Purification of storage brines from the preservation of table olives

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Abstract

The chemical oxidation of the wastewaters generated during storage of table olives in NaCl brines, prior to their manufacturing process, was studied. Ozone alone produced COD removals in the range 14–23%, and a higher average removal of 73% of the aromatic compounds. The additional presence of hydrogen peroxide and UV radiation increased these values to 39% for COD and 86% for aromatics. However, UV radiation alone only gave a removal of 9% for COD and 27% for aromatics, and the additional presence of 0.5 M H_2O_2 led to 13% for COD and 38% for aromatics, respectively. The Fenton's reagent oxidation achieved a COD removal of 24% for the higher concentrations of Fe^{2+} and H_2O_2. The most effective process was the combination $O_3/UV/H_2O_2$ with total removals of 65 and 92% for the COD and aromatics, respectively. The aerobic treatment of these effluents gave a 66% removal regardless of the initial biomass concentration used, and a rate constant of 0.19 per day was obtained for the process by using the Contois model. Finally, the aerobic treatment of the wastewaters previously ozonated alone, and ozonated with UV radiation, gave increases in the COD removal and a final rate constant of 0.44 per day. The enhancements were due to the chemical oxidations, these procedures being suitable technologies as pre-treatments to subsequent biological processes for the purification of these residues.
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Keywords: Preservation brines; Table olives; Ozone; UV radiation; Advanced oxidation processes; Aerobic microorganisms

1. Introduction

The manufacture of table olives (black and green types) in Mediterranean countries like Spain, Portugal and Greece is carried out in numerous industrial plants [1]. Basically, the method of processing the black olives consists of a treatment with dilute NaOH solution

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(lye) to debitter the olives, followed by one to three rinse cycles to eliminate the excess alkali. Finally, the olives are put into sodium chloride brine in which lactic acid fermentation occurs [2]. However, prior to debittering, the olives are subjected to a preservation storage in liquid phase for months. In Spain, the procedure normally used for this preservation stage consists of putting the selected olives into fermentation vessels in 4–6% (w/v) brine under aerobic conditions [3]. During this period, fermentation occurs due to the growth of yeast. Finally, the brines are discarded before the debittering process begins.

These production plants generate each year a large volume of wastewaters from the different manufacturing stages: storage brines, debittering (lyes) and rinsing. The pollution load of these residues is considerable, because the major constituent is organic matter consisting mainly of aromatic and phenolic compounds [4]. Traditionally, these wastewaters have been discharged into city sewers or eliminated through public water courses. More recently, they have been stored in evaporation ponds which have sometimes contaminated groundwaters and caused other environmental problems. However, the brines also contain inorganic compounds, making their evaporation in ponds impractical, so that they require other purification procedures, such as biological treatments [5].

Due to the potential hazards caused by these residues (COD in the range 34–36 g/l, BOD_5 12.5–13.5 g/l and total phenolic content of 1.58 g caffeic acid/l), more demanding requirements are imposed on those wastes, and several investigations have been carried out to examine suitable technologies for reducing their contaminant character by degradation of the toxic organic matter. Among them, chemical oxidation processes have shown themselves to be effective for the destruction of organic matter in general, and refractory pollutants in particular [6]. For this purpose, single oxidants like chlorine, ozone, UV radiation, hydrogen peroxide, etc. are used. Specifically, ozone has many of the oxidizing properties desirable for wastewater treatment [7], and, in some cases, photochemical degradation by UV radiation reveals significant efficiencies in the treatment of wastewaters [8].

On the other hand, systems based on the generation of very reactive free radicals, especially hydroxyl radicals, have experienced increasing interest due to their high destructive power. They are the so-called advanced oxidation processes [9,10] which are constituted by the simultaneous combinations of two or three of the aforementioned oxidants, as well as the combination of hydrogen peroxide plus ferrous ions (Fenton's reagent) [11].

Since few data have been reported in relation to the application of chemical processes for the purification of the effluents produced in the several stages of the manufacture of black table olives, some of these chemical methods are applied in the present research to the degradation of the wastewaters generated by the storage of these olives in brine. Specifically, the oxidants used were ozone and UV radiation alone, as well as the combinations of ozone with UV radiation, ozone plus hydrogen peroxide, UV radiation plus hydrogen peroxide, Fenton's reagent, and the global combination ozone with UV radiation and hydrogen peroxide. In addition, a single aerobic microorganism treatment was performed; and finally, a combined process which consisted in the aerobic treatment of the chemically pre-treated wastewaters. In all these treatments, the objective was to identify removals of the pollutant organic substrate and to develop kinetic studies in order to evaluate kinetic parameters for reactor design.

2. Material and methods

The ozonation experiments were carried out in a batch reactor where the temperature was maintained at 20 °C by means of an external jacket on the reactor, with circulating water from a thermostatic bath. The ozone was generated in a laboratory ozone generator from an oxygen stream. In every experiment, the inlet ozone partial pressure was adjusted to the desired value and the ozone–oxygen gas stream was introduced into the reactor through a porous plate. For the experiments in which UV radiation was used, the reactor was equipped with a radiation source located in an axial position: a Hanau TQ150 high pressure mercury vapor lamp which emitted polychromatic radiation in the range 185–436 nm. Finally, the required amounts of ferrous sulphate and hydrogen peroxide were added to the reactor in the Fenton's reagent oxidation experiments, and only the necessary amounts of hydrogen peroxide in the combined O_3/H_2O_2, UV/H_2O_2 and $O_3/UV/H_2O_2$ experiments to obtain the required initial concentrations of 0.5 and 0.2 M in H_2O_2.

The experiments ran for approximately 8 h and samples were taken periodically to measure the pH, the chemical oxygen demand (COD), aromatic content (aromatics, measured as absorbance at 254 nm with dilution 1:100), outlet ozone partial pressure (pO_{3o}) and the 5-day biological oxygen demand (BOD_5).

The aerobic degradation experiments were conducted in a biological mixed batch reactor, with an air stream introduced into the reacting mass. The biomass created from an activated sludge was previously acclimatized to this substrate (the wastewater of the present study) for 6 weeks, according to the procedure described elsewhere [12]. The bioreactor was loaded with the amount of biomass required to obtain the desired initial concentration of microorganisms for each experiment, and then $500 \, cm^3$ of the raw wastewater was added. The experiment ran for approximately 7 days and samples were withdrawn at regular intervals to determine the COD concentration and the volatile suspended solids (VSSs).

For the aerobic degradation of the pre-treated wastewater with ozone or ozone plus UV radiation, the effluent obtained in the ozonation experiments was loaded into the bioreactor. Aerobic experiments were then conducted as described above, the final COD concentration of the ozonation treatment being the initial COD concentration of the following biological stage.

The analytical methods were as follows: an iodometric method was used to determine the ozone in the inlet and outlet gas stream; the COD was determined in a Lange photometer [13]; the aromatic content was measured in a Hitachi spectrophotometer, with the necessary dilutions to obtain absorbances within the range of the equipment; the phenolic content was determined by the Folin–Ciocalteau method [14]; the BOD_5 by a respirometric method [13]; and the concentration of H_2O_2 by the peroxidase/DPD method [15].

The raw wastewaters used for the experiments were collected from the black table olive industrial plant "Acenorca", located in Montehermoso, Spain. Their main physico-chemical parameters were analysed according to the standard methods [13], giving the following values: pH around 4; total organic content, measured as COD in the range 34–36 g/l, and as BOD_5 12.5–13.5 g/l; absorbance at 254 nm of 0.92; total phenolic content of 1.58 g caffeic acid/l [14]; and total solids content of 55.7 g/l.

Table 1
Degradation experiments performed in the ozonation processes

Experiment	pO_{3o} (kPa)	$[H_2O_2]$ (M)	X_{COD} (%)	X_A (%)	BOD_{5f} (g l^{-1})	pH_f
O-1	1.04		14	67	10.4	3.2
O-2	2.98		17	75	9.5	2.8
O-3	4.48		23	73	7.6	2.7
OP-1	4.38	0.2	24	74	8.2	2.9
OP-2	4.58	0.5	29	75	5.6	2.8
OUV-1	1.04		16	83	9.3	3.3
OUV-2	2.99		29	85	6.5	3.2
OUV-3	4.50		39	86	6.1	2.7
OUVP-1	4.47	0.5	65	92	5.2	2.8

pH = 4, COD_o = 34.9 g l^{-1}, A_o = 0.91, BOD_{5o} = 13.2 g l^{-1}.

3. Results and discussion

3.1. Chemical treatments

The chemical oxidation of the wastewaters from the brine conservation storage of black table olives was performed by means of single ozone and UV radiation, and by the combinations O_3/H_2O_2, O_3/UV radiation, UV radiation/H_2O_2, H_2O_2/Fe^{2+} and O_3/H_2O_2/UV radiation according to the group of experiments described in Tables 1 and 2. Each 8 h experiment was performed at 20 °C, maintaining the natural pH of the water (approximately 4). In these experiments, the reduction of the pollutant organic matter present in the effluent was mainly determined by the COD, a global parameter which seems to be the most suitable for representing the organic load. Other parameters related with the organic matter content, such as the aromatic content and BOD_5 were also determined simultaneously.

In the first stage, oxidation experiments by single ozone were conducted with ozone partial pressures in the ozone–oxygen gas stream ranging between 1.04 and 4.48 kPa (Experiments O-1, O-2 and O-3 in Table 1). In these experiments the outlet ozone partial pressure (pO_{3o}), COD, aromatic content (A), pH, and BOD_5 were determined at regular intervals as described in Section 2. Table 3 depicts the evolution of these parameters in Experiment O-3 taken as example.

Table 2
Degradation experiments performed in the UV radiation and Fenton processes

Experiment	$[H_2O_2]$ (M)	$[Fe^{2+}]$ (M)	X_{COD} (%)	X_A (%)	BOD_{5f} (g l^{-1})	pH_f
UV-1			9	27	9.5	3.9
UVP-1	0.2		11	33	9.1	3.7
UVP-2	0.5		13	38	8.6	3.6
F-1	0.2	1×10^{-2}	12		9.8	2.7
F-2	0.5	2.5×10^{-2}	24		8.3	2.8

pH = 4, COD_o = 34.2 g l^{-1}, A_o = 0.95, BOD_{5o} = 12.5 g l^{-1}.

Table 3
Results obtained in Experiment O-3

Time (h)	pO_{3o} (kPa)	COD (g l^{-1})	A	BOD$_5$ (g l^{-1})	pH
0	0	35.7	0.91	13.5	3.9
0.25	1.21	35.2	0.88		3.7
0.5	2.34	34.7	0.75	12.4	3.5
0.75	2.86	34.3	0.65		3.4
1	3.17	33.8	0.55	10.3	3.3
1.5	3.49	33.3	0.45		3.3
2	3.66	32.6	0.39		3.2
2.5	3.69	32.1	0.36		3.2
3	3.80	31.5	0.33	9.8	3.1
4	3.86	30.4	0.30		3.0
5	3.92	29.6	0.28		3.0
6	3.94	29.0	0.26	8.5	2.9
7	3.95	28.3	0.25		2.8
8	3.98	27.6	0.24	7.6	2.7

During this single ozonation process, the COD decreased continuously with the reaction time. Table 1 lists the final removals obtained (defined as $X_{COD} = 1 - COD/COD_o$) after 8 h of reaction, with values of 14, 17 and 23% for Experiments O-1, O-2 and O-3, respectively. Therefore, when the ozone partial pressure increased, the removal of substrate was also found to increase. Similarly, Table 1 gives the final aromatic compound removals, defined as $X_A = 1 - A/A_o$, and a similar reduction of 67–75% was obtained regardless of the inlet ozone partial pressure. It is interesting to note that most of this aromatic content reduction was already achieved during the first 2 h of reaction (a 57% of reduction in Experiment O-3, Table 3), which probably is a consequence of the high ozone reactivity towards aromatic compounds, especially phenolic compounds [16].

In order to study the enhancement of the degradation of the organic substrate present in these effluents when additional oxidants are used in comparison to the previous single ozonation treatment, oxidation of these wastewaters was performed with the supplementary presence of H_2O_2 or UV radiation in addition to ozone. These combinations constitute some of the advanced oxidation processes mentioned in Section 1, which generate very reactive and oxidizing hydroxyl radicals that react with the organic matter and increase the single oxidant efficiency. Hence, two reaction pathways must be taken into account [10]: a direct pathway with the attack of the organic solutes by the single oxidant, and a radical pathway promoted by a variety of derived oxygen radicals, including the hydroxyl radicals, which can act as secondary oxidants.
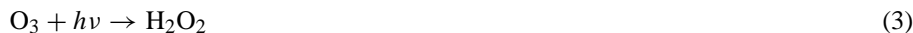
Thus, the direct pathway in the both processes is the ozonation reaction

$$P + O_3 \rightarrow P_{oxid} \tag{1}$$
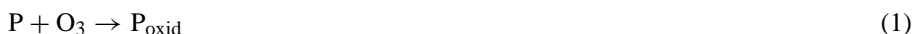
In the case of the combination O_3/H_2O_2 the hydroxyl radicals are generated by the attack of ozone on the hydrogen peroxide [17]

$$O_3 + H_2O_2 \rightarrow {}^{\bullet}OH \tag{2}$$

while in the combination O_3/UV, as Peyton and Glaze pointed out [18], ozone absorbs UV radiation and produces hydrogen peroxide

$$O_3 + h\nu \rightarrow H_2O_2 \tag{3}$$

and later, there is a photolysis of hydrogen peroxide to generate hydroxyl radicals

$$H_2O_2 + h\nu \rightarrow 2\,^\bullet OH \tag{4}$$

Once hydroxyl radicals have been formed, they decompose the organic matter through the radical pathway

$$P + \,^\bullet OH \rightarrow P_{oxid} \tag{5}$$

Given these considerations, two wastewater degradation experiments were carried out with the combination of O_3 plus H_2O_2, with an inlet ozone partial pressure around 4.5 kPa and varying the initial hydrogen peroxide concentration (Experiments OP-1 and OP-2 in Table 1, with $[H_2O_2]_0 = 0.2$ and 0.5 M, respectively). And similarly, three experiments were carried out with the combination of O_3 plus UV radiation, using different ozone partial pressures in the inlet gas stream: 1.04, 2.99 and 4.50 kPa, respectively (Experiments OUV-1, OUV-2 and OUV-3 in Table 1). A final experiment with the global combination O_3/H_2O_2/UV was also performed (Experiment OUVP-1 in Table 1).

The evolution of the COD over the course of each experiment of these processes was quite similar to that of the single ozonation process, and some increases in the COD removal were achieved when hydrogen peroxide was also present. Thus, from a 23% removal in Experiment O-3, 24 and 29% removals were obtained in Experiments OP-1 and OP-2 carried out with the same inlet ozone partial pressure and increasing the hydrogen peroxide dosage. Similarly, the presence of UV radiation enhanced the COD elimination, from 14 to 16%, 17 to 29% and 23 to 39% in experiments with increasing ozone partial pressures. This moderate enhancement in the removals can be attributed to the supplementary generation of hydroxyl radicals due to the presence of hydrogen peroxide or UV radiation, as mentioned above. At the same time, for the aromatic content removal X_A, final values of 75 and 86% were obtained in Experiments OP-2 and OUV-3, exceeding the 73% obtained in Experiment O-3 performed with a similar ozone partial pressure.

Finally, the oxidation of these effluents was examined by the simultaneous action of ozone, UV radiation and hydrogen peroxide (Experiment OUVP-1, Table 1). In this case, in addition to the direct ozonation, an enhanced generation of hydroxyl radicals must also be considered, and increased organic matter elimination can be expected. Indeed, significant increases in the substrate removal were obtained, with $X_{COD} = 65\%$ and $X_A = 92\%$ (almost a total elimination of aromatic compounds), which confirms a higher production of OH radicals in this system.

Regarding the outlet ozone partial pressure pO_{3o} (also measured as a function of the reaction time), Fig. 1 shows the different evolution of this parameter in this group of experiments. Thus, for Experiments O-3 and OP-2, with higher values of inlet ozone partial pressures, it is seen that ozone was completely consumed at the beginning of the reaction, due to fast ozone reactions during the first times of the process, especially with phenolic and aromatic compounds. Later, the outlet ozone partial pressure increased progressively, and a
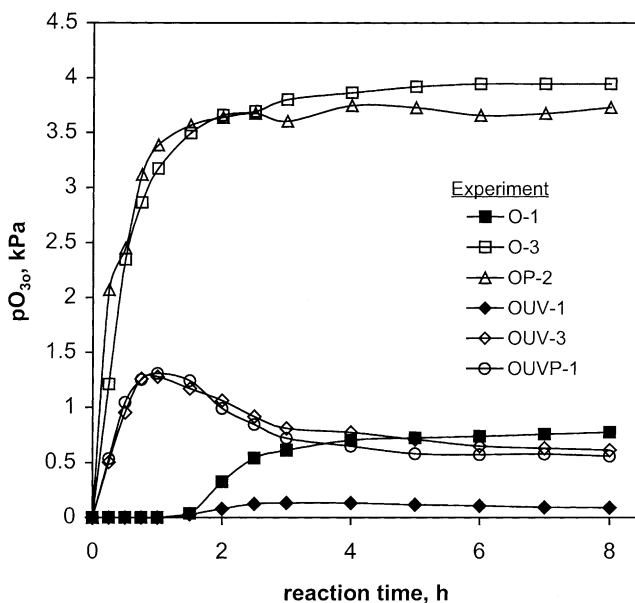
Fig. 1. Evolution of the outlet ozone partial pressure in the ozonation experiments, alone and combined. Experimental conditions given in Table 1.

value close to the inlet ozone partial pressure was reached after 2 h of reaction, which indicates that, then ozone is reacting slowly with the remaining refractory organic compounds. However, Experiments OUV-3 and OUVP-1 showed that the outlet ozone partial pressures increased after 1.5 h of reaction, but later decreased. In these cases ozone, which absorbs in the UV region, competes with the organic matter for the UV radiation. Thus after a certain time, when a major amount of the organic matter has been degraded (see aromatic content removal in Experiment O-3, Table 3), ozone is easily photolyzed even in the gas stream [18] and its concentration in the outlet gas stream decreases. On the other hand, Experiments O-1 and OUV-1, with lower inlet ozone partial pressure, revealed a major consumption of ozone during most of the reaction time (especially in Experiment OUV-1). It indicates that the mass transfer contributes to the control of the process, which, consequently, is not exclusively controlled by the chemical reaction as in the case with the higher inlet ozone partial pressure.

In these ozonation processes, there were decreases in the BOD_5 and pH during the reactions. Specifically, the BOD_5 declined from an initial value around 13.2 g/l to the final values depicted in Table 1, and the pH from an initial value around 4 to final values in the range 2.6–2.8 due to the formation of low molecular weight organic acids.

In the next step, the oxidation of these wastewaters was carried out by means of single UV radiation. In this case, the photochemical decomposition takes place by a direct attack of the radiation on the organic matter

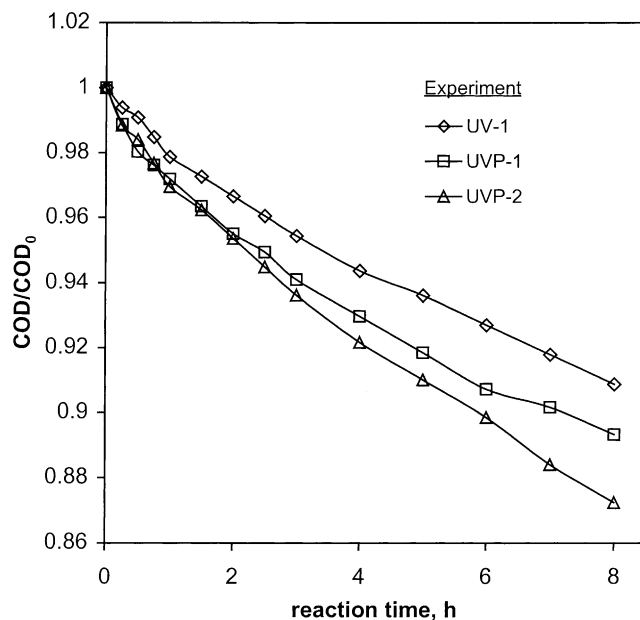$$P + h\nu \rightarrow P_{oxid} \tag{6}$$

Fig. 2. Substrate concentration decay with reaction time in the single UV radiation process and in the combination UV radiation plus hydrogen peroxide. Experimental conditions given in Table 2.

Table 2 lists the COD and aromatic content removals attained, X_{COD} and X_A, in this Experiment UV-1. The lower values obtained in comparison with the ozonation process, 9% for X_{COD} and 27% for X_A, reveals that UV radiation alone is not a good oxidant for the organic content of this effluent, at least with the radiation source used in this research.

In order to improve the efficiency of this single photochemical process, and similarly of the ozonation process, the photodegradation of these wastewaters was subsequently performed with the presence of H_2O_2 in addition to the UV radiation. This combination is another of the aforementioned advanced oxidation process [19]. In this case, the direct pathway is the photochemical reaction given by Eq. (6), while the formation of hydroxyl radicals is due to the direct photolysis of hydrogen peroxide according to the reaction (4).

Two degradation experiments were carried for different initial hydrogen peroxide concentration, with values of $[H_2O_2]_0 = 0.2$ and $0.5\,M$, respectively (Experiments UVP-1 and UVP-2 of Table 2). During these experiments, the evolution of substrate and aromatic compound concentrations were similar to those of the single UV radiation process as can be seen in Fig. 2 for the COD. In addition, two effects can be clearly seen: firstly, a slight positive influence of the combination $UV + H_2O_2$ in comparison with the single photodegradation. Secondly, another moderate positive influence of the H_2O_2 initial concentration on the process, with increasing removals when this variable was increased. Thus for the COD removal, final values of 11% in Experiment UVP-1, and 13% in Experiment UVP-2 were obtained after 8 h, while for Experiment UV-1 the COD removal was 9%. Similarly, for the absorbance removal, final values of 33 and 38% were obtained in comparison with 27% obtained in the single photodecomposition. This slight enhancement in the substrate

removal can be attributed to the additional contribution of the hydroxyl radicals, which are generated in the presence of hydrogen peroxide.

Finally, we studied the decomposition of the wastewaters by means of Fenton's reagent, a mixture of hydrogen peroxide and ferrous ions, which generate hydroxyl radicals according to the reaction [11,20]

$$H_2O_2 + Fe^{2+} \rightarrow OH^- + {}^{\bullet}OH + Fe^{3+} \tag{7}$$

Once the hydroxyl radicals have been formed, they again attack the organic matter in the same way as in the previous combinations (reaction 5). For this process, two experiments were carried out, varying the initial concentrations of Fe^{2+} and H_2O_2. These concentrations were: $[H_2O_2]_0 = 0.2\,M$ and $[Fe^{2+}]_0 = 1 \times 10^{-2}\,M$ in Experiment F-1, and $[H_2O_2]_0 = 0.5\,M$ and $[Fe^{2+}]_0 = 2.5 \times 10^{-2}\,M$ in Experiment F-2. Table 2 lists the COD and aromatic content removals achieved, X_{COD} and X_A, by the end of the reaction. Thus, Experiment F-1 gave a value of 12%, slightly higher than that obtained with the single photodegradation (Experiment UV-1), while Experiment F-2, with higher H_2O_2 and Fe^{2+} concentrations, achieved a greater removal of 24%.

The determination of the kinetic parameters of the chemical reactions that take place in the wastewater purification processes is useful for the design of reactors and contactors where these treatments are carried out.

For ozonation processes, it is assumed that, in most cases, there is no resistance of the liquid phase to mass transfer; and therefore the chemical reaction controls the global process. In addition, several authors have reported [16,21] that the reactions of ozone with organic compounds usually follow overall second-order kinetics, first-order with respect to each reactant. Therefore, second-order kinetics can also be assumed for the present reactions between ozone and the total organic matter represented by the COD, and the rate equation for the overall organic matter decomposition can be expressed by

$$-\frac{dCOD}{dt} = k\,COD\,C_A^* \tag{8}$$

where C_A^* represents the ozone equilibrium concentration in the liquid phase, which is determined from the average value of the inlet and outlet ozone partial pressure in the gas streams using the Henry's law constant of $11{,}395\,kPa\,l\,mol^{-1}$ for this specific process at $20\,^{\circ}C$ [22].

As the outlet ozone partial pressure varies with reaction time during an experiment, the integration of Eq. (8) leads to

$$\ln\frac{COD_o}{COD} = k\int_0^t C_A^*\,dt \tag{9}$$

According to this expression, a plot of $\ln(COD_o/COD)$ versus the integral term should be a straight line whose slope is the second-order rate constant k. Fig. 3 shows this plot for some of the results summarized in Table 1. A least squares regression analysis gave the rate constants in Table 4.

This model was not applied to Experiments O-1 and OUV-1 and the rate constants were not determined because the low inlet ozone partial pressure provided some control of the mass transfer on the overall process, as discussed previously. Therefore, based on
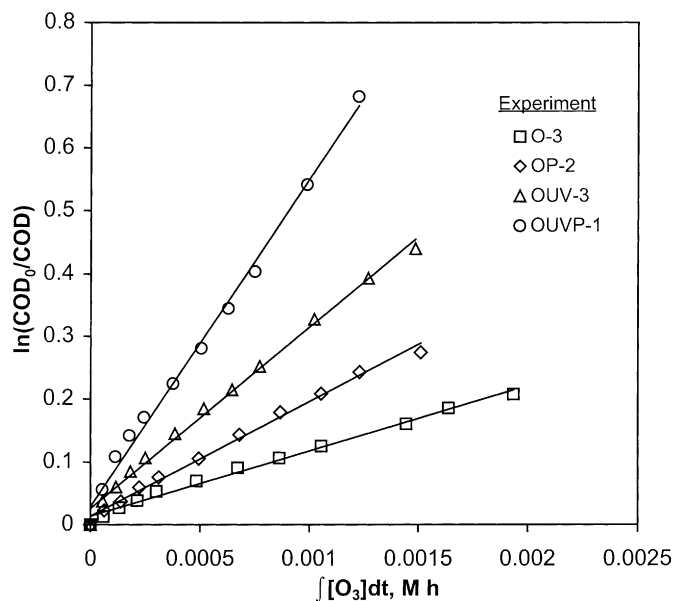
Fig. 3. Determination of the substrate removal rate constant for the single ozonation process and for the combinations of ozone plus hydrogen peroxide and ozone plus UV radiation. Experimental conditions given in Table 1.

the control of the chemical reaction alone, this kinetic model was not appropriate for these experiments. On the other hand, as would be expected for isothermal experiments, similar values were obtained for single ozonation experiments (O-2 and O-3), and for the combined O_3/UV radiation experiments (OUV-2 and OUV-3). For these groups, average values of 101 and 308 l/mol O_3 h can be proposed as global second-order rate constants at 20 °C. In the O_3/H_2O_2 process, there was an increase in the rate constant when the hydrogen peroxide concentration was increased: from 116 to 181 l/mol O_3 h for Experiments OP-1 and OP-2, respectively. Finally, for the total combination O_3/H_2O_2/UV, the highest value of 538 l/mol O_3 h was obtained, as was to be expected. In all cases, the rate constants increased with the

Table 4
Kinetic parameters for ozonation experiments

Experiment	k (l/mol O_3 h)	b (g COD/mol O_3)	k_{O_3} (l/g COD h)
O-1		38.0	
O-2	98	28.8	3.40
O-3	104	37.0	2.81
OP-1	116	25.8	4.39
OP-2	181	26.6	6.82
OUV-1		13.4	
OUV-2	329	16.9	19.50
OUV-3	288	12.9	22.32
OUVP-1	538	21.6	25.60

additional presence of H_2O_2 and UV radiation in addition to ozone, which again confirms the positive effect of these combinations due to the generation of the hydroxyl radicals.

With the organic substrate removal rate constant obtained, the rate constant can also be evaluated with respect to the ozone disappearance k_{O_3} by considering the relationship between the two rate constants

$$k_{O_3} = \frac{k}{b} \tag{10}$$

where b is the stoichiometric ratio of the reaction, in units of grams of substrate degraded per mole of ozone consumed. This ratio can be expressed in the form

$$b = \frac{(COD_o - COD_f)V}{n_i t - \int_0^t n_o dt} \tag{11}$$

where V is the volume of liquid in the reactor. Again, as the outlet ozone partial pressure pO_{3o} varies with reaction time, the total amount of ozone exiting the reactor must be determined by the integration of the outlet ozone flow rate n_o over the reaction time t. The application of Eq. (11) to the experimental data gives the values listed in Table 3. The results suggest average values of 31.3 g of substrate degraded per mole of ozone reacted for the single ozonation (Experiments O-1, O-2 and O-3), and 26.5 and 13.6 g of substrate degraded per mole of ozone reacted for the combinations O_3/H_2O_2 (Experiments OP-1 and OP-2) and O_3/UV radiation (Experiments OUV-1, OUV-2 and OUV-3), respectively. This lower value in the combined O_3/UV process indicates the easy photolysis of ozone in the gas phase. Although this combined process leads to a greater elimination of organic matter, the amount of ozone consumed is greater than in the single ozonation process, with obvious economic consequences.

Finally, Eq. (10) gives the values listed in Table 4 for k_{O_3}. In the case of the single ozonation and combined O_3/UV radiation, average values of 3.1 and 20.9 l/g COD h are proposed, while in the combined O_3/H_2O_2 process, each reaction has a different value according to its initial hydrogen peroxide concentration.

A kinetic study was also performed of the photodegradation experiments, where UV radiation is used alone (Experiment UV-1) or combined with hydrogen peroxide (Experiments UVP-1 and UVP-2). Assuming that the overall reaction follows first-order kinetics with respect to the COD concentration [23], the rate equation can be expressed by

$$-\frac{dCOD}{dt} = k_\phi COD \tag{12}$$

where k_ϕ is the apparent rate constant for this photochemical degradation. The integration of Eq. (12) between $t = 0$ and $t = t$ leads to

$$\ln \frac{COD_o}{COD} = k_\phi t \tag{13}$$

After least squares regression analysis, values for k_ϕ of 1.15×10^{-2}, 1.35×10^{-2} and $1.63 \times 10^{-2} \, h^{-1}$ were obtained for Experiments UV-1, UVP-1 and UVP-2, respectively. Again, the positive influence of the hydrogen peroxide concentration on the organic substrate degradation is observed.

Table 5
Aerobic degradation experiments and combined chemical/biological experiments

Experiment	X_0 (g VSS/l)	X_{COD} (%)	k (per day)
A−1	0.54	66	0.19
A-2	1.44	67	0.19
A-3	3.55	66	0.20
OA-1	1.48	71	0.24
OUVA-1	1.49	71	0.44

$COD_o = 34.2\,g\,l^{-1}$.

3.2. Aerobic treatment and combined chemical and biological treatments

In the following stage, the degradation of these wastewaters was performed by aerobic microorganisms, in the group of experiments described in Table 5. The initial biomass concentration X_0, measured as volatile suspended solids, was varied between 0.54 and 3.55 g of VSS/l (Experiments A-1, A-2 and A-3). The initial substrate concentration of raw wastewater was approximately 34 g COD/l. The substrate concentration COD decreased continuously with reaction time, as in the chemical oxidation processes. The calculated total substrate removals reached at the end of every experiment X_{COD} are given in Table 5. The overall reductions were around 66%. This indicates good efficiency of the aerobic treatment in the degradation of the organic matter for this type of wastes. The biomass evolution agrees well with the typical growth-cycle phases for batch cultivations [24,25]: an acclimatization period (lag phase), increase in the biomass concentration (exponential growth phase), maximum size of population (the stationary phase), and death phase.

For design purposes, a kinetic study employing the Contois model [26] was used. According to this model, the specific substrate decomposition rate q can be related to the substrate concentration S as

$$q = q_{max} \frac{S}{K_1(X + S)} \tag{14}$$

where q_{max} represents the maximum rate of substrate utilization and K_1 is the Contois saturation constant. In those situations when $K_1 X \gg S$ [12], the substrate concentration S can be neglected in Eq. (14), yielding

$$q = \frac{q_{max}S}{K_1 X} = k\frac{S}{X} \tag{15}$$

Using Eq. (15), a least squares regression analysis gave the k values listed in Table 5: a value of 0.19 per day is suggested for the biokinetic rate constant, when the wastewaters from the brine preservation stage of the black table olives have been aerobically degraded.

In the following step, the degradation of the wastewaters was carried out by the combined processes of an ozonation step followed by aerobic degradation, as well as an ozone plus UV radiation oxidation followed by aerobic degradation. These combined treatments were performed with the aim of evaluating the influence of the two chemical pre-treatments on the efficiency of the later biological stage.

Thus, an ozonation experiment was carried out under conditions similar to Experiment O-2, with an inlet ozone concentration of 3.04 kPa. Likewise, another experiment was conducted with UV radiation. These experiments lasted only 2 h: as was discussed previously, the ozone fed to the reactor is absorbed almost completely by the liquid phase in this reaction time, so that longer reaction times lead to an increase of the ozone concentration in the outlet gas, and the efficiency of the process decreases sharply. In addition, most of the phenolic and aromatic compounds are eliminated within this reaction time.

The final effluents of these ozonation experiments were then fed to the aerobic reactor (Experiments OA-1 and OUVA-1 in Table 5). The initial biomass concentration in both experiments was similar to that of Experiment A-2 (around 1.48 g VSS/l), so that the influence of the ozone pre-treatments (alone and with UV radiation) using the substrate removals can be compared with the single aerobic degradation (Experiment A-2). Table 5 gives this COD removal (X_{COD}): a final value of 71% was thus obtained in both processes, with a moderate increase over the removal achieved by the single aerobic process (around 66%).

This improvement in the aerobic stage of the chemically pre-treated wastewaters can also be observed by conducting a similar kinetic study to that described above for the single aerobic treatment, applying the Contois model to the experimental data, Eqs. (13) and (14). Thus, using Eq. (14), a regression of q against S/X gave slopes of 0.24 and 0.44 per day as compared to the 0.19 per day for the single aerobic process of the untreated wastewaters.

Hence, the main kinetic parameter for the substrate decomposition had increased with the previous chemical processes, which indicates a moderate beneficial effect of the first mentioned pre-treatment (single ozonation), and a greater effect of the second (ozonation in the presence of UV radiation). This is probably due to the removal of some fraction of the aromatic and phenolic compounds, which potentially inhibit the later biological oxidation.

4. Conclusions

Different chemical oxidants, alone and combined, were applied to the purification of the wastewaters from the storage in brine of black table olives. The UV radiation presented the lowest efficiency in the degradation of the organic matter, and was slightly improved by the additional presence of hydrogen peroxide. Ozone produced moderate COD removals and higher aromatic compound removals, which increased with increasing inlet ozone partial pressure and with the additional presence of hydrogen peroxide and UV radiation. Fenton's reagent gave COD removals that depended on the initial concentrations of Fe^{2+} and H_2O_2. As was to be expected, the most effective purification process was the overall combination $O_3/UV/H_2O_2$. Aerobic treatment of the effluents gave a major substrate removal that was independent of the initial biomass concentration. The experimental results fit the Contois model well and the kinetic rate constant was evaluated. The removal and the rate constant of this biological process were both proportional to the amount of ozonation or ozone coupled with UV radiation. It can be concluded that the chemical treatments in general, and ozonation processes in particular, are useful for the degradation of organic matter, especially aromatic compounds. These processes can be used as pre-treatment steps for subsequent aerobic degradation in order to meet discharge norms and reach purification efficiencies required by national regulations.

Acknowledgements

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