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Fenton-like Oxidation of Landfill Leachate

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ABSTRACT

The treatment of stabilized leachates by means of Fenton's like reagent [Fe(III)-H₂O₂] has been studied. It has been demonstrated that the oxidation state of the catalyst does not influence the efficacy of the process in terms of chemical oxygen demand depletion profiles. The abrupt increase in temperature experienced in oxidation experiments involves a wastage of hydrogen peroxide diminishing the fraction of this reagent addressed at removing COD. If temperature is kept constant, the hydrogen peroxide uptake is 10 mg of H₂O₂ consumed per mg of COD abated (from 15 to 30°C). Working temperatures above 30°C does not lead to additional COD conversion, contrarily, the percentage of wasted H₂O₂ is increased. A rough economic analysis of the process indicates that this treatment can be a suitable alternative to deal with this type of effluents.

Key Words: Fenton's reagent; Leachates; Wastewater; Hydrogen peroxide; Landfilling.

INTRODUCTION

Landfilling is by far the most widespread method to dispose municipal solid wastes.^[1] In Spain, 44.8 millions of tons are generated of these residues. The management of urban residues is: 48.97% disposed in controlled landfills, 31.28% in uncontrolled landfills, 14.8% addressed at composting and 4.95% is incinerated.

Landfilling is considered an attractive and economical option to deal with these residues, however, some important drawbacks are inherent to its use. Hindrances arising from landfilling are mainly related to leachates formation (due to rainwater percolation) and potential risks for nearby aquifers.^[2] Leachates drag along toxic substances generated in landfills. Thus, the USEPA has determined up to 200 different compounds in leachates. Some of them like organo-halogenated and some heavy metals are extremely harmful for humans and the biota in general. Leachates exhibit a wide range of physical and chemical properties depending on several parameters. Broadly speaking, the principal factor affecting leachate nature is the age of the landfilling facility. Thus, the contamination load and biodegradability of old landfill leachates are characterized by their low values. Contrarily, young landfills generate leachates showing a high level of contamination and biodegradability.^[3] In the first case, (methanogenic landfills) the COD/BOD ratio rules out the implementation of a conventional biological treatment to meet discharge regulations and, therefore, use of alternative technologies is required.

Chemical oxidation may provide a suitable route to deal with this type of effluents. Thus, depending on the specific chemical process used, two distinct objectives could be achieved. On one hand, mineralization of the organic fraction of the leachate may lead to a final stream fulfilling the maximum COD levels allowed for a determined region or country. On the other hand, the recalcitrant substances found in old leachates^[4] can be effectively transformed into oxygenated compounds with lower molecular weights and higher biodegradability. As a consequence, the conventional secondary treatment may now be efficiently applied.

Among the different technologies reported in literature for the treatment of highly contaminated effluents, Fenton's reagent (H₂O₂ + Fe²⁺) is characterized by its cost effectiveness, simplicity and suitability to treat aqueous wastes showing a variable composition.^[5]

In this work, leachates from a municipal landfill have been treated by means of Fenton's reagent by using both, ferrous or ferric iron as the hydrogen peroxide decomposition catalyst. The main variables have been investigated and optimum conditions assessed.

MATERIALS AND METHODS

Leachates were collected from the landfill site of Badajoz (Southwest of Spain) during Winter-Spring of 2001. The main characteristics of the effluent are presented in Table 1. At the sight of values found for chemical oxygen demand (COD) and

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Table 1. Leachate characterization from Badajoz landfill site.

Parameter	gL ⁻¹	Metal	mgL ⁻¹	Metal	mgL ⁻¹
COD	2.30±0.04	Al	1650	P	520
BOD ₅	0.85±0.03	Sb	61.7	Fe	16248
N-Kjeldahl	0.085±0.002	As	<0.1	Mn	707.1
TC	1.31±0.02	Cd	1.4	Hg	<0.1
IC	0.39±0.04	Cu	254	Ni	1358
pH	8.29	Cr	670.1	Zn	2.5

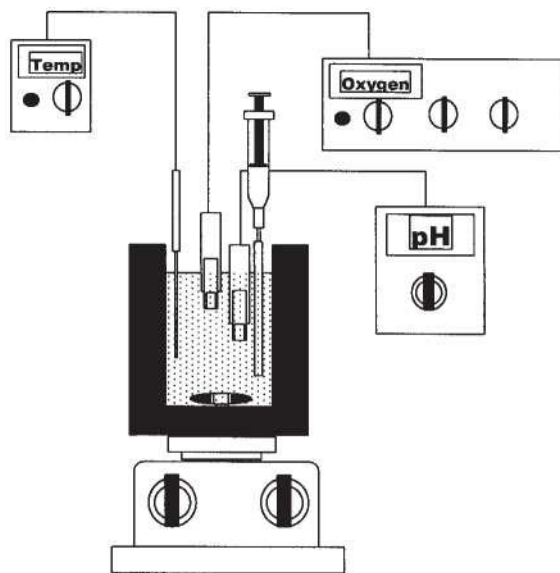


Figure 1. Experimental set-up.

biological oxygen demand after five days (BOD₅) it can be concluded that this leachate can be defined as an old-intermediate leachate and consequently not very

favorable for conventional biological treatment (ratio BOD₅/COD 0.3-0.4).

Experiments were carried out in a perfectly mixed 500 mL glass reactor in the

presence of oxygen and normal laboratory light (Fig. 1). Runs were conducted after addition of a known amount of hydrogen peroxide (30% solution) to the leachate containing the catalyst (Fe²⁺ or Fe³⁺). The solution was thoroughly stirred to avoid concentration gradients. Samples were steadily withdrawn for COD analysis,^[6] total carbon (TC) determination (Dhorman TC analyzer) and hydrogen peroxide titration by the iodometric method. The interference of H₂O₂ on COD analysis was avoided by using both, the expression proposed by Kang and co-workers^[7] and a calibration curve calculated specifically for this type of effluents (see Results and Discussion section). Analytical determinations were completed immediately after sampling to avoid the addition of quenchers and the reaction to progress. Details of the experimental procedure can be found elsewhere.^[8]

RESULTS AND DISCUSSION

To check for the feasibility of the process, two experiments were completed by decomposing hydrogen peroxide (0.5 M) by either Fe(II) or Fe(III) in the presence of undiluted leachates. The evolution of the total normalized COD and increase in temperature of the media has been plotted in Fig. 2(a). As inferred from this plot, COD profiles were similar no matter the oxidation state of iron used as a catalyst. Additionally, the exothermic nature of the process led to a maximum raise in temperature of approximately 50% of the starting temperature value. Nevertheless, given the high concentration of H₂O₂ used in this study, it could not be differentiated if the depletion of COD experienced was only attributable to disappearance of H₂O₂, or

contrarily, a fraction of COD belonging to leachate was also degraded. To account for hydrogen peroxide COD contribution, two procedures were used and "real" COD removal was calculated by means of the arithmetic average given by both methods. The first one was the equation proposed by Kang and co-workers^[7] given by: $C_{COD} = C_{CODm} - fC_{H_2O_2}$, where $f = 0.4706 - 4.06 \times 10^{-5}C_{H_2O_2}$. In the previous expression C_{CODm} and C_{COD} stand for COD with and without considering hydrogen peroxide contribution, respectively, and $C_{H_2O_2}$ is the measured hydrogen peroxide concentration. This equation was only tested for H_2O_2 concentrations below 2000 mg L^{-1} , therefore, a second experimental correlation was adopted, deducing the empirical correlation by mixing different known amounts of H_2O_2 to leachates and measuring the total COD of the mixture. By subtracting the COD concentration without addition of hydrogen peroxide (Fig. 2(b)) the following

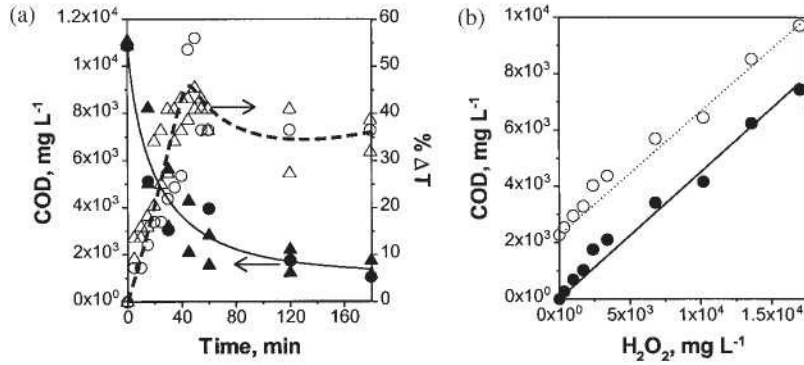


Figure 2. (a) Fenton's treatment of leachates. Evolution of total COD (solid symbols) and percentage of temperature increase (open symbols) with time. Experimental conditions: $C_{Fe} = 0.01 \text{ M}$; $C_{H_2O_2} = 0.5 \text{ M}$; $\text{pH} = 3.0$; $T = 293 \text{ K}$. fs, Use of Fe(II); mi, Use of Fe(III). (b) Influence of hydrogen peroxide on COD analysis. s, Measured COD (C_{CODm}); f, $C_{CODm} - C_{CODleachate}$.

expression was obtained: $C_{COD} = C_{CODm} - 0.4514 C_{H_2O_2}$. In both equations all concentrations are given in mg L^{-1} .

Taking into account all the above, a series of experiments was completed to assess the influence of hydrogen peroxide initial concentration on COD depletion profiles. All experiments were carried out by duplicate, i.e., two runs were completed by adding Fe(II) to the solution, while two more experiments were conducted in the presence of Fe(III). Similarly to results presented in Fig. 2(a), by considering the interference of H_2O_2 on COD analysis, it was observed no influence of the iron oxidation state on the efficiency of COD depletion profiles (results not shown). Figure 3 illustrates the positive effect of initial hydrogen peroxide fed to the reactor. Also, Fig. 3 depicts the conversion of H_2O_2 throughout the reaction period. As observed from Fig. 3, increasing the H_2O_2 dose injected to the reactor results in an appreciable enhancement of the process efficacy in terms of COD removal. Thus, for the lowest H_2O_2 amount tested in this study a COD final conversion of 45-50% was obtained, however, when this reagent was increased up to a value of 1.5 M, the percentage of COD eliminated raised up to roughly 80%. As inferred from experimental results, the consumption of hydrogen peroxide for the treatment of this type of effluents is extremely high, it could be attributed to the inefficient decomposition of this reagent into oxygen and water due to the presence of a significant amount of metal species. However, similar low efficiencies have been experienced when using other powerful oxidants like ozone or ozone based advanced oxidation processes.^[2,9] In any case, higher COD reductions can be attained if a post coagulation- flocculation process is developed to recycle the catalyst^[10] with the subsequent savings in chemicals (catalyst and coagulant).

Other parameters affecting Fenton's reagent efficacy are the initial pH and the presence and concentration of oxygen in the reaction media. Figure 4 presents the experimental results corresponding to runs completed at pHs 3.0 and 5.0 and by bubbling air or nitrogen to the reaction solution. As observed from Fig. 4(a), the

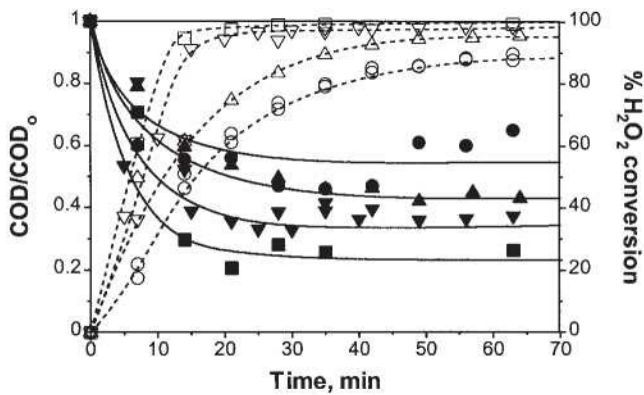


Figure 3. Fenton's treatment of leachates. Evolution of normalized COD (solid symbols) and hydrogen peroxide conversion (open symbols) with time. Influence of initial hydrogen peroxide concentration. Experimental conditions: $C_{\text{COD}_0} = 2\text{gL}^{-1}$ (average value); $C_{\text{Fe(III)}} = 0.03\text{M}$; $\text{pH} = 3.0$; $T = 293\text{K}$. $C_{\text{H}_2\text{O}_2} = \text{f S, } 0.25\text{M; mi, } 0.50\text{M; nr, } 1.0\text{M; g } \square, 1.5\text{M}$.

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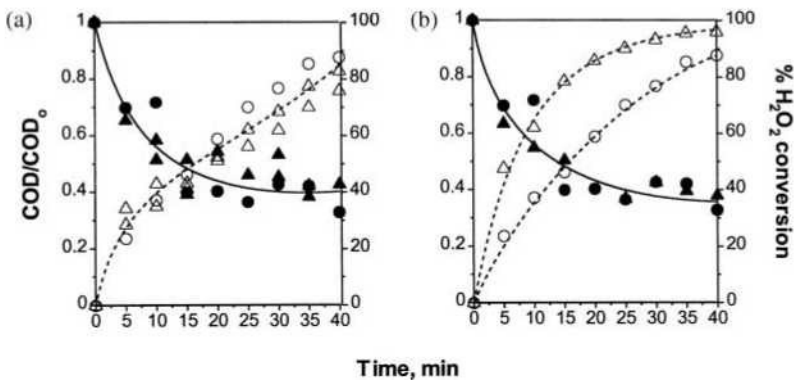


Figure 4. Fenton's treatment of leachates. Evolution of normalized COD (solid symbols) and hydrogen peroxide conversion (open symbols) with time. Influence of (a) oxygen concentration and (b) initial pH. Experimental conditions: $C_{\text{COD}_0} = 2.1\text{gL}^{-1}$ (average value); $C_{\text{Fe(III)}} = 0.02\text{M}$; $\text{pH} = 3.0$ (unless specified); $T = 293\text{K}$. $C_{\text{H}_2\text{O}_2} = 0.7\text{M}$. (a) f S, Air; mi, Nitrogen. (b) fs, $\text{pH} = 3.0$; mi, $\text{pH} = 5.0$.

concentration of oxygen does not influence either COD depletion profiles or hydrogen peroxide decomposition with time. Some authors have found a crucial role played by oxygen when oxidizing model compounds^[11] or even highly contaminated wastewaters,^[12] however, this role strongly depends on the nature of oxidized species and intermediates formed during the Fenton's reaction. The other investigated parameter was pH, in this case two more runs were conducted at initial pH of 3 and 5, respectively. Similarly to oxygen effect, no influence on COD removal rate was observed for this interval of values. Nevertheless, at pH 5 a higher decomposition of hydrogen peroxide was observed. pH effect may be explained by considering the stability of the reactive species implicated in the process. Thus, although Fe(III) is more stable at pH 3 than at pH 5, the sure presence of chelating agents in the reaction media prevents the precipitation of this species. Therefore, since hydrogen peroxide is in large excess, it can be understood that at these operating conditions pH had no influence on the COD conversion. Additionally, hydrogen peroxide decomposition is catalyzed by alkaline conditions according to:



Therefore it is not surprising the higher removal rate of H_2O_2 at pH 5 than at pH 3 and the no influence on COD degradation due to its use in large excess.

From previous results shown in this work, it is deduced that a minimal fraction of the H_2O_2 fed to the reactor is used to reduce the COD content of the leachate and, presumably, most of this reagent is decomposed ineffectively to oxygen and water. To avoid self-decomposition of H_2O_2 by high local concentrations at the moment of injection, some experiments were conducted by adding this reagent in successive steps. Figure 5 shows the results corresponding to the aforementioned series. As seen

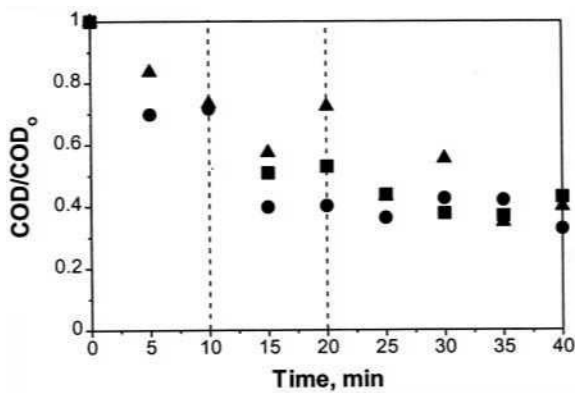


Figure 5. Fenton's treatment of leachates. Evolution of normalized COD with time. Influence of hydrogen peroxide dose stages. Experimental conditions: $C_{\text{COD}_0} = 2.1 \text{ gL}^{-1}$ (average value); $C_{\text{Fe(III)}} = 0.02\text{M}$; $\text{pH} = 3.0$; $T = 293\text{K}$. $C_{\text{H}_2\text{O}_2} = 0.7\text{M}$. (a) f, single addition; g, two stages addition (at 0 and 10 min); m, triple stage addition (0, 10, and 20 min).

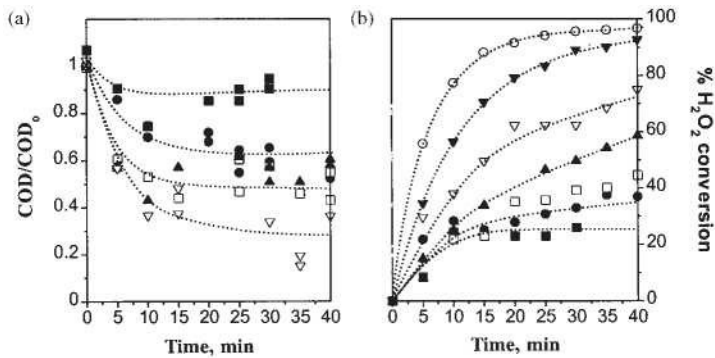


Figure 6. Fenton's treatment of leachates. Evolution of normalized COD (a) and hydrogen peroxide conversion (b) with time. Influence of temperature. Experimental conditions: $C_{\text{COD}_0} = 2.1\text{gL}^{-1}$ (average value); $C_{\text{Fe(III)}} = 0.02\text{M}$; $\text{pH} = 3.0$; $C_{\text{H}_2\text{O}_2} = 0.7\text{M}$. $T =$: g, 10°C ; f, 15°C ; \square , 20°C ; m, 25°C ; j, 30°C ; \blacktriangledown , 35°C ; S, 40°C .

from this plot, no scavenging effects were experienced by local concentrations of H_2O_2 and COD final conversion was similar no matter the number of H_2O_2 injections made to the reactor, provided that the final amount of hydrogen peroxide was identical.

Finally, the influence of temperature was investigated by conducting some experiments under isothermal conditions. Seven different temperatures were used to carry out the Fenton's oxidation runs. Figure 6 shows the results obtained for this series. As observed from Fig. 6(a), this parameter exerted a positive influence on the final COD conversion when its value was raised from 10°C to 30°C . However, a further increase up to 35°C or 40°C (results not shown to avoid crowding of data), did not intensify the oxidation. Moreover, COD abatement profiles were similar to those obtained at $20\text{--}25^\circ\text{C}$. Contrarily, H_2O_2 decomposition was always favored by increasing temperature (Fig. 6(b)). It is noticed a better efficiency in terms of hydrogen peroxide consumed per mass of COD eliminated when temperature is kept under control (below 35°C), indicating that the abrupt raise of temperature experienced in temperature uncontrolled experiments remarkably contributes to inefficient H_2O_2 decomposition. This is corroborated by experiments effectuated at 35 and 40°C where the positive effect of temperature on the kinetic constants involved in the process is counteracted by the higher inefficient decomposition of H_2O_2 .

Experimental results obtained at isothermal conditions have been used to make a rough estimation of operating costs associated to the system. The first step was to calculate the stoichiometric coefficient or ratio H_2O_2 consumed/COD degraded. Thus, hydrogen peroxide uptake was calculated for experiments up to 30°C (above this temperature the efficiency of the system decreased). An approximate value of 10 mg of H_2O_2 per mg of COD degraded was obtained for the complete set of experiments (with the exception of 10°C). Subsequently, by considering the average stoichiometric factor, the price of H_2O_2 (around $300 \text{ USA } \$$ per ton of a 50% solution) and the reduction of COD obtained, the cost associated to hydrogen peroxide consumption can be estimated. This value was estimated around $6.0 \times 10^{-3} \text{ USA } \$$ per m^3 of wastewater treated and ppm of COD removed. The final cost would be $8.0 \times 10^{-3} \text{ USA } \$$ per m^3 of wastewater treated and ppm of COD removed if expenses in H_2O_2 represents 75% of total operating costs.^[12] Similar costs have been previously reported for other authors,^[12] indicating that, even when dealing with high H_2O_2 consuming wastewaters, Fenton's treatment may represent an attractive economical option.

CONCLUSIONS

The system Fe(III)/H₂O₂ has been demonstrated to be a feasible technology to treat stabilized leachates. During the process, the red-ox cycle between Fe(II) and Fe(III) allows for the use of any of them, achieving the same results no matter the oxidation state of the catalyst. The increase in temperature experienced at the beginning of the process contributes to the inefficient decomposition of H₂O₂. If temperature is controlled, the consumption of this reagent is approximately 10 mg of H₂O₂ per mg of COD removed in the interval 15-30° C. A further raise in working temperature does not lead to a higher COD conversion, although it involves a wastage of H₂O₂ not reverting to COD abatement. Recovery of the catalyst by precipitation flocculation may contribute to the economy and efficacy of the process.

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