

Oxone-Promoted Wet Air Oxidation of Landfill Leachates

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Landfill leachates of the city of Badajoz (in the southwest of Spain) have been treated by wet air oxidation at high temperature (180-270 °C) and pressure (40-70 atm). Typical operating variables such as temperature and oxygen partial pressure have been investigated with no effect of any being found and moderate to low chemical oxygen demand conversions (20-30% depending on initial COD concentration). Initial pH shows a positive influence when acidic conditions are used. Addition of hydrogen peroxide (0.01 M) as a hydroxyl radical promoter is able to provide an additional 15% increase in the final COD removal achieved. If a sulfate radical promoter is used (i.e., Oxone) the process is significantly improved, with COD conversions in the range 60- 80%, also depending on the initial COD of the leachates. A first attempt to comprehend the chemistry of this oxidizing system suggests an instantaneous decomposition of Oxone that initiates the radical chain also involving hydroxyl and organic radicals.

1. Introduction

Landfill leachate is an aqueous effluent generated by the action of several phenomena (i.e., rain percolation, biological activity, hydric content of residues, etc.) in landfill sites specifically constructed to take in the municipal residues produced from these normal activities.

Landfill leachate is a potentially polluting liquid that can cause harmful effects to the groundwater and surface water surrounding a landfill if appropriate actions are not considered. The properties characterizing this effluent vary from site to site mainly depending on the age of the landfill. Other factors affecting the production, composition, and contaminant level of leachates include hydrogeological factors, the nature of the deposited wastes, climatic factors, seasonal factors, etc.

As a general rule, it can be said that leachates from young landfills have low values of pH, high values of COD (chemical oxygen demand), and acceptable values of biodegradability. Consequently, in some cases, these effluents can be pretreated by simple biological processes (aerobically or anaerobically), although the persistence of refractory substances and the presence of heavy metals make meeting the regulatory discharge standards difficult.² Stabilized landfills generate leachates characterized by low values of COD (typically below 7-8 g L⁻¹), basic nature (pH above 7-8), and a biodegradability index (i.e., the ratio BOD/COD, where BOD is biological oxygen demand) too low to implement a biological process. As a consequence, alternative technologies are required either as a pretreatment stage to render the effluent more biodegradable or as a separate step to achieve the minimum contamination levels needed for direct discharge.

Among technologies other than bioprocesses the following have been reported:

(i) Coagulation-flocculation: Normally, iron and aluminum salts have been used (with or without polymers) with different results depending on leachate characteristics and methodology.

(ii) Membrane processes: Use of membranes is acquiring an increasing role in the treatment of wastewaters in general and landfill leachates in particular. Examples of nanofiltration, ultrafiltration, or reverse osmosis can be found in the past and recent literature.

(iii) Adsorption processes: Similarly to the previous technologies, the adsorption of landfill leachates onto different solid materials (activated carbon, peat, etc.) has been reported. As in the case of coagulation-flocculation and filtration, the process is characterized by its nondestructive nature, that is, contamination is moved/concentrated from one phase to another (normally a solid phase). Following the treatment, the solid phase needs to be disposed and managed.

(iv) Chemical oxidation: This is the only destructive technology where substances are chemically transformed into biodegradable substrates, harmless end products, or even carbon dioxide and water (total mineralization).

Among the different oxidants used in wastewater treatment, examples include ozone,⁷ Fenton's reagent, electro-Fenton, photolysis, advanced oxidation processes, or even high-frequency ultrasound. However, no attention has been paid to the use of wet air oxidation as an alternative oxidation technology for the treatment of landfill leachates.

Wet air oxidation (WAO) is defined as an oxidation technology carried out in the liquid phase under moderately elevated temperatures and pressures. The oxidizing agent is usually an oxygen-containing gas (i.e., air). Use of WAO to treat different high-strength wastewaters has been reported in the literature.¹⁴ In a number of cases, the presence of catalysts (catalytic wet air oxidation, CWAO) or oxidation promoters (wet promoted oxidation, WPO) has resulted in higher oxidation efficiencies than those obtained in the simple WAO process at similar operating conditions.^{15,16} The effective use of heterogeneous catalysts relies on the activity and stability of the catalyst under the oxidation conditions. Use of homogeneous catalysts involves an

additional stage to recover the metallic salt for reuse and also because of the potential toxicity of the catalyst itself. Among promoters, hydrogen peroxide has been shown

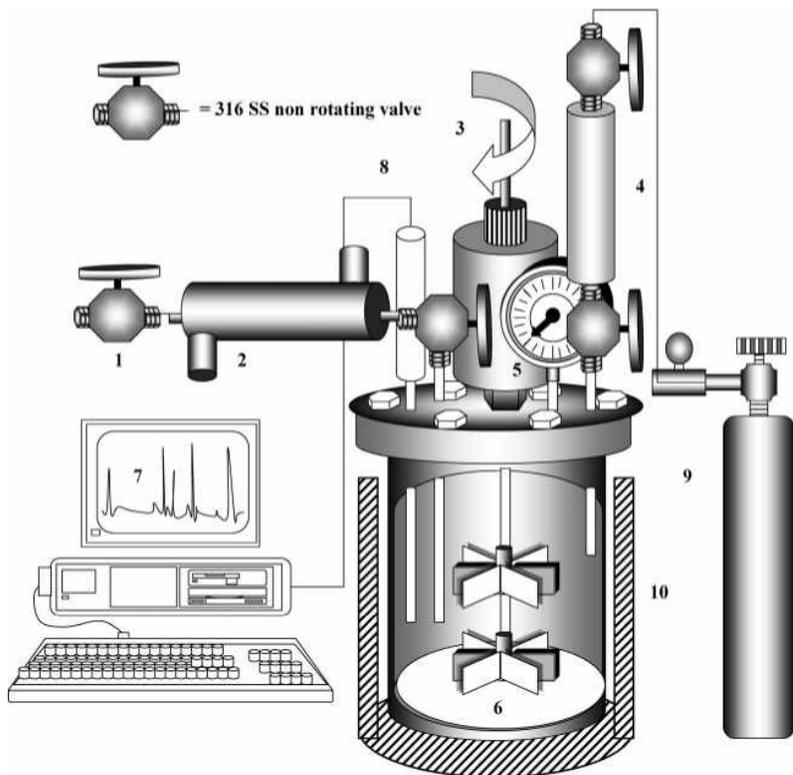


Figure 1. Wet air oxidation of landfill leachates. Experimental setup: 1, sampling port; 2, heat exchanger; 3, agitation system; 4, injection port; 5, pressure indicator; 6, agitation palettes; 7, temperature controller; 8, thermocouple; 9, air cylinder; 10, oven.

to be an environmentally friendly substance capable of generating powerful oxidant species such as the hydroxyl radical. Nevertheless, depending on the nature of the wastewater, inefficient decomposition to oxygen and water can occur, resulting in wastage of the promoter. This study is meant to assess the performance of a different free-radical promoter, peroxomonosulfate. This substance, commercially available as Oxone, is capable of generating, among others, sulfate radicals that might initiate the radical chain mechanism.

2. Experimental Section

Leachates were collected from a municipal landfill site located at the city of Badajoz (in the southwest of Spain). Leachates were stored in plastic barrels at 4 °C for characterization. Thereafter, leachates were frozen at -20 °C until use. The main characteristics of this particular landfill leachate are reported in Table 1. Given the COD and BOD values as well as the pH, this effluent can be considered as barely biodegradable, that is, it can be defined as a stabilized leachate.

The high content of heavy metal species also contributes to the toxic nature of the effluent. This aspect was illustrated by measuring the percentage of fluorescence decrease of *Vibrio fischeri* bacteria.

Wet air and promoted (by either H₂O₂ or Oxone) oxidation experiments were carried out in a Parr stainless steel autoclave of 600-mL capacity. A titanium vessel was placed inside the reactor to avoid corrosion of the reactor walls. The rest of the components inside the reactor were kept in 316 SS. The experimental setup consisted basically of the following components (Figure 1): the sampling port equipped with a heat exchanger to cool the samples; the injection port, used to inject the promoter after the working operating conditions are reached; a magnetic system to agitate the reaction mixture; and finally the corresponding pressure and temperature sensors. The reaction temperature was kept constant with a digital PI controller. The operating procedure was as follows: A 325- or 350-mL sample of leachates was placed inside the reactor and pressurized to 5 bar with air. Thereafter, the heating system was switched on to reach the desired operating temperature. Once the temperature achieved the set point, the reactor was finally air-pressurized to the working pressure, and this was taken as time zero. When a promoter was used, a 25-mL portion of promoter solution of a predetermined concentration was injected immediately after the operating temperature had been reached. After the injection port had been flushed, a 2-mL sample was steadily withdrawn from the reactor to measure different parameters.

Leachates were characterized by measuring the following parameters: Chemical oxygen demand (COD) was determined in a Dr. Lange spectrophotometer, using a procedure based on the standard dichromate reflux method. Total (TC) and inorganic (IC) carbon

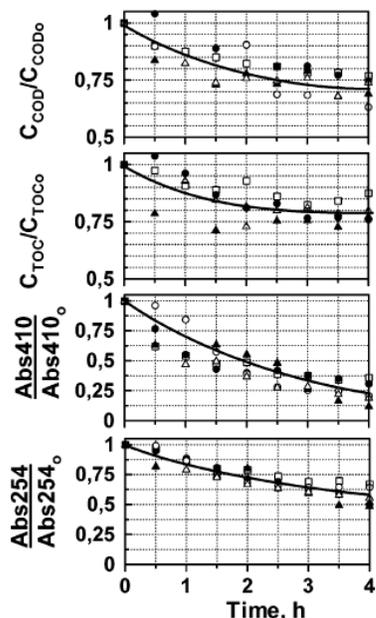


Figure 2. Wet air oxidation of landfill leachates. Experimental conditions (average values): $C_{\text{COD}0} = 3250 \text{ mg L}^{-1}$, $C_{\text{TOC}0} = 1450 \text{ mg L}^{-1}$, $C_{\text{IC}0} = 150 \text{ mg L}^{-1}$, absorbance at 410 nm (after dilution 1:6) = 1.62, absorbance at 254 nm (after dilution 1:31) = 1.45, $\text{pH}_0 = 8.35$, $P_{\text{T}} = 50 \text{ atm}$. Temperature ($^{\circ}\text{C}$): \square , 180; \bullet , 190; \circ , 200; \blacktriangle , 210; \triangle , 220.

concentrations were obtained by means of a DC-190 Dorhman analyzer. BOD was measured following the respirometric method. For this purpose, nonacclimated microorganisms from the municipal wastewater plant of the city of Badajoz were used. Metals in leachates were determined by induced coupled plasma. The toxicity of the samples was measured using a luminometer (ToxAlert); this method is based on the inhibition percentage of a bioluminescent bacteria (*Vibrio fischeri* NRRL B-11177). After dilution, the absorbance of samples at 254 and 410 nm was determined by means of a model U2000 Hitachi spectrophotometer. Details of the analytical procedure can be found elsewhere.

Hydrogen peroxide and Oxone ($2\text{KHSO}_5, \text{KHSO}_4, \text{K}_2\text{SO}_4$) were purchased from Aldrich and used as received. Oxone is a double potassium salt, the active ingredient being the peroxymonosulfate, commonly known as monopersulfate. It derives from the peroxymonosulfuric acid H_2SO_5 (also known as Caro's acid, $\text{pK}_1 = 9.4$) whose structure is a tetrahedron with a S atom in the center surrounded by a perhydroxyl group and two oxygen atoms.

3. Results and Discussion

3.1. Wet Air Oxidation Experiments. Wet air oxidation experiments were conducted to ascertain the efficacy of this process on landfill leachate treatment.

Therefore, a series of experiments was carried out at different temperatures while the rest of operating variables were kept constant. Previous experiments showed no influence of agitation speed (no mass-transfer limitations) or occurrence of nonoxidative processes under an inert atmosphere of nitrogen.

Strikingly, as observed in Figure 2, in the range investigated (180–220 $^{\circ}\text{C}$), temperature has no influence on the depletion profiles or final conversions after 4 h, regardless of the parameter analyzed. Chemical oxygen demand and total organic carbon show limited extents of reduction, achieving roughly 30% and 20% conversions, respectively. The experimental results suggest the elimination of readily oxidizable matter with no effect on a higher fraction of more refractory substances. From the absorbance data at 410 nm, it can be deduced that colored compounds (i.e., humic substances)

are among the substances previously defined as easily oxidizable. The final color removal after 4 h ranges in the interval 75–80%. These experimental findings can be correlated with the fraction of humic substances normally present in a stabilized leachate, which is 35–45% of the total dissolved organic carbon.^{17,18} Thus, by using ozone as the oxidizing system, Imai and co-workers¹⁷ achieved a 60% removal of the total 37% of humic substances present in a stabilized leachate, that is, a 22% removal of the TOC, a value similar to that obtained using WAO. Absorbance at 254 nm is normally related to the presence of aromatic and/or unsaturated compounds.¹⁹ As illustrated in Figure 2, this parameter decreased by up to ca. 40% from its initial measured value. Once again, no temperature influence was noticed in the depletion profiles of the absorbance at 254 nm, indicating the nonrefractory nature of the substances eliminated.

Following the previous analysis, to determine whether oxygen was the limiting reagent, so that no further oxidation could progress after its consumption, a new experimental series was completed at different oxygen partial pressures. For this purpose, the total operating pressure was tested in the interval 40-70 bar while the rest of the parameters were kept constant. As for the temperature series, no appreciable influence was noticed when the oxygen partial pressure was changed, regard- less of the global parameter analyzed (results not shown). Moreover, an additional run was conducted using leachates previously treated under WAO. In this case, no change in any of the analyzed variables was observed, indicating that the process came to a halt not because of a lack of oxygen, but because of the presence of nonoxidizable matter under the operating conditions used.

Finally, the influence of the initial pH was assessed by adjusting this parameter in the interval from 2 to 12 (note that the pH decreased at the end of the experiment by approximately 1-2 units). Figure 3 depicts the results obtained. From this figure, it is observed that pH has a negligible influence on COD depletion for values above 6. However, a higher COD removal was experienced when acidic conditions were used (pH's 4 and 2). It should be pointed out that a decrease in pH to set this parameter below or equal to 4 involved the formation of a precipitate⁷ (i.e., precipitation of humic substances) and consequent removal of COD and TOC. The degree of COD elimination by precipitation depends on the final pH and ranges in the proximity of 25% of COD at room temperature. In any case, COD analysis was carried out with no filtration of samples, so the positive effect observed at low pH is not attributable to precipitate formation. The effect of pH was even more pronounced when measuring TOC; in this case, however, samples were filtered through 0.45- μ m membranes to avoid clogging inside the TOC analyzer. A possible explanation to account for the positive effect of low pH's might be based on the potential catalytic activity of metals leached from the corrosion of some of the 316 stainless steel parts of the reactor; however Fe, Cr, and Ni (the main metallic species for this type of material) have not been reported

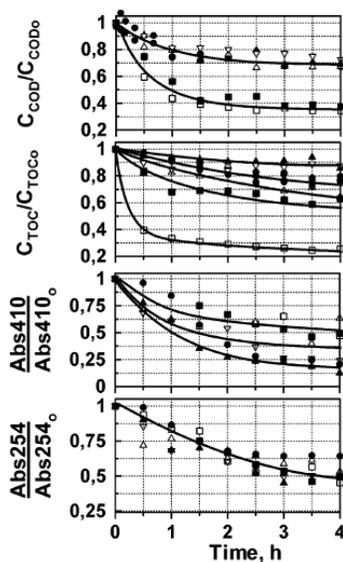


Figure 3. Wet air oxidation of landfill leachates. Experimental conditions (average values): $C_{COD0} = 3250 \text{ mg L}^{-1}$, $C_{TOC} = 1300 \text{ mg L}^{-1}$, $C_{IC0} = 120 \text{ mg L}^{-1}$, absorbance at 410 nm (after dilution 1:6) = 0.95, absorbance at 254 nm (after dilution 1:31) = 1.3, $P_T = 50 \text{ atm}$, temperature = $180 \text{ }^\circ\text{C}$. pH: \square , 2; \blacksquare , 4; \triangle , 6; \bullet , 8.35; \blacktriangle , 10; ∇ , 12.

to exhibit significant catalytic activity in homogeneous WAO processes.

Different trends were observed when measuring the absorbances at 410 and 254 nm. That is, an opposite behavior was noticed regarding the landfill leachate color (410 nm), with a slightly negative effect of pH. This is likely due to (i) the different absorbing natures of substances present at acid-neutral pH and basic pH (initial absorbance values were quite distinct depending on pH) and/or (ii) the different reactivities of neutral or ionic species.

Removal of substances absorbing at 254 nm followed the same pattern as obtained for experiments conducted at different temperatures, that is, an easily oxidizable fraction of these substances is oxidized regardless of the pH, so no influence of this parameter was found.

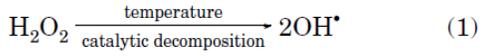
In view of the above results, the following analysis was done: On one hand, WAO of leachates at neutral-basic conditions leads to limited reductions of the indicative contamination parameters measured (except for color removal), and on the other hand, lowering the pH below 5 increases the efficiency of the process, although some corrosion problems are experienced in some parts of the reactor (particularly at pH 2). In any case, at pH 4, only 2000 ppm (or even less) of COD could be removed with this technology, which seems a

poor value for this type of system.

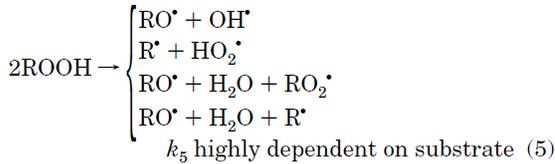
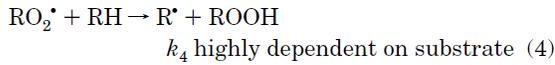
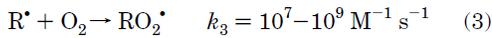
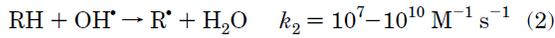
As a consequence, it was decided to study the positive effect, if any, of the addition of free-radical promoters.

3.2. Wet Promoted Oxidation. Experiments carried out in the presence of a free-radical promoter were conducted with leachates showing a higher contamination load than those used in the first part of this study. Consequently, for comparison purposes, some of the previous control experiments were repeated with this new effluent (i.e., WAO at pH 4 and pH 8).

Hydrogen peroxide was first used as a source of hydroxyl radicals through its homolytic excision according to

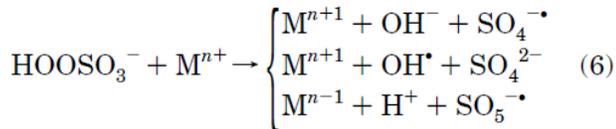


The value of the kinetic constant for reaction 1 depends on a number of factors (e.g., temperature, presence and concentration of catalyst, nature of the reactor wall, etc.). A temperature-dependent value of $7.1 \times 10^8 \exp(-99500/RT)\text{s}^{-1}$ was given by Shibaeva, whereas Rivas and co-workers²¹ reported a slightly higher value with the expression $1.6 \times 10^{10} \exp(-96900/RT)\text{s}^{-1}$. Hydroxyl radicals might initiate a chain mechanism that also involves organic radicals and peroxides formed in the presence of dissolved oxygen



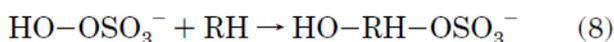
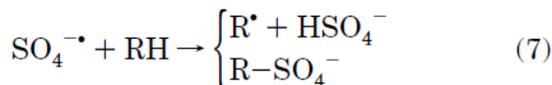
Deactivation of radicals through collisions with the reactor walls or radical-radical recombination would constitute the termination chain stages. As observed in Figure 4, the addition of hydrogen peroxide to the process results in a COD conversion higher than that obtained in the control experiment and similar to that obtained at an initial pH of 4. In any case, as commented previously, the global amount of COD removed for the best conditions applied was in the proximity of 2000 ppm, still a low value.

Therefore, a different free-radical promoter was tested. In this case, a sulfate radical promoter, namely, Oxone, was added to the reaction medium. The oxidizing nature of Oxone at room temperature is mainly due to the following reaction, where M represents a metallic species (Co, Fe, Cu, etc.)



The generation of one radical or another and the rate of reaction 6 depends strongly on the nature of M, the presence of impurities, the pH, the temperature, etc.

Removal of organics by this system is the combined effect of sulfate (eq 7), hydroxyl radicals (eq 2), organic peroxy radicals (eq 4), and/or even direct attack of the HSO_5^- molecule (eq 8) by addition to double bonds.^{24,25} Nevertheless, given the lack of information on the reactions of SOx radicals with organics, other routes cannot be discarded (e.g., attack of peroxosulfate radicals)



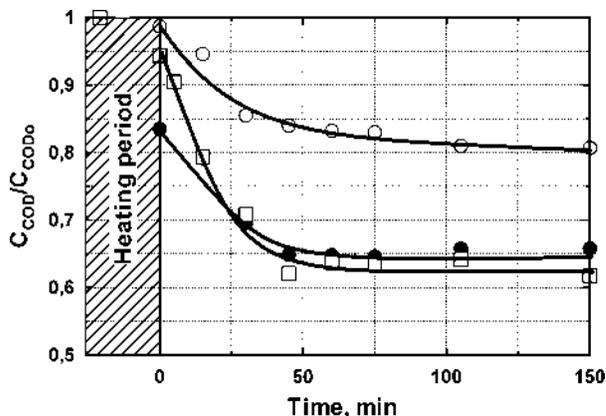


Figure 4. Wet air oxidation of landfill leachates. Experimental conditions (average values): CCOD₀) 6610 mg L⁻¹, PT) 50 atm, temperature) 250 °C, pH₀) 9.2. Symbols: 0, promoted hydrogen peroxide experiment (CH₂O₂) 0.01 M); b, acid experiment (pH₀) 4.0); O, control experiment.

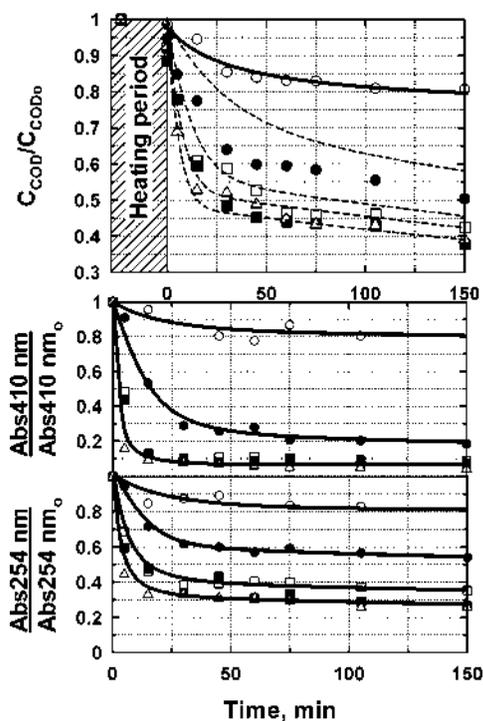
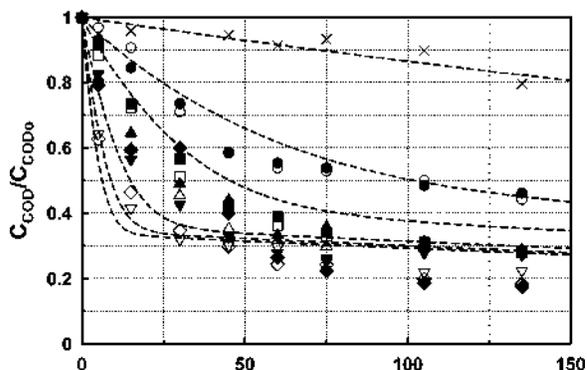


Figure 5. Wet air oxidation of landfill leachates. Experimental conditions (average values): CCOD₀) 6595 mg L⁻¹, PT) 50 atm, temperature) 250 °C, pH₀) 9.2, absorbance at 410 nm (dilution 1:4)) 2.8, absorbance at 254 nm (dilution 1:40)) 1.8. COxone₀ (M): O, 0.0; b, 4.6 x 10⁻³; 0, 1.4 x 10⁻²; 9, 2.3 x 10⁻²; 4, 3.3 x 10⁻². (Dashed lines: model calculations.)

Thus, in a first experimental series, the influence of the initial concentration of Oxone in the range from 4.65×10^{-3} to 3.26×10^{-2} M was investigated. Figure 5 presents the results obtained. As observed from this figure, the addition of Oxone to the reaction medium leads to a significant improvement in the final COD conversion obtained, in the proximity of 60% for promoter concentrations above 5×10^{-3} M. By comparison of Figures 4 and 5, one can infer that monopersulfate is more efficient than hydrogen peroxide. Thus, similar promoter concentrations (roughly 0.01 M, corresponding to an Oxone concentration of roughly 4.65×10^{-3} M) result in COD final conversions of approximately 50% and 35% when HSO₅⁻ and H₂O₂, respectively, are used. Additionally, one can also appreciate that Oxone concentrations above 1.4×10^{-2} M do not necessarily result

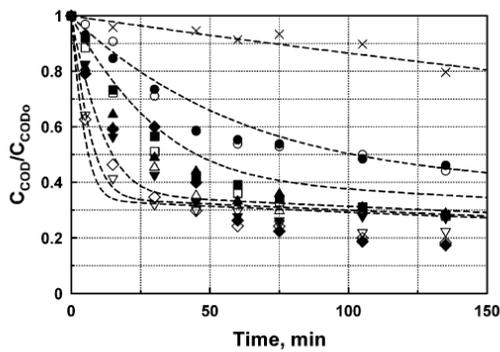
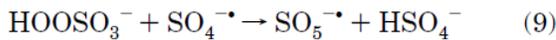


Figure 6. Wet air oxidation of landfill leachates. Experimental conditions (average values): $C_{\text{COD}0} = 3800 \text{ mg L}^{-1}$, $P_T = 50 \text{ atm}$, temperature = $250 \text{ }^\circ\text{C}$, $\text{pH}_0 = 8.8$, $C_{\text{Oxone}0} \text{ (M)}$: \times , 0.0; \bullet , 2.5×10^{-3} ; \blacksquare , 4.6×10^{-3} ; \blacktriangle , 1.4×10^{-2} ; \blacktriangledown , 2.3×10^{-2} ; \blacklozenge , 3.3×10^{-2} . (Open symbols, filtered samples; solid symbols, nonfiltered samples; dashed lines, model calculations.)

in a higher efficiency of the process at the operating conditions investigated. Two plausible reasons can be given. On one hand, an excess of the promoter might behave as a scavenger of the free radicals generated, according to



Notice that this reaction is similar to the scavenging effect of an excess of hydrogen peroxide on hydroxyl radicals. On the other hand, it is likely that, as the reaction progresses, more recalcitrant substances accumulate that cannot be oxidized by this system no matter the amount of oxidizing species present in solution. Similar results have been reported by other authors using the system Oxone/Co(II) at room temperature. In particular, Anipsitakis and Dionysiou²⁶ described a negligible effect of increasing the molar ratio of oxidant to contaminant above 3 in the treatment of 2,4-DCP at room temperature under slightly acidic conditions. Fernandez and co-workers²⁷ even experienced some inhibiting effect (in terms of TOC) of the concentration of Oxone when oxidizing Orange II with the systems VIS/Oxone/ Fe^{3+} and VIS/Oxone/ Cu^{2+} .

The enhancement of the promoted process in comparison to the unpromoted oxidation is also illustrated by the reduction of color and absorbance at 254 nm, with values of ca. 90% and 65%, respectively, for the promoted reaction and barely 20% in each profile when no promoters were added.

The oxidation of the organic content of leachates implies a shift of the pH to acidic conditions and the formation of a blackish precipitate easily separated by filtration. To ascertain the potential contribution of this precipitate to the removal of COD and also to assess the influence of the initial COD of the leachates on the efficiency of the process, a new experimental series was completed in which a less contaminated leachate was used and the samples were analyzed with and without filtration through 0.45- μm membranes. Figure 6 shows the results of this experimental series. As observed, with the exception of some points at the beginning corresponding to the experiments with the highest concentrations of Oxone, there is an acceptable agreement between COD values analyzed with and without filtration. As stated previously, a decrease in pH due to acid formation results in the precipitation of humic sub-

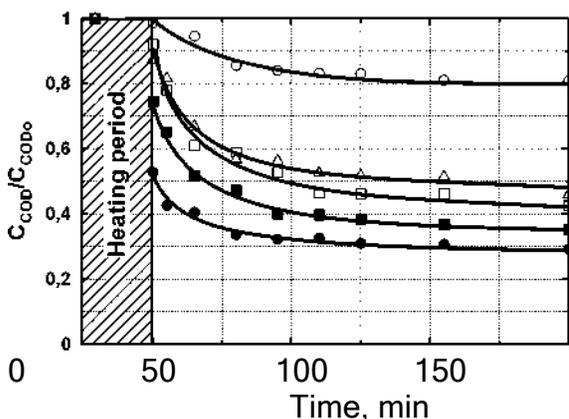


Figure 7. Wet air oxidation of landfill leachates. Experimental conditions (average values): $C_{\text{COD}0} = 6162 \text{ mg L}^{-1}$, $P_T = 50 \text{ atm}$, temperature = $250 \text{ }^\circ\text{C}$, $C_{\text{Oxone}0} = 1.4 \times 10^{-2} \text{ M}$, pH_0 : \circ , 9.2 (no Oxone); \bullet , 3.0; \blacksquare , 6.0; \square , 9.2; \triangle , 12.0.

stances at the beginning (and maybe some adsorbed metallic species). As the reaction progresses, the organic material is destroyed, and likely, complexed metals (either in solution or adsorbed) are transformed into oxides, accounting for the inorganic nature of the final precipitate (metallic oxohydroxides in the highest valence state) and negligible COD.

From Figure 6, two more experimental facts can be derived. That is, an optimum Oxone concentration is confirmed above which no further COD reduction is achieved, and the COD conversions achieved with the less contaminated leachate are higher than those observed in the previous experimental series, although the global removal of COD has decreased (roughly 3000 ppm versus approximately 4000 ppm).

The influence of pH was next investigated in the interval 3-12. Figure 7 shows the normalized remaining concentration of COD for this experimental series. From this figure, one can observe a significant effect of the initial pH used in the experiments, especially in the preheating period (90 min) where COD conversions up to almost 50% were obtained for the run conducted at the initial pH of 3. These results were already reported in the unpromoted WAO of leachates (Figure 2). The final COD removal achieved increased slightly as the initial pH used was decreased; however, serious corrosion problems were experienced when operating at acidic conditions. In this sense, it is worth mentioning that the final pH reached for the most acidic experiment carried out was 1.4. Acidic conditions, high temperatures, and the presence of free chlorine make this atmosphere extremely corrosive, and special construction materials are required for the reactor and its main parts.

Finally, the influence of temperature was assessed by changing this parameter from 200 to 270 °C and keeping the rest of operating parameters constant. Figure 8 displays the results obtained in this series. Temperature exerts a positive effect on COD removal, although, analogously to unpromoted experiments, the influence decreases for temperatures above 230 °C. These data were confirmed by measurements of the absorbances at 410 and 254 nm. In this case, the profiles corresponding to 230, 250, and 270 °C were practically coincident (results not shown).

3.3. Kinetic Considerations. The complexity of both the leachate composition and the radical chain involved in this type of process makes the development of a rigorous kinetic mechanism almost impossible. How-

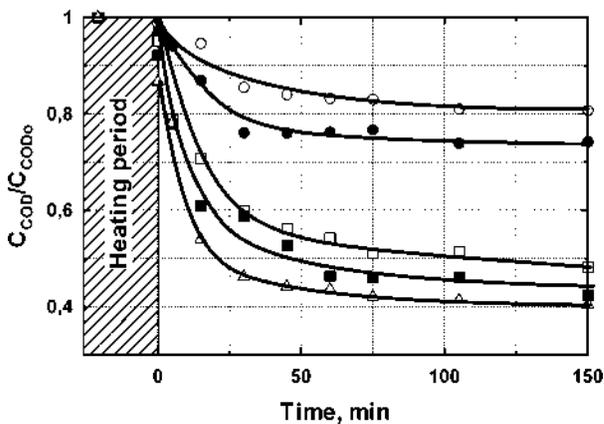


Figure 8. Wet air oxidation of landfill leachates. Experimental conditions (average values): $CCOD_0$) 5958 mg L⁻¹, CO_{xone0}) 1.4×10^{-2} M, pH0) 9.2. Temperature (°C): O, 250 (no Oxone, PT) 50 atm); b, 200 (PT) 24 atm); 0, 230 (PT) 35 atm); 9, 250 (PT) 50 atm); 4, 270 (PT) 58 atm).

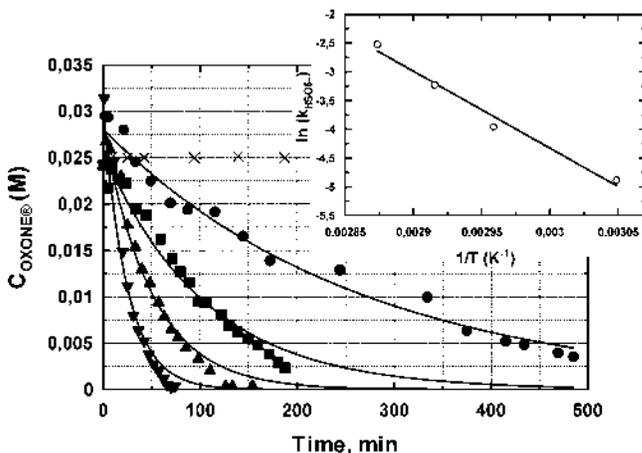
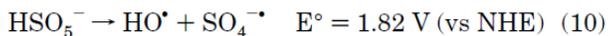


Figure 9. Oxone decomposition in ultrapure water. Influence of temperature (no pressure). Temperature (°C): x , 20; b, 55; 9, 65; 2, 70; 1, 75. (Inset: Arrhenius plot.)

ever, based on some experimental facts, a first attempt can be made to elucidate the main routes of action of the system studied.

It seems clear from the preceding discussion that the addition of a radical promoter is fundamental for the

WAO to proceed at acceptable rates. Sulfate radical promoters appear to be more efficient than hydroxyl radical promoters, as one might expect given the higher redox potential of the former.²⁶ Apparently, the presence of different metallic species in leachates would eventually be responsible for the initiating stage of the mechanism according to reaction 6. Nevertheless, under these conditions, it is more plausible that the breakdown of the HSO₅⁻ molecule occurs in a way similar to that reported for the H₂O₂ molecule under WAO conditions, that is, a scission of the type



Reaction 10 was corroborated by conducting a series of experiments of Oxone decomposition in ultrapure water in the absence of metallic species. Figure 9 illustrates the evolution profiles of Oxone with time for this series. As observed from this figure, Oxone decomposes at acceptable rates at temperatures of 50 °C and above. Although extrapolation of data from the interval 5075 °C to 250 °C seems somewhat audacious, the Arrhe-

Table 2. Proposed Mechanism for the WAO/Oxone System of Leachates^a

	Initiation	
$\text{HSO}_5^- \rightarrow \text{HO}^\bullet + \text{SO}_4^{\bullet-}$	$k_a = ?$	(a)
$\text{COD-OOH} \rightarrow \text{COD-O}^\bullet + \text{HO}^\bullet$	$k_{a'} = ?$	(a')
	Propagation	
$\text{HSO}_5^- + \text{SO}_4^{\bullet-} \rightarrow \text{HSO}_4^- + \text{SO}_5^{\bullet-}$	$k_b < 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	(b)
$\text{SO}_4^{\bullet-} + \text{H}_2\text{O} \rightleftharpoons \text{OH}^\bullet + \text{HSO}_4^-$	$k_c = 360 \pm 90 \text{ s}^{-1}$	(c)
$2\text{SO}_5^{\bullet-} \rightarrow 2\text{SO}_4^{\bullet-} + \text{O}_2$	$k_{-c} = 3.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	(d)
$\text{COD} + \text{SO}_4^{\bullet-} \rightarrow \text{COD}^\bullet + \text{HSO}_4^-$	$k_d = 2.15 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	(d)
$\text{COD} + \text{HO}^\bullet \rightarrow \text{COD}^\bullet + \text{H}_2\text{O}$	$k_e = ?$	(e)
$\text{COD}^\bullet + \text{O}_2 \rightarrow \text{COD-OO}^\bullet$	$k_f = ?$	(f)
	$k_g = ?$	(g)
	Termination	
$2\text{SO}_4^{\bullet-} \rightarrow \text{S}_2\text{O}_8^{2-}$	$k_h = (7.5 \times 10^8) - (3.6 \times 10^9) \text{ M}^{-1} \text{ s}^{-1}$	(h)
$2\text{SO}_5^{\bullet-} \rightarrow \text{S}_2\text{O}_8^{2-} + \text{O}_2$	$k_{h'} = 3.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	(h')
$2\text{HO}^\bullet \rightarrow \text{H}_2\text{O}_2$	$k_i = 5.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	(i)
$\text{SO}_4^{\bullet-} \rightarrow \text{SO}_4^{2-}$	$k_j = ?$	(j)
$\text{COD-OO}^\bullet + \text{COD} \rightarrow \text{COD-OOH} + \text{P}$	$k_k = ?$	(k)
	Additional Reactions	
$\text{S}_2\text{O}_8^{2-} + \text{H}_2\text{O} \rightarrow \text{HSO}_5^- + \text{HSO}_4^-$	$k_l = 7.5 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$	(l)
$\text{HSO}_5^- \rightarrow \frac{1}{2}\text{O}_2 + \text{HSO}_4^-$	$k_m = ?$	(m)
$\text{COD} + \text{O}_2 \rightarrow \text{P}$	$k_n = ?$	(n)
	Chloride-Involving Reactions	
$\text{Cl}^- + \text{HO}^\bullet \rightarrow \text{ClOH}^\bullet$	$k_o = 4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	(o)
$\text{ClOH}^\bullet + \text{H}^+ \rightarrow \text{Cl}^\bullet + \text{H}_2\text{O}$	$k_{-o} = 6.1 \times 10^9 \text{ s}^{-1}$	(o)
$\text{Cl}^\bullet + \text{SO}_4^{2-} \rightarrow \text{Cl}^- + \text{SO}_4^{\bullet-}$	$k_p = 1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	(p)
	$k_r = 2.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	(r)

^a Rate constants from refs 24 and 32–35.

nius plot of the experimental data (see inset of Figure 9) leads to a preexponential factor of approximately $1.6 \times 10^{15} \text{ min}^{-1}$ and an activation energy of 27 kcal mol⁻¹. Consequently, at 250 °C, the global monopersulfate decomposition rate is expected to be close to 500 s⁻¹.

Both sulfate and hydroxyl radicals would initiate a radical chain also involving organic radicals through reactions 3-5. Additionally, as remarked previously, the hydroxylation of organics by direct attack of the HSO₅⁻ molecule has also been reported.²⁵ Nevertheless, as expected, analysis of HSO₅⁻ carried out after the injection of Oxone into the reaction medium revealed the instantaneous decomposition of the molecule. As a consequence, it can be suggested that direct attack can be discarded at the time of proposing a kinetic model. Therefore, based on the results obtained in this study and the available literature on SO_x radicals, the mechanism shown in Table 2 was adopted. At this time, it should be pointed out that, given the number of unknown parameters, it is our intention not to determine a detailed and rigorous model but to obtain some knowledge on the possible main properties of this system.

From the proposed mechanism, the following considerations are stated:

(i) The HSO₅⁻ molecule decomposes through reaction a and also in an ineffective way through reaction m. Both reactions have been taken into account based on the analogies between this species and hydrogen peroxide.²⁹ The value of $k_a + k_m$ must be relatively large (i.e., $k_a + k_m \sim 500 \text{ s}^{-1}$) because of the instantaneous decomposition of HSO₅⁻ immediately after injection.

(ii) COD removal is due to the attack of three different radical species plus the contribution of direct reaction with oxygen. Given the uncertainty in the actual leachate composition, the values of k_e , k_f , and k_k have been

assumed in a generic way. Thus, because of the higher oxidizing character of sulfate radicals in comparison to hydroxyl radicals and the relatively refractory nature of leachates toward the latter species, k_e has been assumed to be approximately 4×10^3 times higher than k_f (10^{10} and $2.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, respectively). Values of k_e in the proximity of $10^9 \text{ M}^{-1} \text{ s}^{-1}$ at room temperature have been reported.³⁰ Therefore, a value of $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ is an acceptable hypothesis under WAO conditions.

The value of k_k depends on the organic structure of the radical and also on the substrate to be oxidized. Again, the unknown nature of leachates implies the adoption of a generic value of $10^5 \text{ M}^{-1} \text{ s}^{-1}$ similar to the one used to model the oxidation of a real wastewater by means of Fenton's reagent.³¹ COD profiles obtained in the absence of any promoter were used to calculate k_n .

(iii) Addition of oxygen to organic radicals is normally an instantaneous step with rate constants on the order of $10^9 \text{ M}^{-1} \text{ s}^{-1}$.³⁰ Consequently, this value has been fixed in the proposed model. Additionally, a fraction of the organic peroxides formed might decompose to generate other active radicals (e.g., hydroxyl radicals) through reaction 5. In this sense, stage a' represents this fraction, with the hydroxyl radicals symbolizing the active species generated.

(iv) A step involving deactivation of the sulfate radicals by means other than the radical-radical recombination (reaction j) has been considered to account for those reactions of $\text{SO}_4^{\cdot-}$ not propagating the mechanism (step e) and other types of deactivation (e.g., against the reactor walls).

(v) Although not measured, the content of chloride in this type of effluent is normally high and close to the COD load. The potential scavenging effect of this species has been considered through reactions o and p. The chloride radical (Cl^{\cdot}) might attack the organics present in solution, but for simplicity, this possibility has not been taken into account, and only the scavenging character of Cl^{\cdot} is assumed. Additionally, Cl^{\cdot} might also propagate and regenerate sulfate radicals through reaction r.

Taking all of these points into consideration, the system of differential equations derived from the mech-

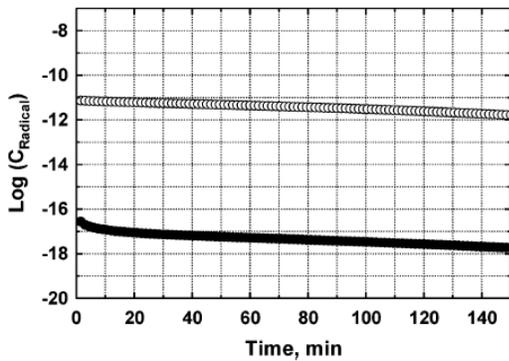
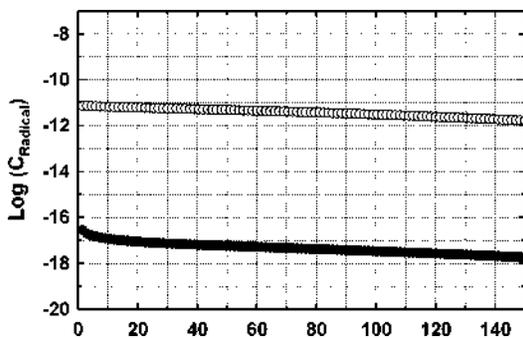


Figure 10. Wet air oxidation of landfill leachates. Conditions: $C_{\text{COD}0} = 3800 \text{ mg L}^{-1}$, $C_{\text{Oxone}0} = 1.4 \times 10^{-2} \text{ M}$, $\text{pH}_0 = 8.8$, $P_T = 50 \text{ atm}$, temperature = $250 \text{ }^\circ\text{C}$. Theoretical sulfate (solid) and hydroxyl (open) radicals evolution with time.

Table 3. Kinetic Constants Used in the Proposed Mechanism for the WAO/Oxone System of Leachates

constant	value	constant	value
k_m/k_a^a	71	k_h	$3.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$
k_a	$8 \times 10^{-2} \text{ s}^{-1}$	k_i	$5.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
k_b	$< 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	k_j	$10^9 \text{ M}^{-1} \text{ s}^{-1}$
k_c	$360 \pm 90 \text{ s}^{-1}$	k_k	$10^5 \text{ M}^{-1} \text{ s}^{-1}$
k_{-c}	$3.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	k_l	$7.5 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$
k_d	$2.15 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	k_n	$3 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$
k_e	$10^{10} \text{ M}^{-1} \text{ s}^{-1}$	k_o	$4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
k_f	$2.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	k_{-o}	$6.1 \times 10^9 \text{ s}^{-1}$
k_g	$10^9 \text{ M}^{-1} \text{ s}^{-1}$	k_p	$1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
k_h	$(0.75-3.6) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	k_r	$2.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$

^a $k_a = 7 \text{ s}^{-1}$.



anism for a discontinuous perfectly agitated reactor was numerically solved. Adjustable kinetic constants were calculated by an optimization procedure minimizing the square error between the experimental and calculated COD values.

Figure 5 shows the theoretical profiles (dashed lines) obtained for experiments conducted in the presence of different amounts of Oxone. Additionally, Table 3 lists the values of the kinetic constants used in the model. As observed in Figure 5, the proposed mechanism calculates the experimental data reasonably well, especially for those runs conducted with Oxone concentrations above 1.4×10^{-2} M.

Additionally, the model was also tested for the experimental series carried out with the less polluted leachate. Figure 6 shows the theoretical evolution profiles for runs conducted with different initial Oxone concentrations. The results obtained corroborate the influence of this variable, although given the different nature of the leachate tested, the optimum value of k_f was set at $5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ instead of $2.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Figure 10 depicts the theoretical evolution of the sulfate and hydroxyl radicals. According to the proposed mechanism, the generation of the most active radicals occurs at the beginning of the process, and their concentrations gradually decrease after roughly 1 h when the COD removal rate also drops. Concentration values for these radicals are on the order of what it is expected for these types of active species.

Logically, this mechanism is not able to model the effect of pH as no heterogeneous stages occurring at acidic conditions (i.e., precipitation of humic substances and subsequent oxidation) have been incorporated into the model. Also, given the lack of information on this type of system, no attempt was made to simulate the influence of temperature. Temperature might affect a number of rate constants in the mechanism, especially those for reactions not involving free radicals. As stated previously, more studies need to be conducted with simpler effluents (i.e., pure compounds) to assess the kinetics of the Oxone-promoted oxidation of organics.

In any case, the sensitivity of the proposed model to some of the more important reactions considered, that is, initiation steps, free radical attack, and sulfate radical deactivation, can easily be investigated. Figure 11 depicts the influence of the values of some rate constants tested. As observed in Figure 11A, logically, the fraction of Oxone (k_a/k_m) leading to the formation of sulfate radicals is of paramount importance in the elimination of the COD content of a determined waste- water. In contrast, regarding the other initiation stage, generating active radicals from organic peroxides (Figure 11B), although fundamental to the propagation of the radical chain, the absolute value of k_a does not have a significant effect on the overall COD removal.

Regarding the reactions of the COD with the radicals, Figure 11C-E illustrates the effect of varying the values

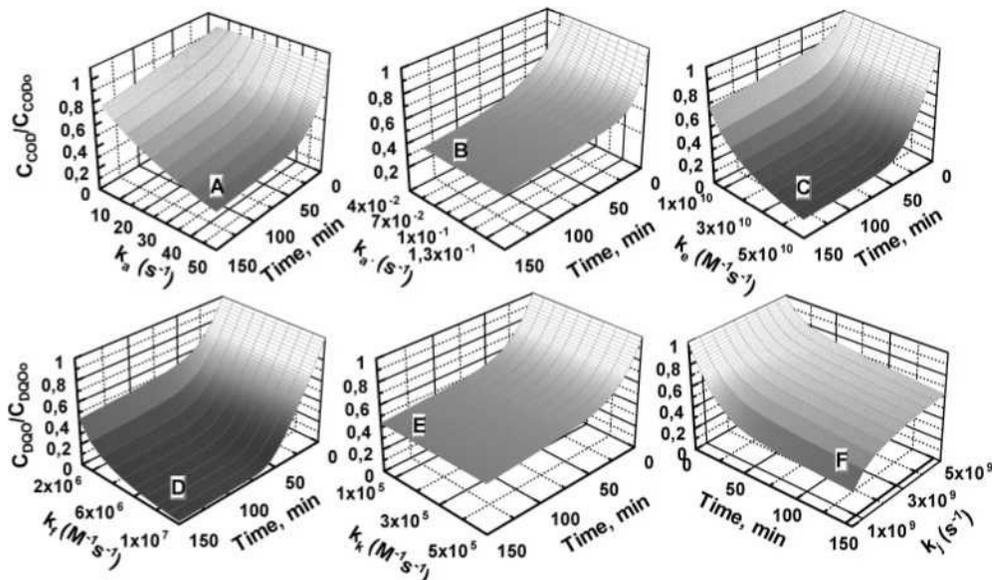


Figure 11. Wet air oxidation of landfill leachates. Influence of k_a , k_a' , k_e , k_f , k_k , and k_j on the theoretical COD removal profiles. Conditions: C_{COD0}) 0.2 mol L^{-1} , P_T) 50 atm , temperature) $250 \text{ }^\circ\text{C}$, pH_0) 9.2 , C_{Oxone0}) $1.4 \times 10^{-2} \text{ mol L}^{-1}$.

of k_e (sulfate radicals), k_f (hydroxyl radicals, and k_k (organic peroxy radicals), respectively. As observed from these plots, both k_e and k_f exhibit a significant influence on the COD depletion rate in the range of values investigated, whereas k_k seems to have a negligible effect on the process, suggesting that the main COD removal route is through reaction with the $\text{SO}_4 \cdot$ and HCO radicals.

Finally, the sulfate radical deactivation step represented by reaction j was investigated (Figure 11F). As expected, an increase on the value of k_j led to a decrease in the final COD conversion, although the influence of this step appears to be less important than that of the direct attack of radicals on COD.

4. Conclusions

From the present work, the following conclusions can be drawn:

- (i) The unpromoted WAO of landfill leachates leads to a moderate removal of COD, with no influence of either temperature or oxygen partial pressure in the range of values investigated.
- (ii) The initial pH of the leachates significantly affects the COD conversion, with initially acidic conditions significantly improving the process.
- (iii) The addition of free-radical promoters enhances the final COD conversion achieved. Hydrogen peroxide (0.01 M) as a source of hydroxyl radicals increases the COD removal up to a value of 35% in comparison to the 20% achieved in the absence of this promoter.
- (iv) Sulfate radical promoters (Oxone) exhibit better properties than hydroxyl radical promoters. Typically, COD conversions in the proximity of 60% are obtained. Similarly to the unpromoted series, pH exerted a beneficial effect at acidic conditions. A slight positive influence of temperature was also experienced.
- (v) Not much information is available on the mechanisms of sulfate radical chemistry in the presence of organics and especially under WAO conditions. Experimental facts suggest that Oxone instantaneously decomposes to initiate a radical mechanism likely propagated by organic radicals. A first attempt to comprehend this system indicates the notable importance of the Oxone decomposition through two different routes, one of them leading to sulfate and hydroxyl radicals and the other to inactive molecular species (oxygen and sulfate). Also, as expected, the rate constant of COD reaction with free radicals determines the oxidation level achieved.

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