



Kinetics of the ozonation and aerobic biodegradation of wine vinasses in discontinuous and continuous processes

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Received 14 November 2002; received in revised form 14 May 2003; accepted 31 May 2003

Abstract

The oxidation of the organic substrate present in wastewaters generated in wine distilleries (“wine vinasses”) is studied by both an ozonation process and by an aerobic activated sludge system. The ozonation process is conducted in a subsequent first discontinuous and a second continuous periods. Values are reported of the organic matter removal, measured as chemical oxygen demand (COD) (5–25.2%) and as total aromatic compounds content (16.8–51.4%). The influences of the inlet ozone partial pressure, the hydraulic retention time in the reactor and the presence of UV radiation and H₂O₂ in addition to ozone are established. Approximate kinetic studies are conducted for both periods which lead to the evaluation of the apparent rate constants for the substrate decomposition 216 l/(mol O₃ h) and 232 l/(g COD h), respectively. In the aerobic degradation by the activated sludge system, the evolution of the organic substrate and biomass are followed during both the discontinuous and continuous stages of the whole process, and COD removals from 31 to 85% are obtained for a hydraulic retention time between 24 and 72 h. For the first stage, a kinetic study is performed by using the Contois model, which applied to the experimental data provides the specific kinetic parameters: $q_{\max} = 0.190$ g COD/(g volatile suspended solids (VSS) h) and $K_1 = 6.48$ g COD/g VSS. For the continuous period, the kinetic study carried out provides the specific rate constant for the substrate decomposition, $q = 0.027$ g COD/(g VSS h).

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Keywords: Wine distillery effluents; Ozonation; Aerobic degradation; Activated sludge system; Kinetics constants

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Nomenclature

A	aromatic content, measured as absorbance at 254 nm
BOD_5	biological oxygen demand (g/l)
C_A^*	ozone equilibrium concentration (mol/l)
COD	chemical oxygen demand (g/l)
H	Henry's law constant (kPa l/mol)
k_A	second order rate constant for the organic matter degradation (l/mol O_3 h)
$k_{A'}$	pseudo first order rate constant for the organic matter degradation (h^{-1})
k_{O_3}	second order rate constant for the ozone disappearance (l/g COD h)
K_1	saturation constant of Contois model (g COD/g VSS)
n	ozone concentration in the gas stream (mol O_3 /l)
$-N_{O_3}$	ozone reaction rate (mol O_3 /l s)
p_{O_3}	ozone partial pressure (kPa)
q	specific substrate decomposition rate (g COD/g VSS h)
q_{max}	maximum substrate specific decomposition rate (g COD/g VSS h)
Q_G	gas phase volumetric flow rate (l/h)
Q_L	liquid phase volumetric flow rate (l/h)
$-r_s$	degradation rate of substrate in an aerobic process (g COD/h)
R	ozonation yield (%)
t	reaction time in a discontinuous period (h)
T	temperature (K or °C)
V	reactor volume (l)
X_A	aromatic content removal (%)
X_{COD}	COD removal (%)
$X_{V,A}$	biomass concentration (g VSS/l)

Greek letter

τ	hydraulic retention time in a continuous period (h)
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Subscripts

i	inlet stream in the continuous period
o	outlet stream in the continuous period
0	initial value in the discontinuous period
t	value any time in the discontinuous period

1. Introduction

Wine distilleries produce great amounts of wastewaters, called "vinasses" which composition varies widely depending on the raw material distilled (wine, lies, pressed grapes, etc.). These wastewaters have an acidic character, with a pH in the range 3.5–5, and a high organic substrate content with chemical oxygen demand (COD) values in the range 10–40 g/l [1], due to the presence of organic compounds like phenols and polyphenols [2]. These effluents

are commonly disposed of into evaporation ponds or eliminated through public sewerages. Because of the generation of bad smells and the possibility of the pollution of surface and ground waters, these methods cause a large-scale environmental problem to which little attention has been paid until recently.

Due to these potential hazards, many countries have recently limited this discharge and have tried to develop several technologies, such as chemical or biological treatments, for reducing the pollutant character by the degradation of the main toxic organic substances and their transformation into more biodegradable residues.

In general, the chemical treatments use several reactives with the main objective of oxidizing refractory organic pollutants. Among them, one of the mostly used oxidants is ozone [3], since it presents desirable properties for water treatments [4], powerful oxidant, soluble in water, readily available and without by-products that need to be removed (unless ion bromide is present, since ozone reacts with this ion and produces bromo-organic derivatives and bromate). Moreover, the additional presence of UV radiation and hydrogen peroxide enhances the efficiency of the single ozonation, due to the generation of free radicals, like hydroxyl radicals, which are very reactive and oxidizing [5].

On the other hand, biological treatments have also been recognized as effective methods for the degradation of wastewaters with high organic pollutant load, as effluents from wine distilleries. Aerobic systems, such as aerated lagoons or activated sludge units, are hence frequently used to remove the contamination generated by wastewaters from agro-industrial plants [6], in spite of the generation of large quantities of waste sludge that must be disposed off. A less costly alternative from an energy point of view is the anaerobic digestion, which produces a biogas containing methane that could eventually cover a part of the energy needs in the plant [7]. However, some disadvantages are also found in the case of winery wastes, like the presence of the mentioned phenolic compounds which are toxic to the methanogenic bacteria and inhibit the efficiency of this anaerobic process to some extent [8].

Since little research has been reported in the specific case of the purification of wine vinasses by these technologies, the present research deals with the degradation of these residues by both chemical and biological procedures. Firstly, an ozonation treatment was conducted with two separate phases in each experiment: a first discontinuous period followed by a second continuous period. Secondly, a biological treatment was carried out by means of an activated sludge system, and again, two different phases were developed in each experiment: a discontinuous step followed by a continuous step. The main aims of these studies were to provide experimental data on the removal obtained and to evaluate the specific kinetic parameters of both chemical and biological treatments. These kinetic parameters are the apparent rate constants in the ozonation reactions and the specific rate constant for the substrate decomposition in the aerobic process, which are useful for the design of industrial wastewaters treatment plants.

2. Material and methods

The raw wastewaters used for the experiments were “vinasses” collected from the industrial distillery “Vinícolas del Oeste”, located in Villafranca de los Barros, Extremadura Community, south-west of Spain. These effluents were analysed according to the

procedures described in the Standard Methods [9], and the values obtained for the main chemical characteristics and compositions were pH = 3.7–4.1; COD = 24.5 g/l; total solids concentration = 21.51 g/l; total suspended solid in the mixed liquor MLSS = 12.51 g/l; alkalinity = 0.45 g CaCO₃/l; volatile acid content = 1.33 g acetic acid/l, and BOD₅ = 11.15 g/l. Prior to any experiment, the vinasses were centrifuged and filtered to remove suspended solids.

The chemical oxidation experiments were conducted in a 1000 cm³ glass column with outlets for sampling and venting. During each experiment two different periods were conducted. Firstly, a discontinuous period, where the process was carried out in a batch mode: the wastewater was initially introduced into the reactor and the gas stream was continuously fed to the reacting mass. This period lasted the time equivalent to the hydraulic retention time selected for the following continuous period. Once the discontinuous period was finished, the second period started and the liquid and gas streams were fed to the reactor continuously, the former at a volumetric flow rate to obtain the selected hydraulic retention time selected for the experiment.

The gas phase consisted of a mixture of ozone and oxygen, and it was fed to the reactor through a porous distributor located at the bottom of the column. The ozone was generated in a laboratory ozone generator (Sander, mod. 301.19) from oxygen taken from a commercial cylinder. The ozonator was able to produce a maximum flow rate of 30 g O₃/h. In the experiments 50 l/h of O₂ at ambient conditions were fed to the unit. With this flow rate, it provided a maximum partial pressure of 5.7 kPa of ozone in the ozone-oxygen exit mixture. Throughout both periods, several liquid samples were taken periodically to analyze the substrate concentration, measured as COD and as aromatic content (absorbance at 254 nm). The inlet and outlet ozone partial pressure in the gas streams were also regularly measured iodometrically by bubbling the gas in a potassium iodide solution. The dissolved ozone in the liquid phase was analyzed by the indigo method as reported by Bader and Hoigne [10].

In addition to ozone, UV radiation was also used in one experiment. In this case, the reactor was equipped with a radiation source, a Hanau TQ718 (700 W) high pressure mercury vapor lamp which, according to the manufacturer, emitted a polychromatic radiation extended from the short UV zone of approximately 185 nm to far into the visible light region. This radiation source was located axially inside the reactor, and was protected with a quartz sleeve which housed the lamp.

The aerobic degradation process was conducted by means of an activated sludge system, comprising an aeration reactor and a clarifier. The temperature was fixed at 25 °C by means of a thermostatic unit. As wine vinasses did not contain microorganisms required for the aerobic degradation, an activated sludge taken from a municipal wastewaters treatment plant was acclimatized to this substrate.

Once this acclimatization period was finished, several aerobic degradation experiments were carried out. Firstly, the discontinuous period of each experiment took place: during that period the reactor tank was initially loaded with the wastewater and it was aerated by introducing an air stream and mechanically stirring the gas–liquid mixture. Similarly to the chemical experiments, this period lasted the same time than that selected as liquid hydraulic retention time for the following continuous period. Thereafter, the continuous period was performed by pumping the wastewater continuously from a reservoir into the aeration reactor at a flow rate required to reach the mentioned hydraulic retention time. The

sludge contained in the outlet effluent from the aeration tank was separated from the treated wastewater in the clarifier and returned to the aeration tank. The substrate concentrations in the samples taken during the discontinuous period as well as in the final effluent during the continuous period were measured as COD. The biomass concentration in the sludge inside the reactor was also determined periodically and measured as volatile suspended solids (VSS).

3. Results and discussion

3.1. Oxidation of wine vinasses by ozone

Chemical oxidation experiments of the wine vinasses by ozone and by the combination of ozone plus UV radiation and hydrogen peroxide (with an initial concentration of 0.168 M) were conducted at 25 °C in the reactor previously described, by varying the hydraulic retention time τ in the reactor and the inlet ozone partial pressure in the gas mixture pO_{3i} according to the values shown in Table 1. The initial organic substrate and the pH were characteristic of these wastes, i.e. around 24.5 g COD/l and around 4, respectively. Due to this pH, only a direct ozone attack can be expected for the degradation of the organic matter in Experiments Q-1 to Q-4. This ozone attack will be reinforced in Experiment Q-5 with the contribution of a radical attack, because of the hydroxyl radicals generated in the combination of ozone plus UV radiation and hydrogen peroxide.

Table 2 depicts the results obtained in Experiments Q-4 of Table 1, taken as example, which allows to observe the evolution followed by the pollutant content in the wastewater by means of the two analyzed parameters in the samples taken from the reactor at regular intervals: the chemical oxygen demand COD and the total aromatic content A. They were selected because both parameters are representative of the global organic matter present in a wastewater. Similar evolutions of COD and A were obtained in the remaining experiments of this group.

It can be seen in Table 2 that the organic substrate represented by the COD, decreased continuously with reaction time during the discontinuous period of the process, as could be expected; and later, during the continuous period, it remained almost constant. Table 1 also depicts the outlet substrate concentration COD_o in this group of experiments (values measured at the end of the continuous period) and the total removal obtained (which is defined

Table 1
Operating conditions and results obtained in the ozonation experiments

Experiment	τ (h)	pO_{3i} (kPa)	COD_o (g/l)	X_{COD} (%)	A_o	X_A (%)
Q-1	3	2.70	22.80	5.0	0.588	16.8
Q-2	3	5.68	23.43	7.5	0.478	31.2
Q-3	6	5.46	22.36	9.1	0.415	40.3
Q-4	9	5.19	18.23	25.2	0.337	51.4
Q-5 ^a	6	5.55	3.80	58.4	0.050	76.9

^a UV + H₂O₂; [H₂O₂]_i = 0.168 M.

Table 2

Illustration of Experiment Q-4 $\text{COD}_i = 24.36 \text{ g/l}$, $p\text{O}_{3i} = 5.19 \text{ g/l}$, $\tau = 9 \text{ h}$, $\text{pH}_i = 3.75$

t (min)	COD (g/l)	A	X_{COD} (%)	X_A (%)
Discontinuous period				
0	24.36	0.693	0	0
60	24.26	0.661	0.4	4.6
120	24.10	0.554	1.1	20.1
200	23.60	0.488	3.1	29.6
240	23.33	0.442	4.2	36.2
300	23.30	0.436	4.4	37.1
360	22.03	0.392	9.6	43.4
495	21.43	0.363	12.0	47.6
540	20.33	0.338	16.6	51.2
Continuous period				
600	19.30	0.344	20.8	50.4
690	18.86	0.343	22.6	50.5
780	18.33	0.344	24.8	50.4
840	18.23	0.342	25.2	50.6
900	17.80	0.335	26.9	51.7
960	18.23	0.337	25.2	51.4

as $X_{\text{COD}} = 1 - \text{COD}_o/\text{COD}_i$). The results of Table 1 indicate that this removal increased when the inlet ozone partial pressure was increased (comparison between Experiments Q-1 and Q-2), as well as when the hydraulic retention time in the reactor also increased (comparison among Experiments Q-2, Q-3 and Q-4). And more pronounced, X_{COD} was found to increase in Experiment Q-5 ($X_{\text{COD}} = 58.4\%$), which was performed with the combination $\text{O}_3\text{-UV-H}_2\text{O}_2$.

In a similar way, the evolution of the total aromatic compounds content is also presented in Table 2, as it is seen, there is an important decrease during the first times of reaction (from 0.693 to 0.554 in 120 min); and a more slight decrease during the remaining time of the discontinuous period of the process. Later, during the continuous period, the A values remain almost constant, as could also be expected.

Table 1 also gives the aromatic contents A_o in the outlet effluents, also measured at the end of the continuous period of the experiments, as well as the aromatic compound removal, which is defined as $X_A = 1 - A_o/A_i$. These values follow the same trend than that observed for the COD, the removal increased from 16.8 to 31.2% with the increase in the ozone partial pressure, also increased, from 31.2 to 51.4%, with the increase in the hydraulic retention time of the wastewater in the reactor (from 3 to 9 h); and a higher increment in Experiment Q-5 ($X_A = 76.9\%$) with the simultaneous presence of UV radiation and H_2O_2 in addition to ozone.

Another parameter measured in the ozonation experiments was the ozone partial pressure in the inlet and outlet gas streams, $p\text{O}_{3i}$ and $p\text{O}_{3o}$, respectively. While the former was always constant throughout each experiment, the latter followed a quite similar evolution in every experiment, which is illustrated in Fig. 1 for Experiment Q-4. The outlet ozone is very limited at the beginning of the reaction, indicating that ozone is mostly consumed in the reactions with the organic matter present. Then, its partial pressure increases rapidly and

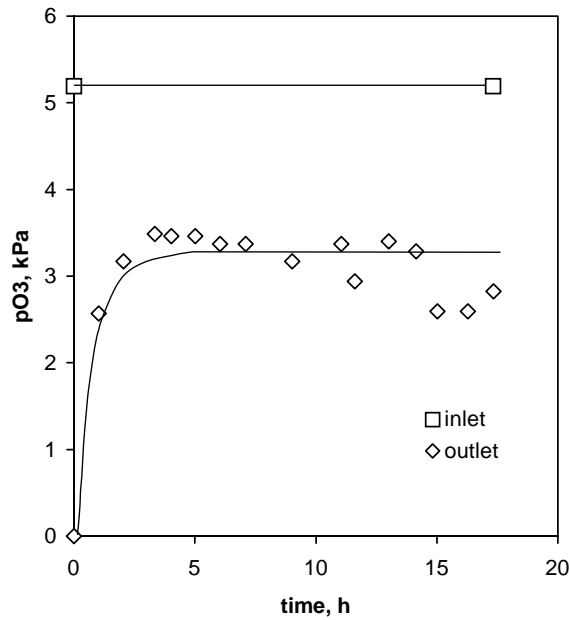


Fig. 1. Evolution of the inlet and outlet ozone partial pressure in the ozonation process. Experiment Q-4.

reaches almost a stationary value, that is also maintained during the continuous period. The difference between both values (inlet and outlet) defines the ozone absorbed in the liquid phase, which is the ozone reacted with the organic matter, since there is no dissolved free ozone in the solution.

The ratio between the absorbed ozone and subsequently reacted in the reacting mass and the ozone introduced into the reactor is the ozonation yield R , a parameter which provides information about the extent of the ozonation process. It can be expressed by

$$R = \frac{pO_{3i} - pO_{3o}}{pO_{3i}} \times 100 \quad (1)$$

Table 3 provides the R values for this group of experiments, where the value taken for pO_{3o} was that corresponding to the end of the continuous period. As it is seen, similar values

Table 3
Ozonation yields and ozone reaction rates in the ozonation experiments

Experiments	pO_{3i} (kPa)	pO_{3o} (kPa)	R (%)	$(-N_{O_3}) \times 10^6$ (mol/l s)
Q-1	2.70	1.30	52	265
Q-2	5.68	2.81	50	526
Q-3	5.46	3.10	43	451
Q-4	5.19	2.85	45	442
Q-5	5.55	1.20	78	824

are obtained (in the range 43–52%) for the single ozonation process (Experiments Q-1 to Q-4). However, Experiment Q-5 (ozonation in the presence of UV radiation and hydrogen peroxide) presented a higher value of 78% which indicates that the ozone absorbed and consumed in the reaction is much higher than the ozone introduced, as could be expected due to the generation of hydroxyl radicals in this system. This behavior can be explained by the fact that ozone, which absorbs in the UV region, is also photolysed even in the gas phase [11].

Also related with this ozonation yield is the ozone reaction rate ($-N_{O_3}$), which provides information about the rate of the global reaction between ozone and the complex matrix of organic compounds which are present in the wastewater. It is defined as

$$-N_{O_3} = \frac{(n_i - n_o) Q_G}{V} \quad (2)$$

where n_i and n_o are the ozone concentrations in the inlet and outlet gas streams, respectively, Q_G is the gas flow rate and V is the reactor volume. Table 3 also compiles the ($-N_{O_3}$) values for this group of experiments, as it is observed, a lower value of 265×10^{-6} mol/l s is obtained in Experiment Q-1 with the lower inlet ozone partial pressure used ($p_{O_{3i}} = 2.7$ kPa). Values, in the range 442 – 526×10^{-6} mol/l s, are obtained with the higher inlet ozone partial pressure (Experiments Q-2, Q-3 and Q-4), which indicate that this rate is almost independent of the hydraulic retention time in the reactor. A much higher value of 824×10^{-6} mol/l s is obtained for Experiment Q-5, because of the additional presence of UV radiation and H_2O_2 .

The design of reactors for water treatments plants where heterogeneous reactions take place, like those occurring in this process between the ozone–oxygen mixture and the organic matter contained in the wastewater, requires the evaluation of the rate constants for these reactions. However, in the present situation, a rigorous kinetic study cannot be performed in detail, since the global reduction of the dissolved organic matter contained in the wastewater by chemical oxidants is a complex process with many individual reactions which take place simultaneously and cannot be defined individually.

From a kinetic point of view, an approximate kinetic study can be conducted by using some of the global parameters that better represent this organic content, like the previously evaluated A or COD. According to these considerations, it was decided in the present research to firstly conduct a kinetic study for the discontinuous period by using the aromatic content A as reference parameter for the organic substrate content; and thereafter, a similar kinetic study for the continuous period, in that case with the COD as reference parameter for the organic matter content. In both studies, the general objective is to provide values for the apparent rate constants which will be useful for the design of reactors.

Regarding to the discontinuous period, and based on the film theory [12], it can be assumed for this type of gas–liquid systems that the reactions occur in the slow kinetic regime, that is, the resistance to the mass transfer in the liquid phase is small, and the process is mostly controlled by the global chemical reaction which takes place in the bulk of the liquid and follows a pseudo first order kinetics with respect to the organic matter concentration, represented by the aromatic content A . Therefore, the rate equation for this organic matter decomposition can be written in the simplified form

$$-\frac{dA}{dt} = k'_A A \quad (3)$$

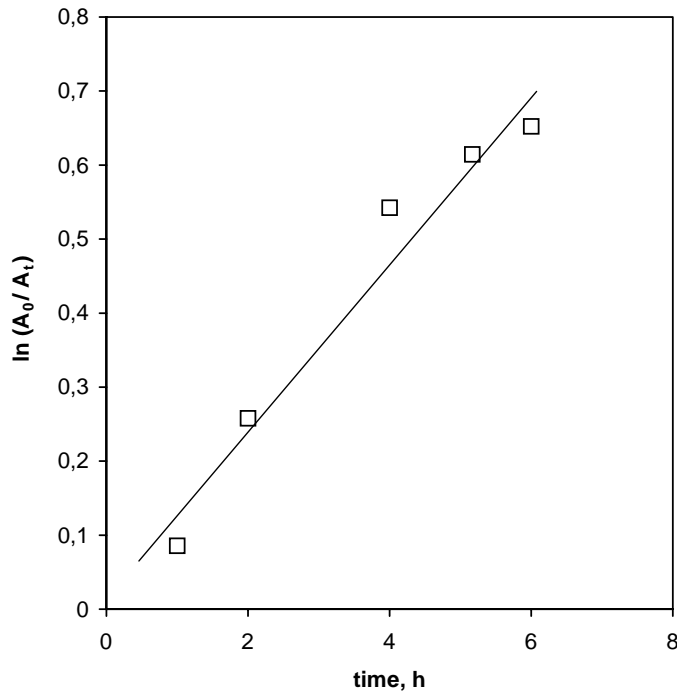


Fig. 2. Evaluation of the apparent rate constant k'_A for the discontinuous period of the ozonation process. Experiment Q-3.

Eq. (3) can be integrated between the initial time ($t = 0$) and any time ($t = t$) in this discontinuous period, leading to

$$\ln \frac{A_0}{A_t} = k'_A t \quad (4)$$

According to this Eq. (4), a plot of $\ln A_0/A_t$ versus t must be linear for every experiment, with slope k'_A . Fig. 2 shows, as an example, the plot corresponding to Experiment Q-3, where it can be seen that experimental points lie satisfactorily around a straight line. Similar results were obtained for the remaining experiments, and after regression analysis, the k'_A values listed in Table 4 were deduced.

Table 4
Evaluation of the apparent kinetic constants k_A and k_{O_3} for the ozonation process

Experiments	k'_A (h^{-1})	$C_A^* \times 10^4$ (mol/l)	k_A (l/mol O_3 h)	k_{O_3} (l/g COD h)
Q-1	0.168	2.37	234	249
Q-2	0.116	4.98	233	248
Q-3	0.115	4.79	240	199
Q-4	0.071	4.55	156	254
Q-5	0.114	4.87	709	3132

These pseudo rate constants k'_A comprise the apparent second order rate constants k_A , according to the expression

$$k'_A = k_A C_A^* \quad (5)$$

where C_A^* is the ozone equilibrium concentration, which can be evaluated for each experiment by using the Henry's law

$$pO_3 = HC_A^* \quad (6)$$

The application of Eq. (6) to the inlet ozone partial pressure of every experiment and to the values of the Henry's law constants reported by Sotelo et al. [13] allows to determine the corresponding value of C_A^* , which are also shown in Table 4. The use of Eq. (5) and the k'_A values previously determined, provides the rate constants k_A which are also included in Table 4. Similar values are obtained for Experiments Q-1 to Q-4 as could be expected, and a mean value of 216 l/(mol O₃ h) is proposed for the apparent kinetic rate constant during the discontinuous period of the ozonation process. The additional presence of H₂O₂ and UV radiation promotes an important increase in this apparent rate constant up to 709 l/(mol O₃ h), due to the presence of the hydroxyl radicals generated in this combined process.

Similarly, the kinetic study for the continuous period of the process implies the evaluation of the apparent rate constant for the substrate decomposition, which in this case is represented by the COD as was previously mentioned. This study must account for (i) the mass balance in the reactor; (ii) the most adequate flow model for both, the liquid and gas phases; and (iii) the kinetics of the reaction.

Regarding to the mass balance, it is assumed that the ozone lost by the gas phase is entirely absorbed by the liquid phase, and once there, reacts with the organic matter present. Therefore, this mass balance can be expressed in the form

$$\frac{Q_G}{RT} dpO_3 = (-N_{O_3}) dV \quad (7)$$

where $(-N_{O_3})$ is the rate of disappearance of ozone in the gas phase, equivalent to the chemical reaction rate in the liquid phase (mol O₃/l h).

On the other hand, with respect to the flow models for both phases, and by considering the bubble column used as ozonation reactor in the present study, it can be proposed for the liquid phase that the mixed flow reactor model fits well the experimental conditions, due to the adequate mixing of the reactor. For the gas phase, the plug flow model seems to be the most adequate for the present study, due to the ascent of the gas bubbles from the porous plate at the bottom of the column to the free liquid surface at the top of the column. For this plug flow model for the gas phase, the following boundary conditions can be established

$$V = 0, \quad pO_3 = pO_{3i} \quad (8)$$

$$V = V, \quad pO_3 = pO_{3o} \quad (9)$$

The application of both conditions to the mass balance given by Eq. (7) leads to the expression which provides the total volume of the plug reactor

$$V = \frac{Q_G}{RT} \int_{pO_{3o}}^{pO_{3i}} \frac{dpO_3}{(-N_{O_3})} \quad (10)$$

In order to evaluate the term $(-N_{O_3})$, and therefore, to solve this Eq. (10), the kinetics of the chemical reaction must be finally taken into account, which can be tentatively represented by the simple expression



According to the film theory [12], it can be assumed that this reaction occurs in the slow kinetic regime, and the process is mostly controlled by the chemical reaction. According to several authors [14,15], this kind of reactions between ozone and organic compounds are of global second order.

With these considerations, the following rate equation can be proposed for the rate of reaction of ozone

$$(-N_{O_3}) = k_{O_3} COD C_A^* \quad (12)$$

where k_{O_3} is the apparent ozone disappearance rate constant. The introduction of Eqs. (6) and (12) into Eq. (10) leads to

$$V = \frac{Q_G}{RT} \frac{H}{k_{O_3} COD_o} \int_{pO_{3o}}^{pO_{3i}} \frac{dpO_3}{pO_3} \quad (13)$$

which integrated provides the final expression for the evaluation of the apparent rate constant k_{O_3}

$$k_{O_3} = \frac{Q_G}{RT} \frac{H}{V COD_o} \ln \left(\frac{pO_{3i}}{pO_{3o}} \right) \quad (14)$$

The application of Eq. (12) to the experimental results obtained (that is, the outlet COD_o showed in Table 1 and the pO_{3i} and pO_{3o} values depicted in Table 3) allows to determine the rate constant k_{O_3} for each experiment. The values deduced are also shown in Table 4, similar values in Experiments Q-1 to Q-4 are observed, as could be expected because the rate constant must not be affected by the inlet ozone partial pressure and the hydraulic retention time in the reactor. Therefore, a mean value of 2321/(g COD h) is proposed for the single ozonation of these wastewaters at 25 °C. Experiment Q-5 presents an important increase in the rate constant, as could be expected too, due to the important generation of hydroxyl radicals which are promoted by the simultaneous presence of O_3 , H_2O_2 and UV radiation. As was previously commented, these radicals are very oxidizing and reactive, and therefore, the rate constant of the oxidation process is clearly enhanced.

3.2. Degradation of wine vinasses by aerobic microorganisms in an activated sludge system

Aerobic degradation experiments of the wine vinasses were performed in the activated sludge system described in Section 3, by modifying the hydraulic retention time of the liquid phase in the reactor (between 24 and 72 h), with the temperature remaining constant at 25 °C. Table 5 compiles the initial operating conditions for these experiments: hydraulic retention time τ , initial concentrations of organic matter present COD_i and initial biomass in the reactor $X_{V,Ai}$ (measured as volatile suspended solids VSS).

Table 5

Experiments performed in the activated sludge system and values obtained for the specific decomposition rate of substrate

Experiments	τ (h)	COD _i (g/l)	$X_{v,Ai}$ (g VSS/l)	COD _o (g/l)	$X_{v,Ao}$ (g VSS/l)	X_{COD} (%)	q (g COD/g VSS h)
B-1	24	19.56	0.90	13.43	3.89	31.3	0.028
B-2	48	19.56	0.90	10.20	6.90	47.9	0.027
B-3	60	16.03	0.91	3.30	7.83	79.4	0.027
B-4	72	19.56	0.90	2.96	9.28	84.8	0.024

Once each experiment was started-up, the biomass in the reactor and the outlet organic substrate were measured at regular intervals during the first discontinuous and the second continuous periods. Regarding the biomass evolution, an increase in the cell number was initially observed which corresponds to the exponential growth phase of the well-known growth-cycle phases for batch cultivations [16,17]. After the maximum value is reached, a decrease in this biomass is observed. Fig. 3 shows the plot corresponding to this biomass evolution in two experiments taken as example (Experiments B-3 and B-4), while Table 5 depicts the final biomass values, which are measured at the end of the continuous period of every experiment conducted, as can be seen, an increase in the hydraulic retention time leads to an increase in the maximum value as well as in this final value $X_{v,Ao}$.

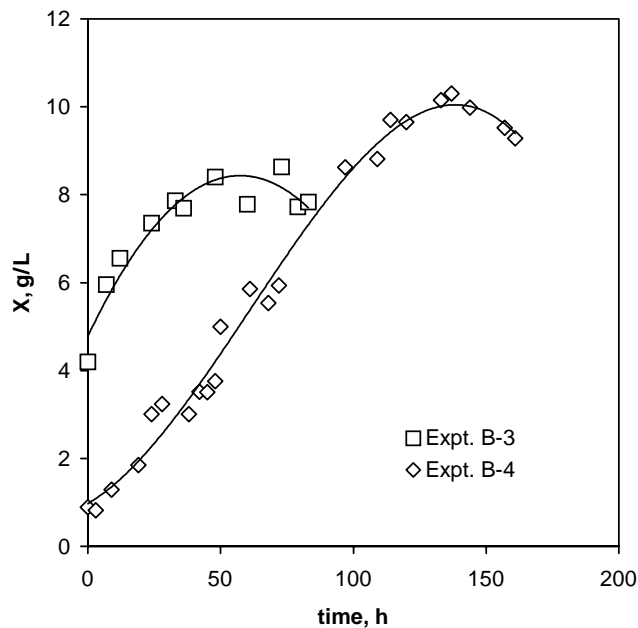


Fig. 3. Biomass evolution in the aerobic process by an activated sludge system. Experiments B-3 and B-4.

The organic matter concentration decreased in relation to the initial COD_i during the discontinuous period, as a consequence of the bacterial growth and the increase in the degrading capacity of the medium. Later, in the continuous period, the outlet organic substrate concentration remained almost constant, as could be expected. Table 5 also shows these final values COD_o at the end of the continuous period of every experiment, as well as the global organic matter reduction obtained X_{COD} . Again, the direct influence of the hydraulic retention time in the reactor on the removal of the organic matter is clearly seen, with values ranging from 31.3 to 84.8% for τ between 24 and 72 h (Experiments B-1 to B-4).

In a similar way as in the chemical oxidation process by ozone of these wastewaters, the first step of the kinetic study was focused on the discontinuous period of the biological process. For this purpose, it must be taken into account that the rate of substrate degraded by the biomass in the aeration tank of this activated sludge system is given by the expression

$$(-r_s) = qX_{V,A}V \quad (15)$$

where q is the specific substrate decomposition rate which characterizes the aerobic degradation process, and is defined in the form

$$q = -\frac{1}{X_{V,A}} \frac{dCOD}{dt} \quad (16)$$

Some empirical relationships are found in the literature [16] which relate this substrate decomposition rate to the substrate concentration. Among them, the Contois model [18] is frequently used because in many cases it provides excellent fits of experimental data. This model establishes for that relation

$$q = q_{max} \frac{COD}{K_1 X_{V,A} + COD} \quad (17)$$

where q_{max} represents the maximum rate of substrate decomposition and K_1 is the Contois saturation constant. In order to obtain the specific kinetic parameters for this model, that is q_{max} and K_1 , Eq. (17) is transformed into

$$\frac{1}{q} = \frac{1}{q_{max}} + \frac{K_1}{q_{max}} \frac{X_{V,A}}{COD} \quad (18)$$

According to this Eq. (18), a plot of $1/q$ versus $X_{V,A}/COD$ must be linear with intercept and slope $1/q_{max}$ and K_1/q_{max} , respectively. Fig. 4 shows the plot obtained in the present case, and after regression analysis, the following values were deduced: intercept = $1/q_{max} = 5.26$ (g VSS h)/g COD, and slope = $K_1/q_{max} = 34.06$ h. It can therefore be proposed that $q_{max} = 0.190$ g COD/(g VSS h) and $K_1 = 6.48$ g COD/g VSS are the final values for the specific parameters of the Contois model in the discontinuous period of the aerobic degradation process of the wine vinasses at 25 °C.

For the kinetic study of the continuous period of this biological process, a mass balance around the aeration tank must be performed. This balance establishes that the difference between the inlet and outlet organic substrate flow rates is equivalent to the flow rate of substrate degraded by the microorganisms in the aeration tank, according to the expression

$$Q_L(COD_i - COD_o) = qX_{V,A}V \quad (19)$$

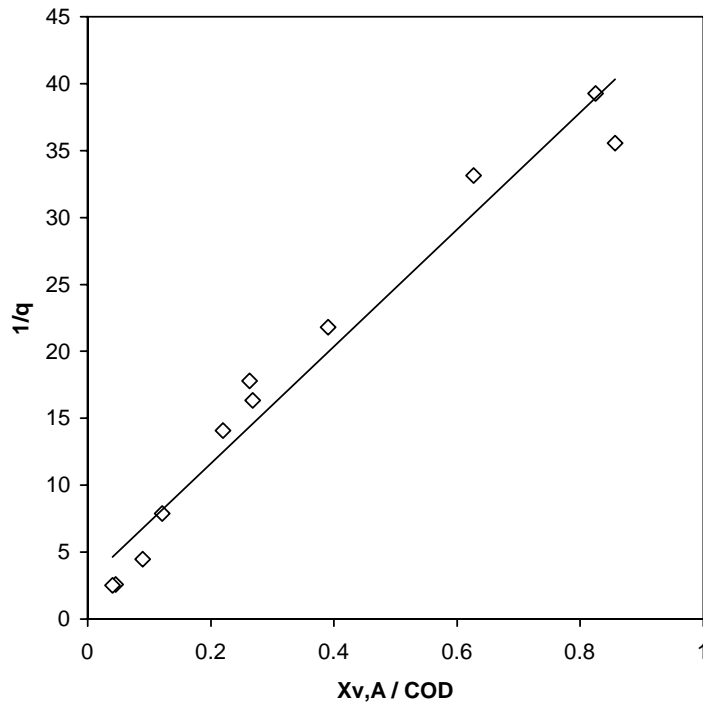


Fig. 4. Evaluation of the kinetic parameters of the Contois model in the aerobic process by an activated sludge system.

where Q_L is the volumetric liquid flow rate introduced in the reactor and V the reactor volume. By considering that the hydraulic retention time is

$$\tau = \frac{V}{Q_L} \quad (20)$$

the introduction of Eq. (20) into Eq. (19) leads to the following expression for the specific decomposition rate of substrate

$$q = \frac{\text{COD}_i - \text{COD}_o}{\tau X_{v,A}} \quad (21)$$

The application of Eq. (21) to the experimental data allows to obtain the values for this decomposition rate, which are also depicted in Table 5 for this group of experiments. As can be seen, they present similar values for q as could be expected, and therefore, an average value of 0.027 g COD/(g VSS h) can be proposed for the aerobic degradation of the wine vinasses by an activated sludge system.

Finally, the degradation of these wastewaters was performed by a combined process of an ozone oxidation followed by an aerobic degradation step in the activated sludge system. The main goal of this combined process was to establish the influence of an ozonation pre-treatment on the subsequent biological treatment.

For this purpose, one ozonation experiment of the wastewaters was carried out, with an inlet ozone partial pressure of 5.5 kPa and a hydraulic retention time of 6 h. The effluent of this stage was then introduced into the activated sludge system unit during 48 h, and the final substrate removal obtained was $X_{\text{COD}} = 39.3\%$. At the same time, an aerobic degradation experiment was conducted with another fraction of wastewater not previously ozonated, and with the same initial operating conditions than the preceding experiment. The final removal obtained was $X_{\text{COD}} = 27.7\%$.

4. Conclusions

From the results obtained in this research, the following conclusions can be drawn.

- Over the range of variables studied, 5–25.2% removal of COD and 16.8–51.4% removal of the total aromatic compounds are attained in the single ozonation process of the wine vinasses, while the consumed ozone yield is around 50% in the single ozonation.
- The kinetic study of the chemical process allows to determine the following average values for the apparent rate constants: 216 l/(mol O₃ h) for the discontinuous period of the process and 232 l/(g COD h) for the continuous period of the process.
- The organic matter removal as well as the kinetic parameters are improved with the simultaneous presence of UV radiation and hydrogen peroxide in addition to ozone, due to the contribution of the hydroxyl radicals generated in these combined processes. Thus, the values obtained in this combined oxidation process are $X_{\text{COD}} = 58.4\%$, $X_{\text{A}} = 76.9\%$, $k_{\text{A}} = 709 \text{ l}/(\text{mol O}_3 \text{ h})$ and $k_{\text{O}_3} = 3132 \text{ l}/(\text{g COD h})$.
- The aerobic degradation of these wastewaters by an activated sludge system leads to COD removal between 31 and 85% for a hydraulic retention time between 24 and 72 h.
- The Contois model provides accurate kinetics for this aerobic purification during the discontinuous period with the following kinetic parameters: $q_{\text{max}} = 0.190 \text{ g COD/g (VSS h)}$ and $K_1 = 6.48 \text{ g COD/g VSS}$.
- A similar kinetic study performed for the continuous period leads to a value of 0.027 g COD/(g VSS h) for the specific substrate decomposition rate.
- The combined process of an ozonation step followed by an activated sludge step provides an enhancement in the substrate removal obtained in relation to that obtained in the single aerobic treatment of wastewater without ozone pre-treatment, i.e. from 27.7 to 39.3%.

Acknowledgements

This research has been supported by the “Comision Interministerial de Ciencia y Tecnologia” (CICYT) of Spain, under Project PPQ2001-0744 and by Junta de Extremadura under Grant 2PR01A004.

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