

KINETICS, CATALYSIS, AND REACTION ENGINEERING

Process Integration: Continuous Anaerobic Digestion–Ozonation Treatment of Olive Mill Wastewater

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The purification of the olive mill wastewaters (OMW) is investigated by the combination of an anaerobic digestion, followed by an ozonation treatment. Continuous anaerobic digestion (CAD) was performed in a laboratory-scale bioreactor at constant hydraulic retention time and influent organic substrate concentration. Chemical oxygen demand (COD), total polyphenolic compounds (TP), methane production, pH, total volatile fatty acids (VFA), and alkalinity were analyzed daily. The COD removal and methane yield coefficient were 81% and 295 L CH₄/kg COD, respectively. A kinetic study is performed using the Monod model, which, when applied to the experimental data, provides the specific kinetic constant of this model. Effluent from CAD was submitted in an ozonation stage, where the temperature and inlet ozone partial pressure were varied. COD, total aromatic compounds (A), and TP removals were established. An approximate kinetic study for design purpose was developed, which leads to evaluation of the apparent kinetic constants for COD and total aromatic compounds.

Introduction

The manufacture of olive oils is performed in numerous small plants that operate seasonally. They produce an aqueous phase (OMW) (~50% of the total volume treated) that arises from the water content of the fruit, combined with the water used to wash and process the original olives. Usually, these effluents are disposed of into evaporation ponds, through public sewers, or are dumped into the environment untreated. They represent a large-scale environmental problem, mainly because of (i) the bad odor that is caused by fermentation processes and (ii) the possibility of the pollution of surface water or groundwaters.¹

Therefore, several treatments have been investigated to reduce the polluting power (mainly biological processes, both aerobic² and anaerobic³ biodegradation). Preferentially, the anaerobic digestion of the material is conducted, because of its advantages, which include (i) low costs, (ii) a need for little energy and very low amounts of nutrients, and (iii) the capability of the anaerobic bacteria to transform most of the organic substances present in the waste into methane. However, some organic compounds, such as phenols, are toxic for methanogenic bacteria and inhibit the anaerobic digestion.^{4,5}

Directive 91/271/CE of the Council of Europe (1991) established efficiencies required for wastewater treatment installations that must be instituted soon. In terms of the objectives promulgated, 70%–90% of biochemical oxygen demand (BOD₅), 75% of chemical oxygen demand (COD), and 90% of suspended solids (SS) should be removed before discharging effluents in

normal areas. On the other hand, the maximum treated effluent concentrations should be set to 25 mg BOD₅/L, 125 mg COD/L, and 35 mg SS/L. Compliance with these criteria implies the construction of new treatment facilities in some countries, with the need for new economic and efficient treatment methods.

Therefore, chemical oxidation treatments have recently been investigated to examine these phenol-rich wastewaters.⁶ Among them, ozonation^{7,8} is a promising technology, because ozone has many of the oxidizing properties that are desirable for wastewater treating. Consequently, it is increasingly used because of its characteristics:^{9,10} (i) it is a powerful oxidant capable of oxidative degradation of many organic compounds, (ii) it is readily available, (iii) it is soluble in water, and (iv) it leaves no byproducts that need to be removed.^{11–13}

In this work, the degradation of OMW has been studied by means of the combined process constituted by an anaerobic digestion followed by an ozonation process. In both steps, the objectives were to report data for the removal of the organic matter (represented by the COD, total aromatic compounds, and total polyphenolic compounds (TP)) and to conduct kinetic studies of each process. The aim of the kinetic study was provide rate constants useful for the design of reactors where these processes could be performed in wastewater treatment plants.

Experimental Section

The original wastewaters used as substrates were collected from an olive oil production plant (Aceitera Valverdeña, Valverde de Leganes) located at the Extremadura Community (in southwestern Spain). These effluents were characterized according to the procedures described in the Standard Methods,¹⁴ and the values

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Table 1. Main Characteristics of Wastewater

parameter	value
pH	4.8
biochemical oxygen demand, BOD ₅	52 g/L
chemical oxygen demand, COD	95 g/L
total polyphenols	2.2 g/L
N-Kjeldahl	0.4 g/L
phosphorus	1.9 g/L
volatile fatty acids	3.4 g/L
alkalinity	2.4 g/L
total solids, TS	130.3 g/L
total suspended solids, TSS	67.1 g/L
volatile suspended solids, VSS	39.9 g/L

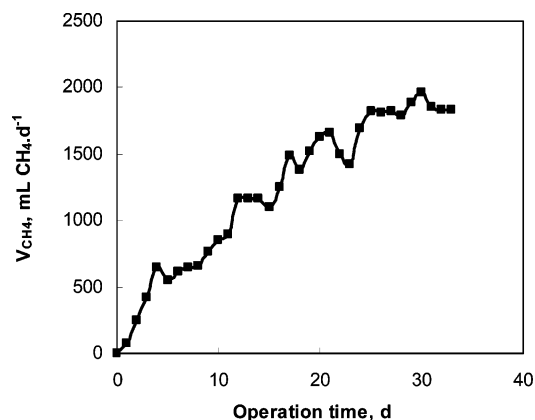
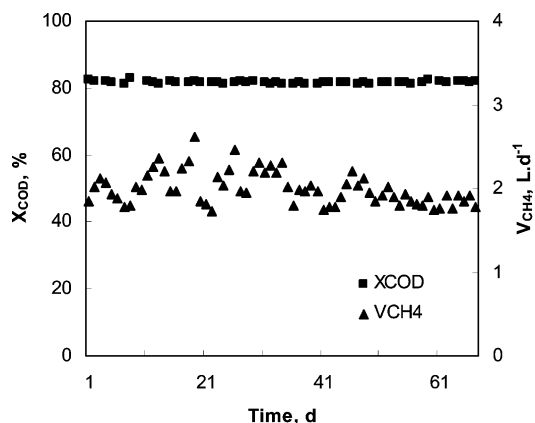
obtained for the main physicochemical characteristics have been summarized in Table 1. Prior to any experiment, OMW was centrifuged and filtered to remove SS.

In the present study, a laboratory continuous anaerobic digester (CAD) was used. It consisted of a 5-L cylindrical Pyrex glass vessel, which was provided with a cover containing an inlet for loading feedstock and an outlet for removing effluents and venting biogas. The substrate was fed continuously to the bioreactor by means of a peristaltic pump (Masterflex, Cole–Palmer) that was controlled by an electronic timer and operated at a volumetric flow rate constant of 90 mL/d. The biogas released volume was measured using the Boyle–Mariotte liquid displacement technique. Temperature was maintained at 35 °C by means of a thermostatic bath, and the biomass content was 12 g/L (measured as volatile suspended solids (VSS)). For the purpose of mixing within the bioreactor, biogas was recirculated by means of a compressor (Dinko, model D-95).

Before the experiment was started, the digester was acclimatized by incrementing the flow rate of OMW loaded from 10 mL/d to 90 mL/d over a period of 1 month. During this time, samples were collected daily and COD and TP were analyzed. The methane content of the gas evolved was also measured daily. Every 15 days, the pH, total volatile fatty acids (VFA), and alkalinity were also analyzed.

The microorganisms that were effecting the anaerobic process were supported on sepiolite, which is a micronized fibrous silicate that retains methanogenic bacteria preferentially. Because of their slow growth, these bacteria are to be retained in the bulk reactor, to avoid any reduction in the overall rate of digestion.

The ozonation experiments were conducted in a 1-L cylindrical Pyrex glass completely mixed batch reactor that was provided with a cover that contained inlets for bubbling the gas and stirring and outlets for sampling and venting. The reactor was submerged in a thermostatic bath with the necessary elements to maintain the temperature constant within ± 0.5 °C. For the ozone generation, oxygen that had been taken from a commercial cylinder was dried with silica gel traps and introduced into an ozone generator (Sander, model 301.7). When the temperature and the inlet ozone partial pressure were adjusted to the desired value, the ozone–oxygen gas stream was fed to the reacting medium through a bubble gas sparger at a constant flow rate of 40 L/h (at 1 atm and 20 °C). After the process started, each experimental series lasted for ~ 4 h. The ozone partial pressure in the outlet gas stream was periodically determined. An iodometric method was used to analyze the ozone in the inlet and outlet gas streams. Several samples were taken periodically to analyze the substrate concentrations, including COD, total aromatic compounds (A) (determined by measuring

**Figure 1.** Evolution of methane production during the acclimatization stage.**Figure 2.** Evolution of substrate removal efficiency and methane production.

the absorbance of the samples at 254 nm), and TP. COD was determined in a Dr. Lange photometer, using the procedure described in the Standard Methods.¹⁴ Absorbances were measured in an Hitachi model U-2000 spectrophotometer, using an 1-cm-optical-path-length quartz cuvette, and the TP was measured via the Folin–Ciocalteu method.¹⁵

Results and Discussion

1. First Stage: Continuous Anaerobic Digestion.

1.A. Startup of Reactor. It is known that the startup of an anaerobic digester fed with high-strength wastewater is a very complex problem. The operating conditions are difficult to control, because of buildup of volatile fatty acids (VFA).^{3,16}

In the present work, during the seeding and maturation period, methane production showed a shaped curve, as depicted in Figure 1. This figure reveals that the maturation period lasted approximately 1 month, with an average methane volume 1828 mL CH₄/d in the steady-state. Next, the reactor started in continuous mode feeding, with a volumetric flow rate of 90 mL/d.

1.B. Substrate Removal and Methane Formation. Figure 2 illustrates the evolution of COD removal and methane formation with time. It can be seen that the biodigester operated under stable conditions during all experiments (2 months), with a mean COD removal of 81% and 95% for BOD₅ (see Table 2). The residual nonbiodegradable organic matter is due to the presence of compounds such as polyphenols, which are very difficult for the flora to break down.

Table 2. Experimental Conditions and Average Values in Continuous Anaerobic Digestion (CAD)

	condition	value	parameter
operation mode	continuous feed	81% ^a	COD
retention time	55 d	95% ^a	BOD ₅
working volume	5 L	95% ^a	TP
OMW feed flow rate	90 mL/d	2.0 L CH ₄ /d	V _{CH₄}
temperature	35 °C	295 L CH ₄ /kg	Y _{P/S}
		COD	

^a Percentage of removal.

One major factor that makes anaerobic digestion preferable to other biological treatments is methane gas production. The specific methane yield (L CH₄/kg COD) varied in the range of 210–315 L CH₄/kg COD during the experiment, with an average value of 295 L CH₄/kg COD (see Table 2); this value is similar to the theoretical value proposed in previous literature of 330 L/kg COD.¹⁶ As it is known, methane is produced from VFA (mainly formic, acetic, propionic, and butyric acids) and carbon dioxide reduction. The conversion of organic matter to VFA is the first phase of the anaerobic system. The formation of these acids does not result in substrate removal. Methanogenic bacteria are responsible for converting VFA to methane and carbon dioxide. A production of 3.6 mg VFA L⁻¹ d⁻¹ was obtained. Also, pH and alkalinity showed an average value of 7.5 and 6.4 g CO₃Ca/L, respectively. According to the literature, these values indicate a very good experimental conditions for anaerobic digestion.¹⁶

1.C. Kinetic Study. The most frequently model used to interpret the experimental data of anaerobic digestion is based on Monod.¹⁷ This model establishes the following relationship among the specific substrate biodegradation rate q and substrate concentration S :

$$q = \frac{q_{\max} S}{k_S + S} \quad (1)$$

where k_S is the saturation constant of Monod and q_{\max} is the maximum specific substrate biodegradation rate. At low substrate load (present study), operating at a volumetric flow rate of 90 mL/d, $k_S \gg S$, and, therefore, eq 1 can be simplified for a continuous reactor:

$$q = -\frac{1}{X_V} \frac{dS}{dt} = \frac{S_i - S_o}{X_V \tau} \quad (2)$$

where S_i and S_o are inlet and outlet organic substrate concentrations, respectively, X_V is the biomass concentration in the bioreactor, and τ is the hydraulic retention time.

Combining eqs 1 and 2 gives the following expression for the kinetic rate constant:

$$k = \frac{q_{\max}}{k_S} X_V = \frac{S_i - S_o}{S_o \tau} \quad (3)$$

Applying eq 3 to the experimental results, the kinetic rate constant was calculated, taking an average value of $(7.8 \pm 0.6) \times 10^{-2} \text{ d}^{-1}$. Similar values were deduced in other works. Phthalic acid esters generated in the wastewater treatment plants were treated by anaerobic digestion.¹⁸ Batch and continuous experiments showed that di-ethyl phthalate and di-*n*-butyl phthalate are rapidly degraded under mesophilic anaerobic conditions

Table 3. Chemical Oxygen Demand (COD), Total Aromatic Compounds (A), and Total Polyphenolic Compounds (TP) Reductions in Ozonation Experiments (OAD)

experiment	T (°C)	p_{O_3} (kPa)	X_{COD} (%)	X_A (%)	X_{TP} (%)
OAD-1	10	4.1	24	35	68
OAD-2	20	4.7	21	42	68
OAD-3	30	4.3	49	57	89
OAD-4	40	4.9	52	69	89
OAD-5	30	1.0	16	8.1	83
OAD-6	30	3.7	27	42	86

Table 4. Evolution of Organic Matter in Experiment OAD-3 ($T = 30$ °C and $p_{\text{O}_3} = 4.3$ kPa)

time (h)	P_{O_3} (kPa)	COD (g/L)	A (g/L)	TP ($\times 10^2$ g/L)
0	0	16.7	1.20	13
0.5	0.5	13.2	0.90	3.1
1	2.3	9.8	0.71	2.2
1.5	2.5	9.5	0.61	1.9
2	2.6	9.4	0.58	1.6
3	2.7	8.5	0.55	1.5
4	3.1	8.4	0.51	1.5

with a first-order kinetic constant of 8.04×10^{-2} and $13.69 \times 10^{-2} \text{ d}^{-1}$, respectively.

2. Second Stage: Chemical Oxidation with Ozone. 2.A. Influence of Operating Variables on the Ozonation Process. The ozonation of OMW from the CAD stage (after reaching a steady state in the anaerobic digester) has been investigated by modifying the temperature ($T = 10, 20, 30$, and 40 °C) and the ozone partial pressure in the gas mixture ($p_{\text{O}_3} = 1.0$ – 4.9 kPa). Table 3 presents the values taken for those operating variables. As was mentioned previously, the evolution of the organic matter reduction was followed through each experiment by measuring the COD and the contents of aromatic and polyphenolic compounds (A and TP, respectively). Table 4 depicts the evolution of these parameters in experiment OAD-3, taken as an example. As can be observed, the organic matter decreases continuously with time. Similar evolutions were observed in all experiments.

Table 3 shows the chemical oxygen demand removal (defined as $X_{\text{COD}} = 1 - S_o/S_i$) at 240 min of reaction. Thus, when the inlet ozone partial pressure (p_{O_3}) increases, the COD removal also increases, with final values of 16%, 27%, and 49% at 240 min for 1.0, 3.7, and 4.3 kPa, respectively. On the other hand, the COD removal increases as the temperature increases at constant p_{O_3} (see Table 3). Final values of 24%, 21%, 49%, and 52% are obtained for 10, 20, 30, and 40 °C, respectively.

Table 3 also shows the aromatic compounds removal, which is defined as $X_A = 1 - A_i/A_o$ and the total polyphenolic compounds removal, defined as $X_{\text{TP}} = 1 - \text{TP}_i/\text{TP}_o$. Values of 8%, 42%, and 57% were obtained in experiments OAD-1, OAD-2, and OAD-5, respectively, for aromatic compounds removal. Most of this reduction was already achieved in the first 120 min of reaction and additional time led to slight increases in that aromatic content: thus, as can be observed in experiment OAD-3 (see Table 4). A small reduction was observed for aromatic compounds from 120–240 min of reaction (that is, from 52%–57% of aromaticity removal). For TP, values of 83%, 86%, and 89% were obtained in experiments OAD-1, OAD-2, and OAD-5, respectively. Also, this reduction was achieved in the first 30 min of reaction, as can be observed in experiment OAD-3 (see Table 4).

Table 5. Values of Ozonation Yields and Ozone Reaction Rates in Ozonation Experiments

experiment	time, <i>t</i> (h)	<i>R</i> (%)	<i>N</i> ($\times 10^5$ mol L ⁻¹ s ⁻¹)
OAD-1	0.5	96	0.9
OAD-1	4	81	0.7
OAD-2	0.5		3.3
OAD-2	4	25	0.8
OAD-3	0.5	86	3.3
OAD-3	4	14	0.5
OAD-4	0.5	75	3.3
OAD-4	4	24	1.0
OAD-5	0.5	88	3.3
OAD-5	4	27	1.0
OAD-6	0.5	95	4.0
OAD-6	4	24	1.0

The ozone partial pressure in the outlet gas stream (p_{O_3o}) was also measured during each experiment. Its values rapidly increased and reached a steady value, close to the inlet ozone partial pressure, especially in experiment OAD-4 with the higher p_{O_3i} value. The difference between both values, p_{O_3i} and p_{O_3o} , is related to the amount of ozone reacted. The ozonation yield (*R*) is a parameter that gives information about the oxidation process:

$$R = \frac{p_{O_3i} - p_{O_3o}}{p_{O_3i}} \times 100 \quad (4)$$

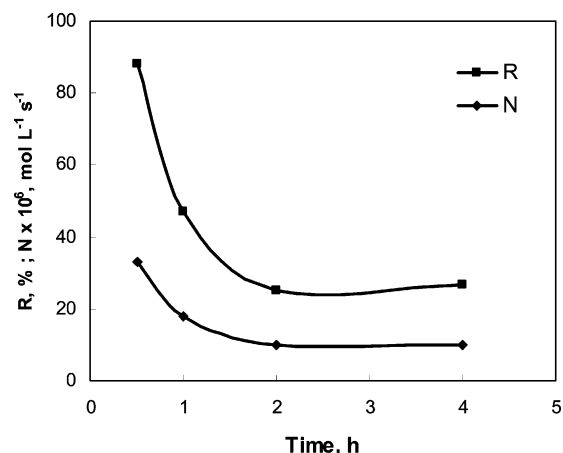
Table 5 provides *R* values for each experiment at two selected reaction times (30 and 240 min). As can be observed, it decreases when the reaction advances, especially at initial reaction times. On the other hand, at a selected time, *R* increases when the p_{O_3i} value decreases: thus, at 240 min, taken as an example, values of 14%, 24%, and 27% were obtained in experiments which the inlet ozone partial pressure p_{O_3i} was 4.3, 3.7, and 1.0 kPa, respectively.

Another interesting parameter in ozonation processes is the ozone reaction rate (*N*), which indicates the global reaction rate between ozone and the different organic compounds present in wastewater. It is defined as

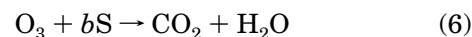
$$N = \frac{(n_i - n_o)}{V} \quad (5)$$

where n_i and n_o are the inlet and outlet ozone flow rates in gas stream, respectively (obtained from the ozone partial pressure), and *V* is the reactor volume (500 cm³). Table 5 also shows the *N* values for each experiment at two selected reaction times (30 and 240 min). Similar to that observed for *R*, the reaction rate decreases with reaction time through each experiment. Figure 3 shows the evolution of ozonation yield *R* and ozone reaction rate *N* for the experiment OAD-5, taken as an example.

2.B. Kinetic Study. During the ozonation of the organic matter contained in the OMW, many reactions which cannot be known individually occur. So, an approximate study of the ozonation kinetics of some wastewaters can be investigated through the use of global parameters, which is the objective: to provide values of apparent kinetic constants for the ozonation reaction of that organic material for design purposes. As the COD and the aromatic compounds content seems to be the most suitable parameters for representing the organic matter reduction in these wastewaters, they are selected for the present kinetic study.

**Figure 3.** Evolution of ozonation yield (*R*) and ozone reaction rate (*N*) in experiment OAD-5.

For that evaluation, the most adequate flow model for the gas–liquid mass reacting, as well as the kinetics of the reaction, must be taken into account. Because of the long reaction times, it can be supposed that the liquid phase fits well to the mixing flow reactor model. In regard to the kinetic reaction, a generalized kinetic model can be proposed, based on a simplified reaction scheme. This model considers that the reaction between ozone and organic matter can be represented by an irreversible reaction as follows:



In a first approximation, according to the film theory,¹⁹ this heterogeneous reaction occurs in the very slow kinetic regime, with almost no resistance to the mass transfer by the liquid phase and the process being controlled exclusively by the chemical reaction. On the other hand, as several authors have noted,^{20,21} the ozone reactions with dissolved organic substances usually follow a global second-order kinetics, which is first order with respect to each reactant. Therefore, the reaction rate equation for the organic substrate removal can be expressed in the following form:

$$-\frac{dS}{dt} = k_{O_3} S C_A^* \quad (7)$$

where C_A^* is the ozone equilibrium concentration in the liquid phase, which is determined from the inlet and outlet ozone partial pressures in the gas streams (p_{O_3i} and p_{O_3o} , respectively) by means of Henry's law:²²

$$H(\text{kPa L}^{-1} \text{mol}^{-1}) =$$

$$2.20 \times 10^7 \exp\left(\frac{-2117.7}{T}\right) [\text{OH}^-]^{0.012} \quad (8)$$

$$p_{O_3} = H C_A^* \quad (9)$$

As the outlet ozone partial pressure p_{O_3o} varies with reaction time during an experiment, the integration of eq 7 between $\tau = 0$ and $\tau = t$ leads to

$$\ln \frac{S_i}{S} = k_{O_3} \int_0^t C_A^* d\tau \quad (10)$$

According to this expression, a plot of $\ln(S_i/S)$ versus the integral term must lead to a straight line whose slope is k_{O_3} , which is the second-order rate constant,

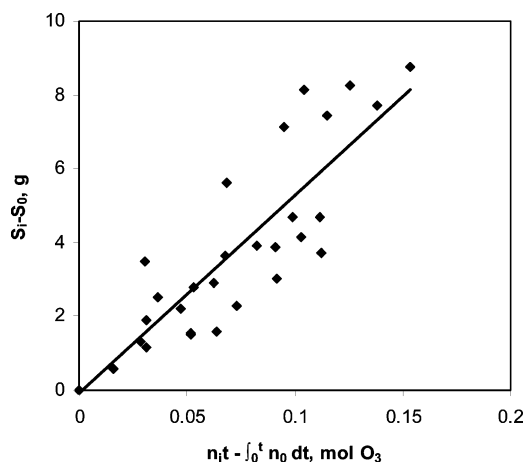


Figure 4. Determination of stoichiometric ratio b for chemical oxygen demand (COD).

with respect to the substrate removal. For this purpose, it is necessary to determine the integral term beforehand, by fitting experimental data (C_A^* , τ) to a polynomial expression and integrating the obtained function between the initial time and each reaction time.

This procedure was applied to the experimental results obtained with COD and aromatic compounds. After least-squares regression analysis, the constants k_{O_3} were determined for both parameters. As could be expected for experiments performed at the same temperature, similar values are obtained for COD and A. In addition, the apparent kinetic rate constants increased when the temperature increased.

Now, the apparent kinetic rate constant can be determined, relative to chemical oxygen demand (k_{COD}) and aromatic compounds (k_A). For this purpose, it is necessary to determine the stoichiometric ratio b , which is defined as the number of grams of substrate degraded by the number of moles of ozone consumed. In this complex reaction system, this ratio has a role that is similar to the stoichiometric coefficient in a simple chemical reaction, and it can be expressed in the following form:

$$b = \frac{(S_i - S_0)V}{n_i t - \int_0^t n_0 dt} \quad (11)$$

Again, because the outlet ozone partial pressure p_{O_3} varies with reaction time t , the total amount of ozone leaving the reactor is determined by integration of outlet ozone flow rate n_0 with reaction time t . The application of eq 11 for all experimental data yields a value of 55.5 ± 6.1 and 5.3 ± 0.3 g substrate degraded/mol O_3 reacted for COD and A, respectively. Because of the limited accuracy of the experimental data, one should treat the suggested method of studying the kinetics of the ozonation process with caution. Figure 4 shows the determination of stoichiometric ratio b for COD. Finally, by considering the relationship between both constants:

$$k_{COD,A} = \frac{k_{O_3}}{b} \quad (12)$$

Table 6 shows the values of k_{COD} and k_A for all experiments. It can be observed that the apparent kinetic rate constants increase with temperature and do not vary greatly, relative to the ozone partial pressure p_{O_3} .

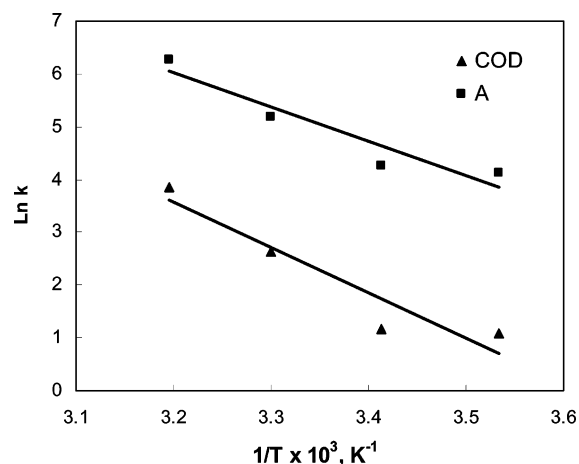


Figure 5. Arrhenius's plot for the apparent kinetic rate constant of ozone–COD and ozone–aromatic compounds.

Table 6. Values of Apparent Kinetic Rate Constants and the Hatta's Number in Ozonation Experiments

experiment	temp, T (°C)	k_{COD} (L g COD ⁻¹ h ⁻¹)	k_A (h ⁻¹ abs ⁻¹)	Hatta's Number	
				Ha_{COD}	Ha_A
OAD-1	10	3.0	62	0.018	0.022
OAD-2	20	3.2	71	0.028	0.029
OAD-3	30	13.9	180	0.034	0.031
OAD-4	40	47.6	531	0.047	0.036
OAD-5	30	24.2	114	0.035	0.032
OAD-6	30	11.3	153	0.035	0.032

To verify the slow kinetic regime for ozone absorption that was supposed previously, the Hatta's number (Ha) must be calculated. For a second-order reaction (first order with respect to ozone and COD and A), this number is defined as follows:¹⁹

$$Ha = \sqrt{\frac{k_{COD,A} C_{COD,A} D}{k_L^2}} \quad (13)$$

where D is the ozone diffusivity in water. The value of this parameter, as a function of temperature, were taken from the literature,²³

$$D(\text{m}^2/\text{s}) = 1.10 \times 10^{-6} \exp\left(\frac{-1896}{T}\right) \quad (14)$$

and k_L is the individual liquid-phase mass-transfer coefficient. Its values were taken from the literature:²⁴ $k_L \times 10^4 = 2.04, 2.47, 3.58$, and 4.64 m/s at temperatures of 10, 20, 30, and 40 °C, respectively. The Ha values were calculated under the initial experimental conditions of each experiment. Table 6 shows these Ha values for the reaction rate of both COD and aromaticity. It can be seen that the Ha values are always <0.05 , which is the upper limit for a reaction to develop in the slow kinetics regime.

The apparent kinetic rate constants can be related to the temperature T by an Arrhenius expression. Figure 5 shows that these kinetic rate constants fit well to give the following equations:

$$k_{COD}(\text{L g}^{-1} \text{h}^{-1}) = 4.1 \times 10^{13} \exp\left(\frac{-8678}{T}\right) \quad (15)$$

$$k_A(\text{abs}^{-1} \text{h}^{-1}) = 5.4 \times 10^{11} \exp\left(\frac{-6567}{T}\right) \quad (16)$$

Conclusions

The results show that olive mill wastewaters (OMWs) can be effectively treated by an anaerobic digestion,

which resulted in a gas production rate that averaged ~ 295 L CH₄/kg COD and COD removal efficiencies of $\sim 81\%$. The application of the Monod model provides the value of the kinetic constant of the substrate degradation rate, $(7.8 \pm 0.6) \times 10^{-2} \text{ d}^{-1}$.

The post-treatment of OMW with ozone considerably reduces the total polyphenolic compounds and, in a lesser grade, COD and aromatic compounds. An approximate kinetic study for design purposes was developed: assuming the slow kinetic regime for ozone absorption, the apparent kinetic rate constants for COD and aromatic compounds are evaluated and correlated as a function of temperature.

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Nomenclature

A = total aromatic compounds [abs]
 abs = absorbance at 254 nm
 b = stoichiometric ratio [g substrate per mol ozone]
 BOD₅ = biochemical oxygen demand [g/L]
 CAD = continuous anaerobic digestion
 C_A* = equilibrium ozone concentration in liquid phase [mol/L]
 COD = chemical oxygen demand [g/L]
 D = diffusivity of ozone in water [m²/s]
 H = Henry's law constant [kPa L mol⁻¹]
 Ha = Hatta's number
 HRT = hydraulic retention time [d]
 k_A = rate constant for A [h⁻¹ abs⁻¹]
 k_{COD} = rate constant for COD [L g COD⁻¹ h⁻¹]
 k_L = individual mass transfer coefficient [m/s]
 N = ozone reaction rate [mol L⁻¹ s⁻¹]
 OAD = ozonation anaerobic digestion
 OMW = olive mill wastewater
 p_{O₃} = ozone partial pressure [kPa]
 q = specific substrate biodegradation rate [g COD L⁻¹ d⁻¹]
 q_{max} = maximum specific substrate biodegradation rate [g COD L⁻¹ d⁻¹]
 R = ozonation yield [%]
 S = substrate concentration [g COD/L]
 τ = hydraulic retention time, HRT [d]
 TP = total polyphenolic compounds [g caffeic acid/L]
 TS = total solids [g/L]
 TSS = total suspended solids [g/L]
 V_{CH₄} = volume of methane produced [L/d]
 VFA = volatile fatty acids [g acetic acid/L]
 VSS = volatile suspended solids [g/L]
 Y_{PS} = methane production yield coefficient [L/kg COD]

Superscripts and Subscripts

i = inlet
 o = outlet

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