstream waste treatment, waste disposal facilities must guarantee adequate control over the two main sources of contamination, i.e., gas emissions and leachate generation.

A feasible leachate disposal and management methodology is at present one of the greatest challenges to face. An additional drawback for the appropriate treatment of these effluents is their heterogeneity in production and composition depending on several factors. Leachate is normally classified depending on the age of the landfill into young, medium, or stabilized leachates. Among the different types of leachates, stabilized leachates show the lowest values of contamination in terms of chemical oxygen demand (COD); however, they also present the lowest biodegradability properties, with ratios of biochemical oxygen demand (BOD)/COD below 0.1. This biological refractory nature involves the necessity of developing alternative methodologies other than biodegradation processes to effectively reduce the contaminant load of these effluents.

A literature survey of different technologies used for leachate remediation reveals that in most of cases a single technology is insufficient to achieve acceptable levels of pollution decrease and integrated methods have to be developed. In this work, several options have been contemplated, for instance, a chemical oxidation step, a coagulation - flocculation (CgFc) process, and a final adsorption stage. These single operations have been combined and the results have been analyzed. The chemical oxidation technologies utilized are based on the use of the following:

(i) Ozone: This agent is an attractive oxidizing reagent due to the high redox potential and its environmentally friendly nature and also because it presents an alternative route of action through decomposition to generate free hydroxyl radicals.

(ii) Fenton's reagent. This cost-effective system is characterized by its wide range of applications and simplicity of execution. Additionally, the presence of Fe(III) as a part of the reagent allows for the implementation of a CgFc stage.

(iii) Wet air oxidation. This technology is meant to deal with contaminated effluents by carrying out the oxidation of organic and inorganic species at high temperatures and pressures and in the presence of an oxygen-containing gas. A variation of this process consists of the utilization of a free radical promoter to initiate the radical mechanism. Among promoters, hydrogen peroxide is characterized by the generation of hydroxyl radicals, while OXONE is capable of inducing the formation of sulfate and hydroxyl radicals.

Table 1. Statistic Descriptives for Leachates from Badajoz Landfill Site^a

	COD	BOD ₅	N-Kjedahl	TC	TIC	pH	Al	Cr	Fe	Mn	Ni
N	14	13	9	8	7	12	7	10	10	10	9
min	2.30	0.29	0.085	0.83	0.17	7.9	950	534	8329	213	0
max	11.10	0.85	0.330	4.30	1.6	9.4	1650	1240	23109	4316	13470
mean	5.04	0.49	0.164	1.68	0.43	8.5	1355	817	15979	1507	1839
SD	2.59	0.14	0.089	1.12	0.17	0.42	279	249	4547	1502	4380
Huber	4.69	0.47	0.134	1.38	0.42	8.5	1372	773	16239	966	353
Tukey	4.50	0.46	0.118	1.30	0.43	8.5	1368	767	16244	718	261
Hampel	4.80	0.47	0.137	1.32	0.43	8.5	1358	791	16087	842	310
Kurt	0.78	2.39	-0.5	5.69	-0.38	-0.02	-1.6	-1.34	-0.46	0.24	8.7
Asym	1.04	1.23	0.95	2.27	0.11	0.5	-0.4	0.56	-0.28	1.27	2.9
this work leachate	11.10 (17.7) ^b	0.35	0.152	4.3	1.6	9.4		1240	12350	213	590

^aUnits in g L⁻¹; except metals in µg L⁻¹. Analyses correspond to samples after filtration through Whatmann 1 filtration paper. Last file depicts the characterization of leachates used in this study. N = sample size; min = minimum value, max = maximum value; mean = arithmetic mean; SD = standard deviation; Huber, Tukey, and Hampel = estimators of the center of the distribution; Kurt = Kurtosis; Asym = asymmetry. ^b COD value before filtration.

In both cases, other radicals might be formed (i.e., organic radicals).

2. Materials and Methods

2.1. Landfill Leachates. Landfill leachates used in this work were taken in April 2004 from a municipal landfill site located at the city of Badajoz (southwest of Spain). The effluent was stored in plastic barrels at 4 °C for characterization. Thereafter, landfill leachates were frozen at -20 °C until use. Because of the heterogeneity of these residues depending on sampling season, raining levels, sampling methodology, solid wastes nature, etc., the leachate collected to perform this study showed a higher contaminant load than previous samples from the same landfill site monitored for a period of 3.5 years.² Fe, Ni, and Cr are the most abundant heavy metals present in these leachates with other species also present at lower levels. Table 1 shows the variability of the leachate composition by calculation of some of the most common statistical descriptives (only Al, Cr, Fe, Mn, and Ni are included in the results). The descriptive procedure is useful for obtaining summary comparisons of approximately normally distributed scale variables and for easily identifying unusual cases across those variables by computing z scores. Additionally, some estimators of the average value were calculated to avoid the influence of extremely scattered data. The normality of the different sample distribution was ascertained by applying the one-sample Kolmogorov-Smirnov procedure. This procedure is used to test the null hypothesis that a sample comes from a particular distribution. It does this by finding the largest difference (in absolute value) between two cumulative distribution functions, one computed directly from the data, the other, from mathematical theory, for instance, the normal distribution. Broadly speaking, all the variables analyzed in this work showed a Gaussian distribution as indicated by the two-tailed asymptotic significance of the proof. Some metallic species did not follow normality, likely due to the small size of the sample analyzed.

2.2. Procedure. Ozonation experiments were carried out in a glass bubble column of 1 L of capacity. The mixture of ozone and oxygen was fed through a porous plate situated at the column base. Ozone was produced from oxygen in a laboratory SANDER 301.7 ozone generator with a maximum capacity of 12 g h⁻¹. Details of the experimental procedure can be found elsewhere.² Unbuffered runs were conducted for 1-2 h by using a gas flow rate of 50 L h⁻¹ with an O₃ concentration of 1.5 x 10⁻³ mol L⁻¹. Thereafter, the effluent was analyzed and refrigerated for additional treatments (i.e., CgFc, adsorption onto activated carbon). The previous experiments were conducted either with raw leachates or after precipitation of the humic substances at acidic pH (AcPp).

Precipitation treatments of CgFc were conducted in 1-L beakers mechanically agitated at 40 rpm by using a FC-4 SBS conventional jar-test apparatus. Fenton runs were carried out in batch mode in 1-L beakers, magnetically agitated, with no control either of temperature or pH. Experimental details can be found in previous literature.

Wet air promoted oxidation experiments were performed in a PARR stainless steel autoclave of 600-mL capacity. To avoid corrosion of the reactor walls, a titanium vessel was placed inside. The autoclave was equipped with the following components: the sampling port with a heat exchanger, injection port to add the promoter (OXONE) after reaching the operating conditions, a magnetic system to agitate the reaction mixture, and the corresponding pressure and temperature sensors. A schematic drawing of the apparatus and experimental procedure can be consulted elsewhere.

Adsorption experiments were accomplished by using a commercial activated carbon (Norit 0.8) denoted hereafter as C*. The main properties of this adsorbent are specific surface area 1150 m² g⁻¹, bulk density 0.39

gcm^{-3} , moisture content 2 wt %, ash content 7.0 wt %, and particle size below 0.6 mm. These experiments were sufficiently extended in time to reach equilibrium conditions.

2.3. Analysis. All experiments were carried out at least by duplicate, and samples were always analyzed by triplicate. Results obtained permitted the calculation of the range of 95% of confidence by considering the standard deviation of samples and the number of replicates of the analysis.

Leachates were characterized by measuring the following parameters: COD was determined in a Dr. Lange spectrophotometer, the method based on the standard dichromate reflux method. Total (TC) and organic (TOC) carbon concentrations were obtained by induced coupled plasma. The latter was measured after acidification of samples followed by CO_2 stripping. BOD was measured following the respirometric method. For this purpose, nonacclimated microorganisms from the municipal wastewater plant of the city of Badajoz were used. Since microorganisms in the nature are not acclimated to any specific effluent, use of nonacclimated

Table 2. Sequences of Treatment Used in This Investigation

sequence	stages	summary of experimental conditions
1	O_3	$\text{CO}_{3\text{inlet}} = 1.5 \times 10^{-3} \text{ M}$; $\text{Q}_{\text{Gas}} = 50 \text{ L h}^{-1}$; $V = 1 \text{ L}$; ozonation time = 2 h; $T = 20 \text{ }^\circ\text{C}$.
2	$\text{O}_3 + \text{C}^*$ (pH = 8)	sequence 1 + 15 g L^{-1} of Norit 0.8 activated carbon
3	$\text{O}_3 + \text{C}^*$ (pH = 3)	similar to sequence 2
4	acidic precipitation (AcPp)	addition of H_2SO_4 up to pH = 2
5	AcPc + O_3	sequences 4 + 1 (ozonation time = 1 h)
6	AcPc + $\text{O}_3 + \text{Fe(III)-CgFc}$	sequence 5 + addition of $\text{Fe(III)} 0.01 \text{ M}$ and coagulation–flocculation at pH = 3.5
7	AcPc + $\text{O}_3 + \text{Fe(III)-CgFc} + \text{C}^*$	sequence 6 + 15 g L^{-1} of Norit 0.8 activated carbon
8	AcPc + Fe(III)-CgFc	sequence 4 + addition of $\text{Fe(III)} 0.01 \text{ M}$ and coagulation–flocculation at pH = 3.5
9	AcPc + $\text{Fe(III)-CgFc} + \text{Fenton}$	sequence 8 + addition of $\text{Fe(III)} 0.01 \text{ M}$ and $\text{H}_2\text{O}_2 1.0 \text{ M}$
10	AcPc + $\text{Fe(III)-CgFc} + \text{Fenton} + \text{Fe(III)-CgFc}$	sequence 9 + Fe(III) coagulation–flocculation at pH = 3.5
11	AcPc + $\text{Fe(III)-CgFc} + \text{Fenton} + \text{Fe(III)-CgFc} + \text{C}^*$	sequence 10 + 15 g L^{-1} of Norit 0.8 activated carbon.
12	wet air oxidation (WAO)	$P_{\text{T}}(\text{air}) = 50 \text{ atm}$; time = 1 h; $T = 250 \text{ }^\circ\text{C}$; $V = 0.35 \text{ L}$
13	WAO + wet promoted oxidation (WPO)	sequence 12 + injection of OXONE $3 \times 10^{-2} \text{ M}$ (time = 3 h)
14	WAO + WPO + Fe(III)-CgFc	sequence 13 + addition of $\text{Fe(III)} 0.01 \text{ M}$ and coagulation–flocculation at pH = 3.5
15	WAO + WPO + $\text{Fe(III)-CgFc} + \text{C}^*$	sequence 14 + 15 g L^{-1} of Norit 0.8 activated carbon

microorganisms in BOD tests results in a less biased analysis. In any case, an attempt to gradually acclimate biological sludges from the municipal wastewater plant failed, indicating the significant toxic nature of the effluent. Metals in leachates were also determined by induced coupled plasma. Absorbance of samples at 254 and 410 nm after dilution were determined by means of a U2000 model HITACHI spectrophotometer.

Norit 0.8, hydrogen peroxide, FeCl_3 , and OXONE ($2\text{KHSO}_5\text{KHSO}_4\text{K}_2\text{SO}_4$) were purchased from Aldrich. OXONE is a double potassium salt being the active ingredient, the peroxymonosulfate, commonly known as monopersulfate.

3. Results and Discussion

As stated in the introduction, several physical- chemical processes have been combined to reduce the contaminant load of landfill leachates. Thus, up to 15 different sequences have been investigated and analyzed. Table 2 depicts the aforementioned sequences describing the single stages and summarizing the experimental conditions used for each of the simple steps.

As inferred from the leachates description section, after a period of 3.5 years of analysis, the effluent used in this study shows the highest level of contamination. This means that all the results presented hereafter were obtained in the worst of cases (normally, stabilized leachates present lower contamination levels).

3.1. Ozone Involving Processes. 3.1.1. Ozonation + Adsorption onto Activated Carbon. In a previous paper,² the integration of a preozonation stage followed by an adsorption step was shown to be a feasible technology to deal with landfill leachates of relatively low COD content (i.e., 5 g L^{-1}). In the aforementioned study, a moderate effect of the chemical oxidation step was observed in terms of COD removal after 1 h of reaction. In this study, given the higher contaminant load present in the leachates used, it was considered to feed a higher amount of ozone for a longer period. Thus, leachates were first ozonated for 2 h (sequence 1) by feeding an ozone-oxygen mixture of $1.5 \times 10^{-3} \text{ M}$ of the former (gas flow-rate 50 L h^{-1}).

As observed from Figure 1A, the single ozonation process reduces the COD level only by roughly 38% of the initial COD value even after 2 h of treatment. Contrarily, absorbances at 254 and 410 nm are decreased

by a factor of 71 and 94%, respectively. These results are in agreement with the data previously reported for the ozonation of the same stabilized leachates (albeit a slight inferior COD conversion is experienced in this work due to the higher value of this parameter in the raw effluent). Accordingly, the mineralization level achieved in this step was practically negligible.

Given the insufficient COD reduction achieved by the chemical oxidation stage (the remaining value is of the order of 7g L^{-1}), an additional step is therefore needed. Thus, an adsorption step on a commercially available activated carbon (Norit 0.8) was assayed. In a first attempt, this stage was carried out with no change of the pH media (around 8.0) after the oxidation (sequence

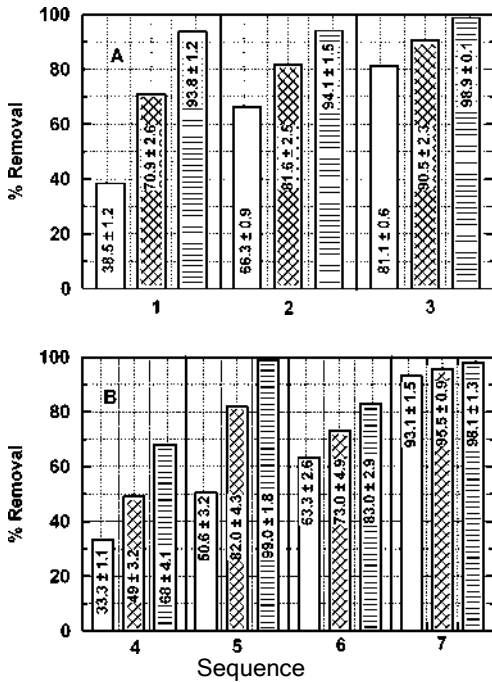


Figure 1. Integrated ozonation activated carbon adsorption of landfill leachates. Experimental conditions (average values): CO_3inlet) 1.5×10^{-3} M; QGas) 50L h^{-1} ; V) 1 L; Norit 0.8 MassC^*) 15g L^{-1} ; T) 20°C . (A) CCOD_0) 1100mg L^{-1} ; pH_0) 9.2; $\text{Abs}_{254\text{nm}}$) 0.945 (dilution 1:101); $\text{Abs}_{410\text{nm}}$) 0.644 (dilution 1:21); ozonation time) 2 h. (B) CCOD_0) 9975mg L^{-1} ; pH_0) 8.9; $\text{Abs}_{254\text{nm}}$) 1.093 (dilution 1:101); $\text{Abs}_{410\text{nm}}$) 0.681 (dilution 1:21); Ozonation time) 1 h. Patterns: COD, (0); $\text{Abs}_{254\text{nm}}$, (cross-hatched bars); $\text{Abs}_{410\text{nm}}$, (bars with horizontal lines).

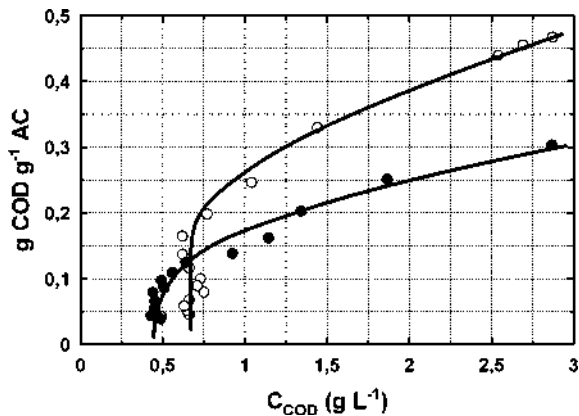


Figure 2. Ozonated landfill leachates isotherms (20°C) onto Norit 0.8. (b) pH) 8.0; (O) pH) 3.0.

2). The amount of Norit 0.8 utilized was 15g L^{-1} with a COD reduction in the range of 66%. Although absorbance at 254 nm and color showed an important reduction, the overall COD elimination still represents a poor value if it is considered that activated carbon is not a cheap technology. The next step was then focused to achieve the improvement of the adsorption process by varying one of the most influential parameters, i.e., pH.

Consequently, to ascertain the influence of pH on the adsorption process, the isotherm curves in terms of COD were determined at pH 8 and 3. Figure 2 depicts the results obtained.

As inferred from Figure 2, both isotherms show a characteristic profile, typical of the existence of a fraction of species recalcitrant to the adsorption, that is, isotherms do not intersect the origin.¹⁰ Also, it can be seen how acidic conditions favor the efficiency of the adsorption process; the observed improvement increased as the COD equilibrium concentration in the liquid is increased. Consequently, the ozonated leachates were acidified up to pH 3 and subsequently contacted with the activated carbon (sequence 3). The

COD removal experienced after this stage rose to a maximum of ca. 81% also accompanied by the almost total discoloration of the effluent (see Figure 1A). Metallic species were also partially eliminated along the overall process.

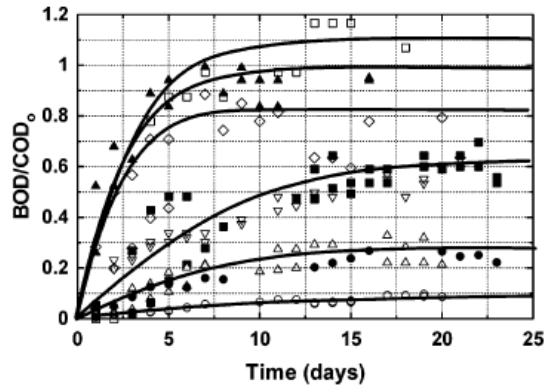


Figure 3. Ratio BOD/COD of raw and treated landfill leachates. Sequences applied: ○, none (raw leachate); △, 1; ●, 3; □, 7; ■, 10; ◇, 11; ▽, 14; ▲, 15.

Table 3 illustrates the concentration of some of the most abundant species after the combined treatment. The reduction percentage achieved is added in parentheses. As observed from this table, different behaviors were experienced. Thus, Pb, Zn, Cu, and Ni were removed to a high extent, while Co, Cr, and Fe did not appreciable change their concentrations, especially for the latter metal. The carbon content of the effluent was also reduced an average of 60% of the initial value.

Although a relatively high COD removal was obtained with the two-stage process, in absolute terms, the remaining COD concentration ranged in the interval 2000-2200 mg L⁻¹. With this in mind, the direct discharge into natural environments (rivers, lagoons, etc.) or municipal wastewater treatment plants (maximum COD) 500 mg L⁻¹) is not allowed by the regulatory directives, and a polishing step is necessitated. The preferred option to treat moderately contaminated effluents is the co-treatment with municipal wastewaters.¹¹ Consequently, to avoid any disruption into the normal operation of the urban wastewater treatment plant, the biodegradability characteristics of the effluent (besides of the pollution load) are considered of paramount importance. Figure 3 shows the biodegradability (in terms of the ratio BOD to COD) of the treated leachates after the first chemical oxidation step (sequence 1) and after the combined oxidation-adsorption process (sequence 3).

Table 3. Total Carbon and Metal Elimination from Landfill Leachates under Different Processes^a

	sequence 3	sequence 4	sequence 5	sequence 6	sequence 7	sequence 10	sequence 11	sequence 14	sequence 15
TC	1700 ± 145 (60.5)	1338 ± 145 (58)	1209 ± 125 (62)	863 ± 86 (73)	191 ± 65 (94)	525 ± 20 (87.8)	564 ± 32 (86.8)	1174 (73)	316 (93)
Cd		<0.1 (>92)	< 0.1 (>92)	23.8 ± 6.7 (-1804)	11.8 ± 6 (-860)	24.3 ± 1.2 (-1844)	< 0.1 (>92)	87.5 (-6900)	40.4 (-3132)
Co	93 ± 10.8 (23)	81.5 ± 6 (21)	67.8 ± 9 (34)	110.9 ± 12 (-7.7)	109.7 ± 23 (-7)	220.8 ± 5.3 (-82)	56.5 ± 2.5 (53)	100.4 (17)	72.6 (40)
Cu	3.9 ± 2.1 (85)	35.3 ± (46)	28.1 ± 5 (57)	37.5 ± 17 (44)	9.2 ± 1.5 (86)	156.7 ± 3.0 (-491)	1.2 ± 0.1 (95)	59.4 (-124)	5.94 (78)
Cr	835 ± 25 (33)	771.6 ± 36 (23)	638.8 ± 230 (36)	955.7 ± 68 (4)	592 ± 15 (40)	4619 ± 129 (-272)	791.1 ± 18 (36)	485.3 (61)	< 0.1 (>99)
Fe	13500 ± 1800 (-10)	9710 ± 956 (34)	9540 ± 825 (35)	457300 ± 2355 (-2980)	218600 ± 3225 (-1374)	153800 ± 426 (-1145)	378.1 ± 33 (97)	53760 (-335)	216.1 (98)
Mn		256 ± 62 (-20)	168.8 ± 54 (20)	1666 ± 105 (-682)	1983 ± 325 (-831)	4321 ± 58 (-1928)	1965 ± 128 (-822)	2542 (-1093)	2619 (-1129)
Ni	170 ± 16 (71)	267.8 ± 24 (27)	189.9 ± 32 (49)	282 ± 24 (24)	134.8 ± 35 (63)	2306 ± 134 (-291)	1218 ± 90 (-106)	121.3 (79)	50.5 (91)
Pb	<0.1 (>99)	< 0.1 (>99)	< 0.1 (>99)	29 ± 3 (20)	< 0.1 (>99)	28.3 ± 1.4 (21)	29.3 ± 3.2 (19)	<0.1 (>99)	< 0.1 (>99)
Zn	<0.1 (>90)	2.73 ± 1.1 (13)	4.58 ± 2.5 (-52)	13.5 ± 5 (-350)	24.9 ± 5 (-733)	10.9 ± 0.8 (-24)	< 0.1 (>99)	5.17 (41)	< 0.1 (>99)

^a In parentheses percentage of elimination relative to raw leachates. Units in μg L⁻¹; except TC in mg L⁻¹). Percentages are calculated regarding the analysis of raw leachates used in each sequence.

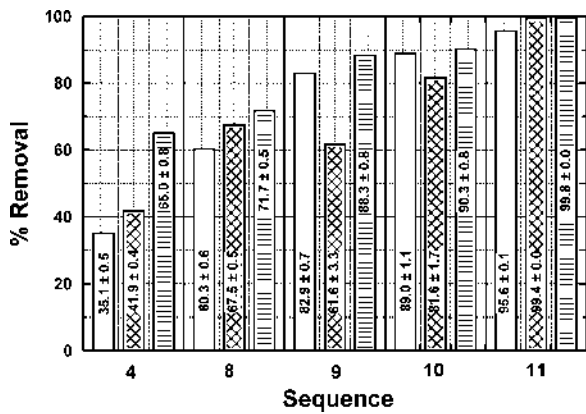


Figure 4. Integrated precipitation-Fenton's reagent-activated carbon adsorption of landfill leachates. Experimental conditions (average values): CCODo) 11275 mg L⁻¹; pHo) 9.3; Abs254 nm) 0.939 (dilution 1:101); Abs410 nm) 0.620 (dilution 1:21). Patterns: COD (0); Abs254nm, (crosshatched bars); Abs410n, (bars with horizontal lines).

From Figure 3, it is observed how the oxidation step is capable of transforming nonbiodegradable high molecular weight compounds into smaller molecules with a higher ratio BOD/COD.¹² Thus, biodegradability is increased by a factor of 3 if compared to the raw leachate (from 0.1 to 0.3). Strikingly, the further COD removal due to the adsorption stage does not result in a further increase of the biodegradability, likely attributable to preferential adsorption of substances readily biodegradable.

3.1.2. Acidic Precipitation + Ozonation + Fe(III)- CgFc + Adsorption onto Activated Carbon. Although not excessively disappointing, results from the previous sequence of treatments were not completely satisfactory. Thus, as stated previously, COD values obtained do not permit direct discharge into the sewage wastewater municipal system, while the biodegradability of the effluent is below the limit (i.e., 0.5 BOD/ COD) considered as the minimum to implement an effective biological treatment. Consequently, additional physical-chemical steps were introduced in the sequence.

The first stage applied to the raw leachate was the acidification (pH 2) with mineral acid to precipitate a fraction of the humic substances present (sequence 4). Figure 1B shows the efficiency of this stage. As observed from this figure, 33% of COD is removed by simple acidification of the effluent. Feeding of ozone for a period of 1 h attains a further 20% removal (up to 50.6% COD total elimination) and the discoloration of the sample (99% color elimination).

Use of Fe(III) in CgFc processes is a normal practice in wastewater treatment. Therefore, before applying the final adsorption step, Fe(III) at a concentration of 0.01 M was introduced, dissolved, and precipitated at pH 3.5 (sequence 6). The CgFc process develops at acceptable rates, so the solid separation does not represent an added drawback (see Figure 5C).

As inferred from Figure 1B, the contaminant load of the effluent in terms of COD was reduced 63.3% of the initial value; however, the presence of remaining ferric species in solution after precipitation involves a slight negative effect when measuring absorbances.

This negative effect is also experienced in terms of some metallic species. Thus, as observed from Table 3, impurities of the FeCl₃ salt used in sequence 6 bring as

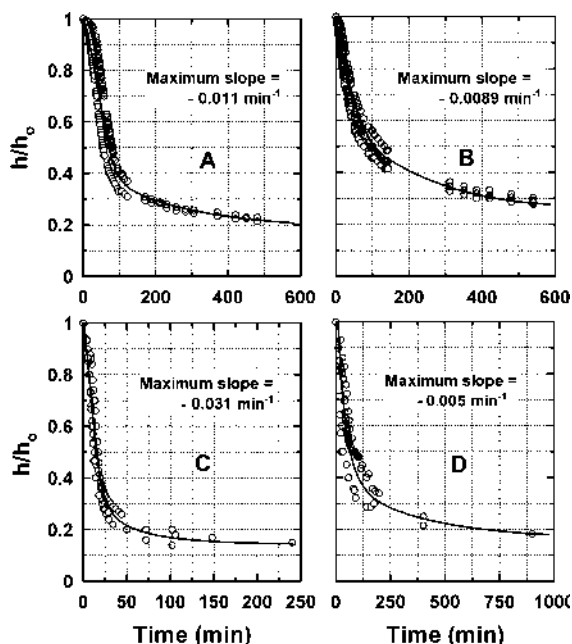


Figure 5. Settling rate of the solid formed after sequence: (A) 4; (B) 8; (C) 6; (D) 14.

a consequence a significant increase in some transition metals such as Fe, Mn, Zn, Co, etc. An opposite trend is experienced when measuring the total carbon content of the effluent: a 73% removal indicates not only the elimination of organic matter from the leachate but also the stripping of carbon dioxide formed from the corresponding carbonates.

The final adsorption of the pretreated leachates onto Norit 0.8 activated carbon (sequence 7) is carried out at the more favorable conditions of acidic pH. This stage allows for the 93-94% of elimination in both COD and TC. Moreover, although the content in some metallic species is still high (i.e., Fe), the biodegradability of the effluent has been significantly improved. Hence, Figure 3 shows a considerable increase of the ratio BOD/COD if comparing the final effluent and the raw leachate (1.16 vs 0.1).

3.2. Fenton's Involving Processes. 3.2.1. Acidic Precipitation + Fe(III)-CgFc + Fenton's Oxidation + Fe(III)-CgFc + Adsorption onto Activated Carbon. Use of Fenton's reagent as the chemical oxidation stage involves two premises. On one hand, a ferrous/ ferric salt needs to be added to the reaction media. Hence, the presence of ferric species might constitute an additional benefit as precipitating agent. On the other hand, optimum operating pH when utilizing the Fenton's reagent is usually set at acidic conditions (i.e., in the range 2.5-3.5). By combining the aforementioned needs, in a previous study the following sequence of stages was optimized before applying the final adsorption step: (1) precipitation by acidification up to pH 2 with mineral acid (sequence 4), (2) precipitation of ferric species (after addition of Fe(III)) 0.01 M) at pH ~ 3.5 (sequence 8), (3) oxidation of the supernatant with Fenton's reagent (Fe(III)) 0.01 M and H₂O₂) 1.0 M), (sequence 9), and (4) precipitation of ferric species at pH 3.5 (sequence 10). Figure 4 portrays the consecutive COD and absorbance removals obtained after application of the previous stages.

As observed from Figure 4, by the only application of precipitation treatments (sequence 8), an important COD reduction is already achieved (60%) in a straightforward mode. Thus, both precipitates (sequence 4 and 8) present acceptable settling properties (see Figure 5A,B) and floc size with a sludge production of 12200 (1173 and 18986 (2774 mg L⁻¹ total suspended solids for the first and second precipitations, respectively).

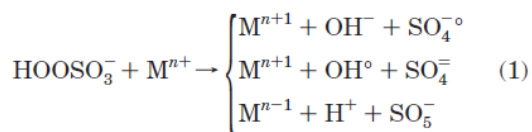
Oxidation of the supernatant by hydrogen peroxide in the presence of Fe(III) increases the overall COD removal up to 83% if compared to the COD content of the raw leachate. Use of H₂O₂ as the oxidizing agent results in a slight negative effect in terms of absorbance at 254 nm, which is undoubtedly due to the presence of small amounts of non reacted H₂O₂. Precipitation of Fe(III) at pH 3.5 further increases the COD elimination up to 89%, the pH of the leachate (pH 3) being the optimum for the final adsorption process. The integrated treatment achieves an outstanding 96% of COD removal and the practical discoloration of the effluent, both in the UV and visible regions (> 99%).

As observed from Table 2, again impurities of the FeCl₃ salt used in precipitation stages imply an increase in the heavy metal content of leachates (Fe, Cr, Mn, Ni, etc.). However, with the exception of Mn and Ni, the ultimate adsorption onto Norit 0.8 is capable of partially eliminating the majority of these metallic species.

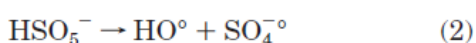
The amount of carbon eliminated from the effluent is slightly lower than in the preceding treatment (around 84%).

The biodegradability of the effluent before the adsorption stage was enhanced (see Figure 3) to a value slightly above 0.5. After the whole treatment was completed, the ratio BOD/COD was further raised to a value beyond 0.8, which implies an 800% improvement.

3.3. Wet Oxidation Involving Processes. 3.3.1. Wet OXONE Oxidation + Coagulation-Flocculation + Adsorption onto Activated Carbon. Finally, a third system was investigated based on the use of a chemical oxidation stage carried out at high temperature in the presence of a free radical promoter. In this work, a sulfate radical promoter was added to the reaction media. The salt of Caro's acid catalytically decomposes at room temperature in the presence of certain metallic species according to the following set of reactions:



Additionally, the peroxidic structure of the HOOOSO₃⁻ molecule induces the possibility of a nonmetal-mediated decomposition due to the high temperatures used, similar to the case of hydrogen peroxide under WAO conditions:



The kinetic parameters of the first-order OXONE decomposition have been calculated as $111.3 \text{ kJ mol}^{-1}$ and $3.1 \times 10^{13} \text{ s}^{-1}$, respectively. Notice that the activation energy obtained is similar to the reported value for the autodecomposition of hydrogen peroxide (i.e., 99.5 kJ mol^{-1} was reported by Shibaeva¹⁵). Taking into account the Arrhenius expression, it can be assumed that OXONE decomposition at these high temperatures must

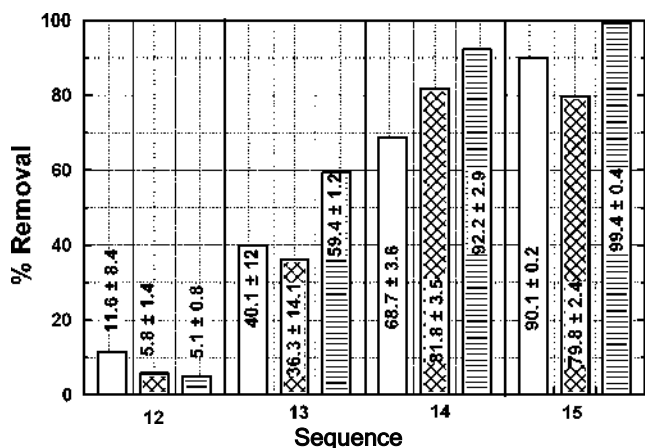


Figure 6. Integrated wet oxidation + precipitation + activated carbon adsorption of landfill leachates. Experimental conditions (average values): CCODo) 9500 mg L^{-1} ; pHo) 9.3; Abs254 nm) 0.930 (dilution 1:101); Abs410 nm) 0.668 (dilution 1:21). Patterns: COD (0); Abs254nm, (cross-hatched bars); Abs410n, (bars with horizontal lines).

occur instantaneously, initiating therefore a radical chain mechanism involving radicals of the type sulfate, hydroxyl, organics, etc.

The integrated process used in this study consisted of a first step in which the reactor was heated from room temperature to the operating temperature of $250 \text{ }^\circ\text{C}$ (initial pressure 5 atm). Thus, during the heating period a fraction of the COD content of the leachates was degraded by a simple wet air oxidation process (sequence 12). Figure 6 illustrates that the efficiency of the WAO process shows an average value in the proximity of 12%, although experimental results presents a high degree of scattering. Once the operating temperature was achieved, 25 mL of an OXONE concentrated solution was injected into the reactor, so the initial OXONE concentration was approximately $3 \times 10^{-2} \text{ M}$ (sequence 13), and the operating pressure was adjusted to 50 atm. Samples analyzed after 180 min of reaction led to a COD decrease of the order of 40 (12% (95% of confidence)). The effluent obtained from the chemical oxidation stage presented a blackish color due to the existence of a precipitate. This precipitate could be eliminated by simple sedimentation due to gravity without the need for the addition of settling reagents. However, to accelerate the process, an intermediate CgFc step, before the adsorption process, was included. For this purpose, some previous tests were conducted at different pH's and with distinct reagent concentrations. Table 4 depicts a scheme of these previous assays. As inferred from this table, the best results were obtained with no alteration of the pH after the oxidation and in the presence of 0.015 M of Fe(III). Figure 5D shows the settling capacity of the flocs formed in the aforementioned experiment.

Therefore, the series of CgFc experiments conducted after the promoted oxidation was carried out under these optimum conditions. The averaged COD conversion obtained in the experimental series rose to 69%.

Use of 15 g L^{-1} of activated carbon finally increased the COD elimination percentage up to 90%. With the exception of Cd and Mn (introduced as impurities after Fe(III) addition) the rest of metals are acceptably eliminated after the adsorption stage.

Also, from Figure 3 it is observed how the oxidation (sequence 13) is capable of increasing the

Table 4. Coagulation–Precipitation Tests after Wet OXONE (0.03 M) Promoted Oxidation of Landfill Leachates

pH	reagent	conc	observations	% COD removal ^a
2			Sedimentation too slow. Results after 5 days of clarification.	≈65%
2	cationic polyelectrolyte	100 ppm	Fast formation of sludge. Poor sedimentation tendency of flocs. Presence of bulking phenomena.	
3.5			No precipitation.	
3.5	FeCl ₃	0.01 M	Sedimentation too slow. Results after 5 days of clarification.	≈65%
3.7 → 5.3	FeCl ₃	0.01 M	Acidification at pH 3.7 + addition of Fe(III) and final increase to pH 5.3. Fast sedimentation.	≈68%
5.8	FeCl ₃ + cationic polyelectrolyte	0.01 M + 100 ppm	Instantaneous sludge formation. High sedimentation rate.	≈71%
6.6	FeCl ₃	0.01 M	No pH change after chemical oxidation. Poor sedimentation tendency of flocs. Presence of bulking phenomena.	
6.6	AlCl ₃	0.01 M	No pH change after chemical oxidation. Poor sedimentation tendency of flocs. Presence of bulking phenomena.	
6.6	FeCl ₃	0.015 M	No pH change after chemical oxidation. Instantaneous sludge formation. High sedimentation rate.	≈76%
8.9	FeCl ₃ + cationic polyelectrolyte	0.01 M + 100 ppm	Instantaneous and dense sludge formation. High sedimentation rate.	≈59%
6.1 ^b	FeCl ₃	0.01 M	No pH change after chemical oxidation. Poor sedimentation with the presence of bulking phenomena.	≈70%
6.1 ^b	FeCl ₃	0.01 M	No pH change after chemical oxidation. Fe(III) addition after filtration of oxidized effluent.	≈73%
6.1 ^b	FeCl ₃	0.05 M	No pH change after chemical oxidation. Poor sedimentation with the presence of bulking phenomena.	≈68%

^a % of COD removal with respect to raw leachate. % of COD removed after the chemical oxidation: 54% (0.03 M OXONE) and 67% (0.06 M OXONE). ^b Chemical oxidation carried out with 0.06 M of OXONE.

Biodegradability of the effluent above five times the biodegradability of the original leachate. The complete integrated process (sequence 15) leads to an effluent with more than satisfactory biodegradation characteristics (almost a 1000% increase regarding the original effluent).

Conclusions

From the previous study, the following conclusions and considerations can be noted:

(i) Under the operating conditions applied, none of the integrated systems tested are capable of reducing the COD levels below the limits for direct discharge into natural watercourses. As a consequence, a final biodegradation polishing stage is needed, and the final biodegradability of the effluent, therefore, is of paramount importance. In this sense, the three integrated processes investigated were capable of significantly increasing the ratio of BOD/COD.

(ii) The best results in terms of COD removal were achieved by the Fenton's based integrated process (although no significant differences were found between the three integrated systems). These results are likely attributable to the coagulation stages implicated rather than to a higher efficiency of this oxidative system in comparison to ozonation or wet air oxidation.

(iii) Use of an Fe(III) salt in the sedimentation stages involves the addition of other metallic impurities. After the coagulation and adsorption steps some of these impurities are significantly reduced, although some metals remain in solution. Utilization of modified activated carbons (surface treated) to increase the metal capacity adsorption might represent a potential solution.

(iv) On top of all the above conclusions, the economy of the different processes will ultimately dictate the preferential option. In this work, no effort has been focused to assess the economic characteristics of each technology, albeit some initial considerations should be taken into account at the time of performing the economic assessment.

Thus, the presence of sedimentation stages involves the disposal and management of generated solids. In the case of Fenton's based technologies, this problem can be partially overcome by redissolution of sludges and Fe(III) recirculation to the oxidation step.¹⁶ Alternatively, the highest fraction of sludges is composed of Fe(III) oxohydroxides; sludges can be dried and calcinated to recover the Fe(III) oxides, which may be reintroduced into the different processes.

Use of activated carbon also involves the need for a regeneration stage. Oxidative regeneration systems conducted at temperatures significantly below thermal regeneration temperatures are gaining acceptance. Thus, ozone or WAO can be employed in the same leachate treatment plant to regenerate exhausted adsorbents.

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