Wine Distillery Wastewater Degradation. 1. Oxidative Treatment Using Ozone and Its Effect on the Wastewater Biodegradability

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Laboratory-scale experiments were conducted to investigate the impact of ozonation on the degradability of wine distillery wastewaters, usually called vinasses, with the goal of developing combined chemical−biological methods for their treatment. Chemical oxygen demand (COD), biological oxygen demand (BOD), total organic carbon (TOC), and ultraviolet absorbance at 254 nm (UV_{254}) were taken as reference parameters to follow the pollution level. The vinasses were treated both directly and after being mixed with domestic sewage. Ozonation of pure vinasses required high ozone doses to achieve a significant efficiency for removing the organic matter. Mixing vinasses with domestic sewage allowed higher degradation rates with ozone. Ozone was also demonstrated to be an appropriate oxidizing agent to improve vinasses's biodegradability and organic matter removal. A mathematical model of the ozonation kinetics based on the film theory concept is also presented.

Keywords: *Wastewater treatment; ozonation; biodegradation; ozonation kinetics; wine distillery wastewater; domestic sewage*

INTRODUCTION

Liquid wastes from food processing and related industries are significant sources of water pollution. Organic effluents from agroindustrial activities often find their way into water courses with disastrous results. The extreme toxicity of some of these effluents arises from their high biological oxygen demand, resulting in local fish kill and damage to other aquatic biota (Middlebrooks, 1979; Niranjan and Shilton, 1994). A common agroindustrial activity is the production of ethanol from agricultural materials. Production of ethanol from agricultural materials for use as an alternative fuel has been attracting worldwide interest because of the increasing demand for limited nonrenewable energy resources and variability of oil and natural gas prices (Sitton et al., 1979; Rosillo-Calle and Cortez, 1998). Wine, lees, and pressed grapes are usually raw material sources for distilleries in Spain (López and Ovelleiro, 1978). Vinasses are the main liquid wastes of the alcohol industry from the distillation process. They are acidic effluents with high organic content, including acids, carbohydrates, phenols, and unsaturated compounds. As a result, vinasses have a high BOD, COD, and solid concentration (Sales et al., 1982, 1987), and their release to surface waters causes significant environmental problems. Thus, prior to vinasse disposal in the environment, an efficient treatment should be applied.

So far, a number of studies on the treatment of vinasses have been reported (i.e., physicochemical treatment or biological oxidation); however, there is no widespread agreement on the most suitable methods, which depend mainly on the distillery type (Sheehan and Greenfield, 1980; Maiorella et al., 1983). Although

many of the vinasse compounds are, in fact, biodegradable, there are also other recalcitrant compounds (i.e., phenols, pesticides, and heavy metals) that cannot be removed and may create problems in the operation of a standard sewage treatment plant (Jaworski and Lee, 1987; Cabras et al., 1992; Revilla et al., 1997; Cugier and Reulet, 1997; Mena et al., 1997). In addition, capital and operating costs of the available physicochemical and biological treatment processes of this waste stream are inevitably high (Kim et al., 1997). Thus, when companies located in urban areas need to dispose of an industrial effluent (i.e., winery effluent), the usual method is to discharge the effluent to the public sewage system, to be treated as a mixture with domestic wastewater. Although this method of disposal is generally considered best for dealing with some industrial effluents, it is also necessary that the mixed sewage can be effectively and economically treated by the technology employed at the treatment facility (Childs, 1981). As aerobic biological treatment is the most common practice in municipal wastewater treatment plants, the wastewater influent should contain only biodegradable compounds.

For more than a decade, ozone has been used in water and wastewater treatment (Leist, 1992; Rice, 1997). Ozonation is a technology that offers an innovative approach to solve the problems outlined above. One of the most important characteristics of ozone in industrial wastewater treatment is its ability to convert biorefractory compounds into less toxic and more readily biodegradable compounds, thereby significantly decreasing the time necessary for bioremediation (Scott and Ollis, 1995; Van Kemenade et al., 1996). In this regard, some recalcitrant compounds present in vinasses are very reactive toward ozone (Beltrán et al., 1993, 1998; Benítez et al., 1997). The efficient use of ozone in any wastewater treatment depends on the selection and

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Table 1. Main Characteristics of Vinasses

parameter	unit	value
COD	mg/L	21715 ± 1236
BOD_5	mg/L	13440 ± 1578
TOC	mg/L	7363 ± 697
IC	mg/L	147 ± 44
UV_{254}[a]		1.214 ± 0.320
total phenols	mg/L as gallic acid	735 ± 127
TS	mg/L	748 ± 132
TSS	mg/L	485 ± 74
conductivity	mS/cm	3.12 ± 0.40
pH		3.5 ± 0.3
total acidity	mg/L as $CaCO_3$	2750 ± 360
TKN	mg/L	1354 ± 432

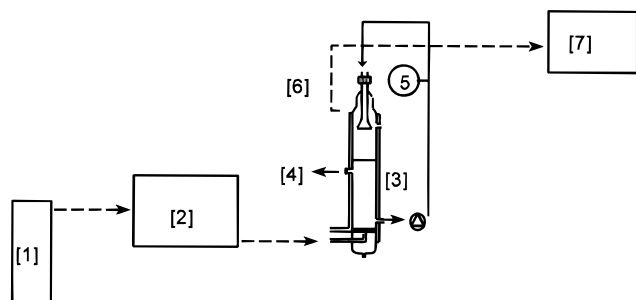[a] Measured with 1 cm path length quartz cell; $\pm$ standard deviation.

Figure 1. Schematic of experimental apparatus: 1, oxygen bottle; 2, ozone generator; 3, reactor; 4, sample point; 5, temperature and pH meter; 6, gas outlet; 7, ozone gas analyzer.

design of the contact equipment for the water–ozone system. Thus, knowledge of the process microkinetics must be available. In the literature, values of rate constants of the reactions between ozone and different organics present in the vinasses, like phenols, have been given (Hoigné and Bader, 1983). However, the effect of the simultaneous interaction of ozonation intermediates, in addition to the lack of information concerning other compounds present, makes process design difficult.

The present paper describes the first part of a study on the use of ozone to treat municipal waters containing high concentrations of vinasses. The main aims were to find optimal reaction conditions for treatment and parameter values for an empirical kinetic equation. Following papers will report results of aerobic biological and continuous integrated ozone-activated sludge treatments of these wastewaters.

MATERIALS AND METHODS

Wastewaters. Wine distillery wastewater was taken from a processing plant in Villafranca de los Barros (Badajoz province, Spain). The main physicochemical characteristics of the wastewater are given in Table 1. In most of cases, vinasses were diluted with domestic sewage taken from the municipal plant at Badajoz. The dilution was made to simulate the concentration of typical wastes entering treatment plants that receive combined domestic and agroindustrial effluents, including vinasses.

Apparatus and Procedure. A scheme of the experimental setup is shown in Figure 1. The reactor was a glass bubble column (i.d. = 9 cm; length = 45 cm) provided with a diffuser plate (pore diameter = 16–40 μm) at its bottom. The reactor was charged with the feed wastewater, and the volume of the reaction mixture in the column was kept constant in each experiment. In some cases the pH was changed by adding an aqueous sodium hydroxide solution. A peristaltic pump was used to circulate the wastewater at a 20 L/h flow rate, thus providing appropriate mixing conditions. Ozone was produced

Table 2. Effect of Vinasse Dilution on the Overall Degradation by Ozonation

Range of Operating Conditions	
gas flow rate, F	30 L/h
ozone concn in the feeding gas, C_{O_3i}	10–50 mg/L
reaction vol, V_T	1–1.5 L
reaction temp, T	20 °C
initial pH	3.5–6.4 and 7.8[a]

Experimental Results

run	f[b]	ozone appld, g/h	run time, h	initial COD, g/L	final COD, g/L	initial TOC, g/L	final TOC, g/L	initial UV_{254}	final UV_{254}
1	0	1.51	5	21.71	14.39	7.36	6.61	1.214[c]	0.833[c]
2	5	0.62	1	4.58	3.90	1.57	1.46	0.657[d]	0.501[d]
3	10	0.58	1	2.47	2.00	0.85	0.75	2.114	1.416
4	15	0.62	1	1.70	1.26	0.59	0.45	1.692	1.315
5	20	0.59	1	1.32	1.00	0.47	0.35	1.532	1.301
6	a	0.30	1	0.30	0.22	0.12	0.11	1.045	0.888

[a] Only domestic sewage. [b] f = vol of domestic sewage/vol of vinasse. [c] Sample diluted 10 times. [d] Sample diluted 5 times.

from oxygen in a Model 500 Fisher ozone generator and was supplied at the bottom of the reactor through the diffuser. Most of the experiments were conducted at 20 °C, and wastewater samples were withdrawn periodically to analyze the following parameters: pH, oxygen demand (COD and BOD), total and inorganic carbon content (TC and IC), dissolved oxygen (DO), 254 nm ultraviolet absorbance (UV_{254}), and ozone concentration.

Analytical Methods. The dichromate method (APHA, 1985) was used to measure COD in the liquid samples, whereas BOD was determined following a standard respirometric method (Ramalho, 1991). DO and pH were measured on-line using a YSI 58 oxygen meter and a pH-meter (Radiometer Cophenhagen PHM-82), respectively. The residual total carbon (TC) and inorganic carbon (IC) concentrations of the aqueous phase samples were measured by means of an Dohrmann DC-190 analyzer. TOC was calculated as the difference between TC and IC. UV_{254} measurements were made in a Hitachi 2000 spectrophotometer with 1 cm path length quartz cells. Ozone in water was analyzed according to the Indigo method (Bader and Hoigné, 1981); in the gas (at the column inlet and outlet), an Anseros Ozomat analyzer was used. Also, the following parameters were determined to characterize the wastewater: nitrogen as total Kjeldahl nitrogen (TKN), total and suspended solids (TS and TSS), conductivity, and total acidity. All of these analyses were carried out in accordance with standard methods (APHA, 1985). Finally, total phenol content was determined according to the Folin–Ciocalteu method using gallic acid as the standard (Vázquez et al., 1974).

RESULTS AND DISCUSSION

Ozonation of aqueous systems is a heterogeneous gas–liquid reaction that consists of the following steps: ozone generation from an oxygen-containing gas, transfer of ozone from the gas phase to the gas–liquid interface, and transfer from the interface to the bulk liquid accompanied by chemical reaction. Depending on the nature of chemicals dissolved and hydrodynamic conditions, the chemical reaction may take place at different points: gas–liquid interface, film liquid close to interface, and bulk liquid phase (Charpentier, 1981).

Preliminary Work: Influence of Dilution. Vinasses and domestic sewage to be ozonated were first mixed at different ratios. Experimental conditions and results obtained are presented in Table 2. A plot of the ozone mass transferred and COD–ozone stoichiometric consumption versus the domestic sewage to vinasse volumetric ratio is presented in Figure 2. Table 2 and
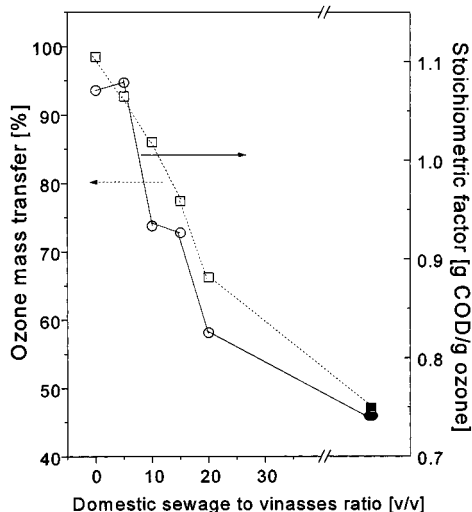
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Figure 2. Influence of domestic sewage-to-vinasse ratio on the ozone mass tranfer and COD removal during ozonation. Conditions: $T = 20$ °C; pH 5.4; $V_T = 1$ L; $F = 30$ L/h; $C_{O_3i} = 20$ mg/L; reaction time = 1 h. Black symbols correspond to domestic sewage without vinasses.

Figure 2 imply that ozone transfer and pollution removal efficiencies during ozonation are suitable when the percentage of vinasse in the wastewater is high. This is in accordance with the high reactivity of several organic pollutants present in the vinasses (e.g., phenols) toward ozone (Beltrán et al., 1998). Thus, on the basis of previous results (Beltrán et al., 1991) and according to those reported here, ozonation could be an efficient treatment to remove dissolved organic pollutants from vinasses. However, excessive consumption of ozone is needed to obtain significant organic matter removal, resulting in prohibitive costs (e.g., only 33.7% COD removal is reached after 5 h of treatment in run 1, see Table 2). On the other hand, wine distillery industries often discharge to the public sewage system, frequently with no complete treatment or even without any treatment. In these cases, vinasses are diluted with domestic sewage. Because these mixed wastes contain a moderate organic content after the dilution, ozonation can be used without excessive consumption as a pretreatment step before conventional biological oxidation. To ascertain the most effective integrated chemical (ozone)−biological process conditions, studies of the influence of the main variables, pH and temperature, on biodegradability and ozonation kinetics were undertaken. Herein the ratio of domestic sewage to vinasses was kept at 10 to 1 by volume, as it is in some wastewater treatment facilities.

Influence of Operating Variables on the Oxidation Process: pH and Temperature. It is well-known that pH is the parameter with the highest influence on water and wastewater ozonation. This is because dissolved ozone decomposes into free radicals (mainly hydroxyl free radicals, HO•) at high pH, and therefore ozone indirectly oxidizes the organic matter through these species (Staehelin and Hoigné, 1985). Figures 3 and 4 show the evolution of residual normalized COD and dissolved carbon (TC and TOC) with time during ozonation experiments carried out at different pH values and fixed ozone dose and temperature. An increase of pH yields slight increases of COD and TOC removal rates. The smaller decrease observed in TC, compared to that observed in TOC, is due to the accumulation of carbonate/bicarbonate formed from CO_2 produced during ozonation, especially at pH 10. On the other hand,
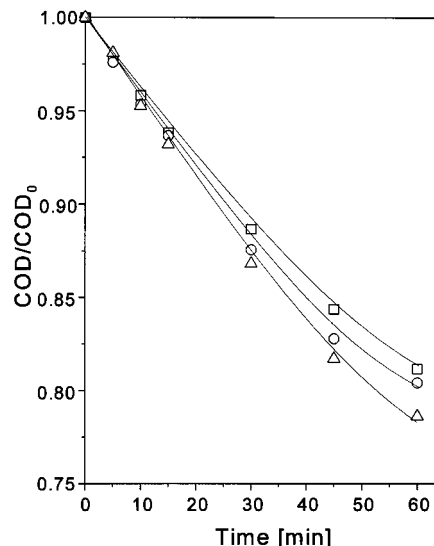

Figure 3. Influence of pH on COD removal during wastewater ozonation: (□) pH 5.4; (○) pH 7.0; (△) pH 10. Conditions: $T = 20$ °C; $V_T = 1$ L; $F = 30$ L/h; $C_{O_3i} = 20$ mg/L; $f = 10$.
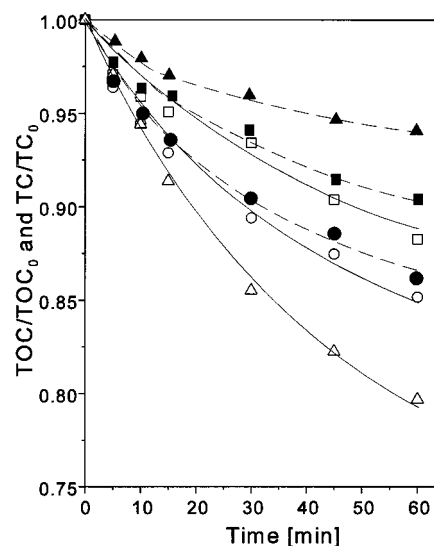
Figure 4. Influence of pH on TOC and TC removal during wastewater ozonation: (□, ■) pH 5.4; (○, ●) pH 7.0; (△, ▲) pH 10. Conditions: $T = 20$ °C; $V_T = 1$ L; $F = 30$ L/h; $C_{O_3i} = 20$ mg/L; $f = 10$. Black symbols and dotted lines correspond to TC data.

it was also observed (not shown) that low pH favored overall UV_{254} disappearance rate (UV_{254} decreases after 1 h of ozonation were 33, and 22% at pH 5.4 and 10, respectively). In no case was dissolved ozone detected in water. The absence of ozone, according to the film theory concept, suggests that all ozone reacts in the diffusion film, a situation defined as fast reaction (Charpentier, 1981). Under these circumstances no formation of hydroxyl radical from ozone−hydroxide ion reaction can be considered (Beltrán, 1995). Therefore, the beneficial effect of high pH on COD and TOC removals can most likely be attributed to the fast hydroperoxide ion (HO_2^-)−ozone reaction. Hydrogen peroxide is formed as an intermediate during phenol ozonolysis (Bailey, 1982). Formation of the hydroperoxide ion is favored at high pH ($pK = 11.8$). Reaction between ozone and the hydroperoxide ion initiates a free radical mechanism in which RO• and HO• are the main propagating species (Staehelin and Hoigné, 1982). Thus,

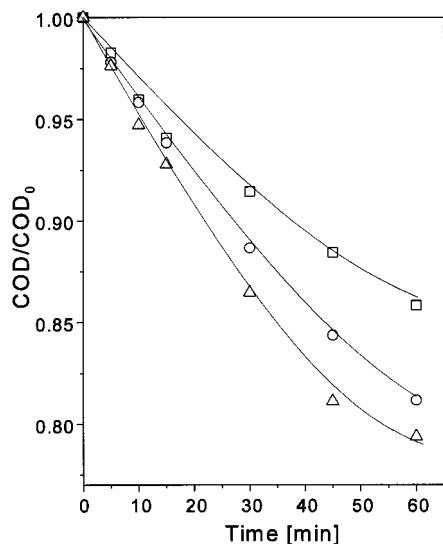**Figure 5.** Influence of reaction temperature on the COD removal rate during wastewater ozonation: ($\square$) 10 °C; ($\bigcirc$) 20 °C; ($\triangle$) 30 °C. Conditions: pH 5.4; $V_T = 1$ L; $F = 30$ L/h; $C_{O_3i} = 20$ mg/L; $f = 10$.

as long as the concentration of the hydroperoxide ion is low (i.e., low pH), the initiation step of the radical mechanism is inefficient and hence only the direct reaction between ozone and organic matter takes place. It should be kept in mind, however, that the direct or molecular reactions of ozone (i.e., electrophilic substitution and cycloaddition reactions) are very selective toward specific compounds such as unsaturated and aromatic substances, most of them with high UV_{254} absorption (Traina et al., 1990).

The effect of temperature on the oxidation rate is illustrated in Figure 5. As can be seen for experiments completed at identical ozone dose and pH conditions, an increase in temperature leads to a positive effect on COD removal rate. The increase in COD conversion with temperature is a logical consequence of the increasing rate constants of the reactions between dissolved matter and ozone or free radicals.

Biodegradability Induced by Ozonation. The effects of ozonation on the biodegradability of distillery and domestic wastewater were observed through changes in COD and BOD during runs carried out at different applied ozone doses, percentages of vinasse in the feeding wastewater, and pH values. Some authors have chosen the BOD/COD relationship as an index of the water biodegradability (Gilbert, 1987; Zimmerman and Richard, 1990; Adams et al., 1994). In this research changes in the BOD/COD ratio under batch conditions were followed to determine the ozonation conditions that improve the biodegradability of the wastewater tested. Measurements of BOD after 5 days do not usually provide a good estimate of the concentration of the biodegradable organic matter, due to the lack of microorganism acclimation to the ozonated wastewater (Beltrán et al., 1997). However, BOD measurements after 10 days could be misleading because consumption of oxygen due to nitrification reactions is possible. Therefore, in this work, BOD tests were performed up to 10 days. The improvement of biodegradability induced by ozonation has been associated with partial oxidation of different organic compounds to low molecular weight compounds, which are readily biodegradable, rather than complete oxidation to CO_2 (Scott and Ollis, 1995).
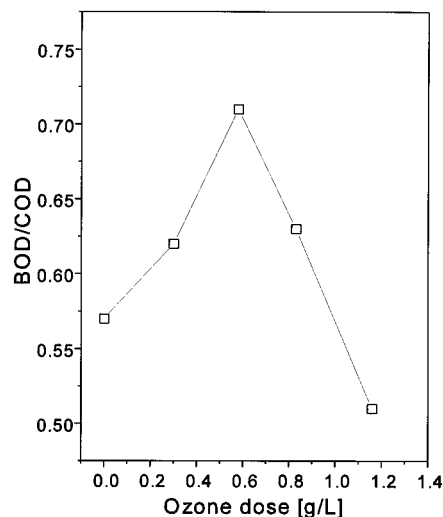

Figure 6. Influence of the ozone dose on the biodegradability induced by ozonation. Conditions: $T = 20$ °C; pH 5.4; $V_T = 1$ L; $F = 30$ L/h; $f = 10$.
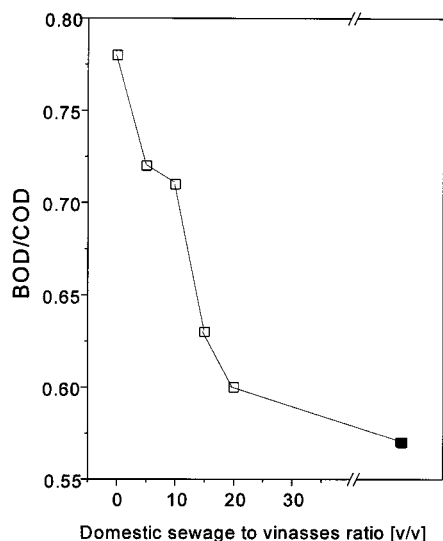

Figure 7. Influence of domestic sewage-to-vinasse ratio on the biodegradability induced by ozonation. Conditions: $T = 20$ °C; pH 5.4; $V_T = 1$ L; $F = 30$ L/h; $C_{O_3i} = 20$ mg/L; $f = 0$–20. Black symbol corresponds to domestic sewage without vinasses.

From experiments completed at different ozone doses it was observed (see Figure 6) that addition of 0.58 g of ozone per liter of wastewater (vinasse/domestic sewage, ratio 1:10 by volume) led to a maximum change of BOD/COD ratio. This suggests that ozone doses smaller than the optimum one are not enough for the conversion of all refractory organics present in the wastewater to others more amenable to microorganisms included in the BOD seeding. However, some improvement in BOD/COD ratio was observed in ozonated samples compared to the nonozonated ones, regardless of the ozone dose applied. On the other hand, when ozone doses higher than the optimum one were applied, COD and BOD diminished, indicating that biodegradable organics were also oxidized. This explains the marked drop observed in biodegradability (i.e., BOD/COD).

Figure 7 shows the evolution of BOD/COD ratio with the sewage/vinasse volume ratio for ozonated wastewaters. The BOD/COD ratio diminished with the increase of domestic sewage fraction. This implies that certain

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chemicals included in vinasses, which are refractory to biotreatment like phenols, can be partially oxidized by ozonation, whereas the compounds found in municipal sewage are more refractory to ozonation.

Finally, the increase of pH has a negative effect on the changes of BOD/COD ratio when results from original and ozonated wastewaters are compared. For example, when ozonation was carried out at pH 10, BOD/COD decreased from 0.60 (without preozonation) to 0.55, whereas at neutral and acid conditions (pH 5.4) the ratio BOD/COD increased from 0.60 to 0.63 and from 0.61 to 0.75, respectively. As indicated above, the pH can alter the mechanism of ozonation. At high pH, ozone reacts directly via free radicals with the organics present in the wastewater, whereas in acid media the formation of free radicals from ozone is negligible. Therefore, acid conditions that favor direct ozonolysis instead of free radical reactions ameliorated the ozone-induced biodegradability.

Kinetic Study. Mathematical Model. Despite the beneficial effects of ozonation in wastewater treatment, there are only a few works supporting the kinetics of ozonation of complex wastewaters. Almost all of the studies on reaction kinetics of ozone have been carried out in synthetic wastewaters with model pollutants. In this work, all simultaneous reactions that ozone undergoes in water were grouped in reaction 1

$$\text{organic matter} + z\text{O}_3 \rightarrow \text{products} \qquad (1)$$
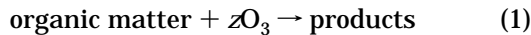
where the organic matter concentration is expressed as COD and the reaction order was assumed to be 1:1 as has been observed in most water pollutant−ozone reactions (Hoigné and Bader, 1983; Kuczkowsky, 1984; Yao and Haag, 1991).

The proposed model is based on film theory to address the problem of gas (ozone) absorption accompanied by irreversible chemical reaction (eq 1). According to this model, the ozone absorption rate can be expressed by eq 2 (Charpentier, 1981)

$$N_{O_3} = k_L a C^*_{O_3} E \qquad (2)$$

where $k_L a$ is the volumetric mass transfer coefficient, $C^*_{O_3}$ the ozone concentration at the gas−liquid interface, and E the reaction factor. As ozonation is a gas−liquid reaction, degradation rates can be controlled by mass transfer and/or chemical reaction. Accordingly, to develop the kinetic study, the kinetic regime of ozone absorption must be established. As no free dissolved ozone was detected in water, a fast absorption regime with a pseudo-first-order reaction was assumed (Beltrán et al., 1995). For this case the film theory proposes that E and Ha, the dimensionless Hatta number, coincide. The Hatta number is defined as

$$\text{Ha} = \sqrt{\text{COD} \times D_{O_3} k}/k_L \qquad (3)$$

where D_{O_3} is the diffusivity of ozone in water, k the rate constant of the global reaction 1, and k_L the individual liquid-phase mass transfer coefficient.

The fast absorption regime with pseudo-first-order reaction pertains when the following condition is satisfied:

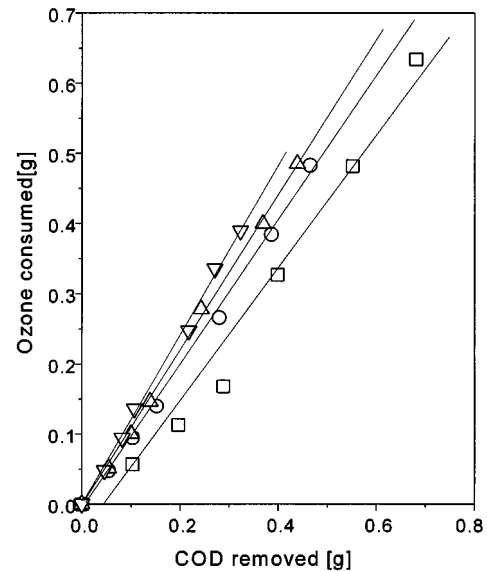$$3 \leq \text{Ha} \leq E_i/2 \qquad (4)$$

Figure 8. Determination of stoichiometric coefficient, z, according to eq 7. Domestic sewage-to-vinasse ratio, f: (□)5; (○) 10; (△) 15; (▽) 20. Conditions: $T = 20$ °C; pH 5.4; $V_T = 1$ L; $F = 30$ L/h; $C_{O_3i} = 20$ mg/L.

The instantaneous reaction factor, E_i, is defined as

$$E_i = 1 + (D_{OM}/D_{O_3})(z\text{COD}/C^*_{O_3}) \qquad (5)$$

where D_{OM} is the diffusivity of the dissolved matter.

Estimation of the Physicochemical Parameters. The stoichiometric factor, individual mass transfer coefficients, and diffusivities must first be evaluated to apply the kinetic model. Thus, a series of experiments and assumptions were made. Given the fact that dissolved ozone was not found, the stoichiometric factor, z, was calculated from the ozone absorbed and consumed as

$$(C_{O_3i} - C_{O_3o}) \frac{F}{V_T} = z\left(\frac{-\text{dCOD}}{\text{d}t}\right) \qquad (6)$$

where C_{O_3i} and C_{O_3o} are the ozone concentrations in the gas at the reactor inlet and outlet, respectively, F is the gas flow rate, and V_T is the reaction volume. If eq 6 is applied to a finite time interval, Δt, eq 7 is obtained:

$$(C_{O_3i} - C_{O_3o}) \frac{F}{V_T} \Delta t = z \times \Delta\text{COD} \qquad (7)$$

For a constant value of z, according to eq 7, a plot of the left side versus the COD removed during each finite interval time, COD, should yield a straight line. As an example, Figure 8 shows this plot corresponding to experiments carried out with different concentration of vinasses. From the least-squares analysis of the straight lines plotted z was found (see values in Table 3).

Determination of the volumetric mass transfer coefficient, $k_L a$, involved another series of experiments of oxygen absorption in the specific treated wastewater (Gurol and Nekouinaini, 1985). At these conditions no variation of COD was noticed. Hence, the absorption of oxygen was due only to mass transfer. The rate of absorption of oxygen is

$$N_{O_2} = \text{d}C_{O_2}/\text{d}t = k_L a_{O_2} C^*_{O_2} - k_L a_{O_2} C_{O_2} \qquad (8)$$

Table 3. Stoichiometric Coefficient, Mass Transfer Coefficient, and Pseudo-First-Order Rate Constant for Vinasse−Domestic Sewage Wastewater Ozonation

f^a	initial pH	z, g of O_3/ g of COD	$k_La \times 10^2$, s^{-1}	$k \times 10^{-4}$, L/(mol·s)	COD range,[b] g/L
0	3.5	0.985	0.95	0.08	14.4−21.7
5	4.4	0.955	1.03	0.64	3.9−4.6
10	5.4	0.991	1.14	0.95	2.0−2.5
15	5.8	1.114	1.13	1.06	1.2−1.7
20	6.4	1.121	1.07	1.14	1.0−1.3
10	7.0	1.116	1.13	1.48	2.0−2.5
10	10.0	1.111	1.07	1.62	1.9−2.4

[a] f = vol of domestic sewage/vol of vinasse. [b] Range of COD for which pseudo-first-order kinetics was checked.

Assuming that the oxygen concentration at the gas−liquid interface, $C^*_{O_2}$, is constant, a plot of the rate of oxygen absorption against the dissolved oxygen, C_{O_2}, led to a straight line, the slope of which is $k_La_{O_2}$. Application of least-squares analysis to the resulting straight lines allowed $k_La_{O_2}$ to be determined. The volumetric mass transfer coefficient referred to ozone, k_La, was then calculated according to the film theory by

$$k_La = k_La_{O_3} = k_La_{O_2}(D_{O_3}/D_{O_2}) \qquad (9)$$

where diffusivities, D_{O_3} and D_{O_2}, were obtained from the literature (Johnson and Davis, 1996; Gurol and Singer, 1983). With this procedure $k_La_{O_3}$ was found to be slightly dependent on the vinasse concentration and pH as shown in Table 3.

The individual liquid-side mass transfer coefficient, k_L, was calculated from Calderbank's equation, valid for contactors similar to the bubble column used in this work (Froment and Bischoff, 1979). From k_La and k_L the specific interfacial area, a, was obtained. Finally, for the diffusion coefficient, D_{OM}, a value of 5×10^{-10} m²/s was taken as an average value of those corresponding to the diffusion of organics in water (Reid et al., 1977).

Rate Coefficient Determination. According to the geometric characteristics of the reactor and flow rates used in this work, ideal plug flow behavior of the gas phase and perfect mixing of the water through the bubble contactor were assumed. The ozone mole balance applied to a differential element in the reactor was then expressed by

$$-\frac{m_T}{P_T} dP_{O_3} = N_{O_3}\beta \, dV + \frac{dC_{O_3g}}{dt} dV \qquad (10)$$

where m_T is the total molar gas flow rate, P_T the total pressure within the system, dP_{O_3} the ozone pressure drop in the differential volume element, and β the liquid hold-up. The last term of the right side of eq 10 represents the accumulation rate of ozone in the gas phase and can be considered negligible compared to the other terms (Beltrán et al., 1995). The ozone concentration at the gas−water interface can be expressed as a function of the ozone partial pressure according to Henry's law

$$C^*_{O_3} = P_{O_3}/He \qquad (11)$$

where He is the Henry's law constant. Values of He were taken from previous work (Beltrán et al., 1995). From eqs 2, 3, 10, and 11, the differential ozone mole balance equation becomes
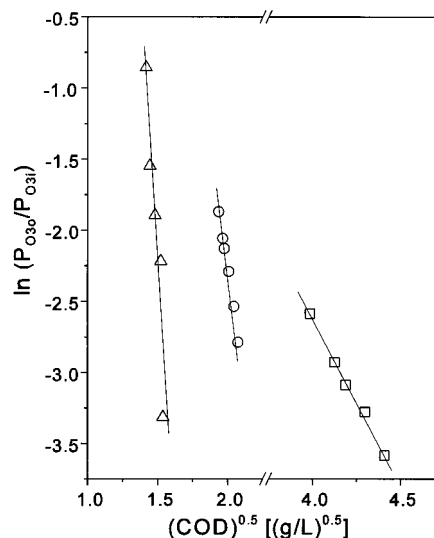

Figure 9. Determination of the rate constant, k, according to eq 14. Domestic sewage-to-vinasse ratio: (□) 0; (○) 5; (△) 10. Conditions: $T = 20$ °C; pH 5.4; $V_T = 1$ L; $F = 30$ L/h; $C_{O_3i} = 20$ mg/L.

$$-\frac{m_T}{P_T} dP_{O_3} = \frac{aP_{O_3}\beta\sqrt{COD \times D_{O_3}k}}{He} dV \qquad (12)$$

By rearranging and integrating eq 12 with the boundary conditions (eq 13)

$$V = 0 \quad P_{O_3} = P_{O_3}i; \qquad V = V_T \quad P_{O_3} = P_{O_3}o \qquad (13)$$

eq 14 is obtained:

$$\ln(P_{O_3}/P_{O_3}i) = \alpha\sqrt{k}\sqrt{COD} \qquad (14)$$

In eq 14 α is

$$\alpha = P_T a\beta V_T\sqrt{D_{O_3}}/m_T He \qquad (15)$$

According to eq 14, a plot of the left-hand side versus $COD^{1/2}$ should yield a straight line of slope $\alpha k^{1/2}$. As an example, Figure 9 shows this plot for experiments carried out under different conditions. The experimental points lie on straight lines, corroborating eq 14. Table 3 summarizes the values of k obtained from the slope $\alpha k^{1/2}$ corresponding to different vinasse wastewater concentrations, pH values, and temperatures. Finally, condition 4 was satisfactorily checked for the COD range investigated.

ABBREVIATIONS USED

C_{O_3i}, gas ozone concentration at the reactor inlet, mg/L; C_{O_3g}, gas ozone concentration within the reactor, mg/L; C_{O_3o}, gas ozone concentration at the reactor outlet, mg/L; $C^*_{O_3}$, ozone concentration at the gas−liquid interface, mg/L; D_{OM}, diffusivity of organic matter in water, m²/s; D_{O_2}, diffusivity of oxygen in water, m²/s; D_{O_3}, diffusivity of ozone in water, m²/s; E, reaction factor, dimensionless; E_i, instantaneous reaction factor defined by eq 5, dimensionless; F, volumetric gas flow rate, L/h; Ha, Hatta number, defined by eq 3, dimensionless; He, Henry's law constant, atm·L/mol; k, rate constant of the ozone−organic matter reaction, L/mol·s; k_La, liquid-phase volumetric mass transfer coefficient, s⁻¹; m_T, total molar gas flow rate, mol/h; N_{O_3}, ozone

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absorption rate, mol/L·s; P_T, total pressure within the system, atm; P_{O_3}, ozone partial pressure within the reactor, atm; P_{O_3i}, ozone partial pressure at the reactor inlet, atm; P_{O_3o}, ozone partial pressure at the reactor outlet, atm; V_T, reaction volume, L; z, stoichiometric ratio of the reaction ozone−organic matter reaction, mol of O_3/mol of O_2; α, parameter defined by eq 15; β, liquid hold-up, dimensionless; BOD, biological oxygen demand, mg/L; COD, chemical oxygen demand, mg/L; DO, dissolved oxygen, mg/L; IC, inorganic carbon, mg/L; TC, total carbon, mg/L; TKN, total Kjeldahl nitrogen, mg/L; TOC, total organic carbon, mg/L; TS, total solids, mg/L; TSS, total suspended solids, mg/L; UV_{254}, ultraviolet absorbance at 254 nm.

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