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Treatment of Wastewater from Table Olive Industries: Quantum Yield of Photolytic Processes

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Table olive production is an important industrial activity in European Mediterranean countries like Spain, Greece or Italy. The process is carried out through a series of steps: selection of olives, cleaning, debittering, washing, fermentation and packing. Debittering and washing steps consume important quantities of water that become polluted with different compounds like polyphenols extracted from olives. Final COD in these wastewater varies between 12 and 16 g/L. Although these industries are seasonally working (during about three months in a year) the highly contaminated wastewater they release deserves special attention. In most of cases these wastewaters are sent to ponds where they receive a slow biological treatment. However, this treatment presents important problems related to bad odors, presence of insects or surface and underground water contamination. As a result different alternative treatments have been investigated to both recover part of the sodium hydroxide and sodium chloride used or eliminate the remaining organic matter. Among these treatments one can cite: membrane processes, anaerobic biological oxidation or advanced oxidation processes (Beltrán et al. 1999; Brenes and Garrido, 1988a and 1988b; García et al. 1989; Garrido, 1975; Kopsidas, 1990).

UV radiation combined with different oxidants like ozone or hydrogen peroxide with and without metal cations (Fe^{2+}) has been used to generate hydroxyl radicals (Glaze et al. 1987; Pertersen et al. 1988). In this type of process, however, part of the radiation directly decomposes the organic matter by direct photolysis. Therefore, determination of the quantum yield is fundamental to quantify the relative importance of the photolytic process.

In this work, wastewater generated during the debittering and washing steps of table green olive preparation has been treated with UV radiation emitted by two different UV lamps with the aim of determining the quantum yields.

MATERIALS AND METHODS

Table olive wastewater was prepared by treating 5 kg of green olives with 5 L of a 1% w/v sodium hydroxide solution during 8 hours (debittering step). After wastewater separation, olives were washed with water in the same proportion: 1 liter

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of water per 1 kg (washing step). COD of wastewater obtained (determined according to the dichromate procedure (Moore et al. 1948)) was 20.95 and 18.5 g/L for the debittering and washing steps, respectively, while pH was about 12. Since in practical application these wastewaters are usually diluted with others of lower COD (for example, with water from subsequent washing steps and/or cleaning processes), in this work, both wastewaters were also diluted with distilled water (1:25 by volume).

Experiments were carried out in a 1000 mL photochemical reactor described in a previous work (Beltrán et al. 1993). The reactor had a central inlet to situate a quartz well to insert the UV lamp. Two different UV lamps were used: a TNN 15/32 Hanau low pressure mercury lamp emitting radiation mainly a 254 nm and a TQ 150 Hanau high pressure mercury lamp of polychromatic radiation between 200 and 600 nm. Photochemical parameters of these systems were first obtained from actinometry experiments by using hydrogen peroxide (monochromatic system) or uranile oxalate (polychromatic system) as actinometers as reported in literature (Nicole et al. 1990; Alfano et al. 1986). Intensity of incident radiation was found to be 3.7×10^{-6} and 3.4×10^{-5} Einstein/(L·s) for the monochromatic and polychromatic UV lamps, respectively. These represented only 20.3 and 19% of the total power of lamps reported by the manufacturer.

RESULTS AND DISCUSSION

Figure 1 shows the evolution of remaining normalized COD corresponding to the wastewater studied when treated with monochromatic (low pressure UV lamp) and polychromatic (high pressure UV lamp) radiation. It is seen that both radiations yield similar photolytic rates regardless of the type of wastewater treated. It is also observed that reduction of COD is rather low, specially for the case of debittering wastewater (after 1 hour treatment, 9-10% against 27-31 % for the case of washing wastewater). It should be kept in mind that UV radiation is usually applied in combination with oxidants (ozone, hydrogen peroxide, etc) to improve a free radical oxidation step. In this work, however, UV radiation alone has been studied to determine the process quantum yield.

Quantum yield determination

In a photochemical process, the rate of photolysis of a given compound, N, can be expressed by the following equation (Leifer, 1988):

$$-\frac{dC_N}{dt} = \sum_{\lambda} \left\{ \Phi_{N\lambda} F_N I_{0\lambda} f_{\lambda} \left[1 - \exp\left(-2.303 L \sum_j \varepsilon_{j\lambda} C_j \right) \right] \right\} \qquad [1]$$

where F_N is the fraction of radiation of λ wavelength that N absorbs, defined as follows:

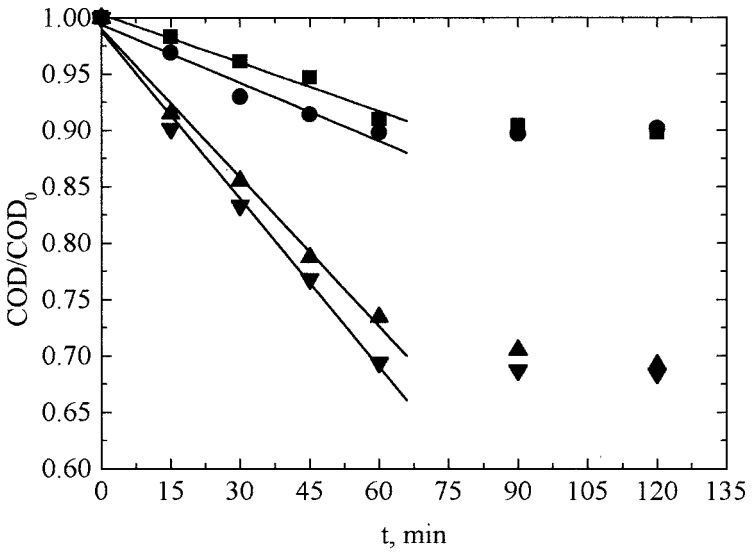

Figure 1: Variation of chemical oxygen demand (dimensionless form) with time of table olive wastewater photochemically treated. Debittering wastewater (COD_0 = 722 mg O_2/L): ■ monochromatic radiation; ● polychromatic radiation. Washing wastewater (COD_0 = 743 mg O_2/L): ▲ monochromatic radiation; ▼ polychromatic radiation. Conditions: T = 20 °C; pH = 10.3 -12.1

$$F_N = \frac{\varepsilon_{N\lambda} C_N}{\sum_j \varepsilon_{j\lambda} C_j} \qquad [2]$$

and subindexes j and λ refer to any compound present in water that absorbs radiation and to the wavelength of radiation, respectively, $\varepsilon_{j\lambda}$ represents the extinction coefficient of compound j at λ wavelength, L the apparent path of radiation through the photorreactor (4.9 cm in our case, see Beltrán et al. 1993), $\Phi_{N\lambda}$ and f_λ the quantum yield of N and the fraction of total intensity of radiation being emitted at the given wavelength, respectively.

In the case of wastewater, COD is usually taken as a surrogate parameter to follow the concentration (Beltrán et al. 1992 and 1995a; Preis et al. 1988). On the other hand, F_{COD} can be considered unity and eq. [1] becomes:

$$-\frac{dDQO}{dt} = \sum_\lambda \left\{ \Phi_\lambda I_{0\lambda} f_\lambda \left[1 - \exp\left(-2.303 L \varepsilon_\lambda DQO \right) \right] \right\} \qquad [3]$$

Table 1. Fractions of total intensity of polychromatic radiation, f_λ, and extinction coefficients, ϵ_λ, for debittering and washing wastewaters

λ	f_λ	ϵ_λ [1]	ϵ_λ [2]	λ	f_λ	ϵ_λ [1]	ϵ_λ [2]
238	$1.51\ 10^{-2}$	$8.43\ 10^{-3}$	$8.42\ 10^{-3}$	313	$8.52\ 10^{-2}$	$2.26\ 10^{-3}$	$1.12\ 10^{-3}$
248	$1.10\ 10^{-2}$	$8.03\ 10^{-3}$	$8.03\ 10^{-3}$	334	$1.06\ 10^{-2}$	$1.50\ 10^{-3}$	$8.75\ 10^{-4}$
254	$6.43\ 10^{-2}$	$8.01\ 10^{-3}$	$8.02\ 10^{-3}$	366	$1.48\ 10^{-1}$	$1.07\ 10^{-3}$	$7.62\ 10^{-4}$
265	$2.35\ 10^{-2}$	$7.97\ 10^{-3}$	$7.99\ 10^{-3}$	390	$2.47\ 10^{-3}$	$8.68\ 10^{-4}$	$6.93\ 10^{-4}$
270	$1.03\ 10^{-2}$	$7.66\ 10^{-3}$	$7.66\ 10^{-3}$	406	$8.22\ 10^{-2}$	$7.91\ 10^{-4}$	$5.24\ 10^{-4}$
275	$5.22\ 10^{-3}$	$7.48\ 10^{-3}$	$7.47\ 10^{-3}$	436	$1.16\ 10^{-1}$	$4.36\ 10^{-4}$	$2.89\ 10^{-4}$
280	$1.24\ 10^{-2}$	$7.16\ 10^{-3}$	$7.16\ 10^{-3}$	492	$3.11\ 10^{-3}$	$3.12\ 10^{-4}$	$1.06\ 10^{-4}$
289	$9.15\ 10^{-3}$	$6.08\ 10^{-3}$	$6.01\ 10^{-3}$	546	$1.76\ 10^{-1}$	$2.30\ 10^{-4}$	$8.94\ 10^{-5}$
297	$1.88\ 10^{-2}$	$4.16\ 10^{-3}$	$3.85\ 10^{-3}$	579	$1.72\ 10^{-1}$	$1.19\ 10^{-4}$	$8.01\ 10^{-5}$
302	$3.44\ 10^{-2}$	$3.36\ 10^{-3}$	$2.66\ 10^{-3}$				

[1] Debittering wastewater; [2] Washing wastewater. Units: λ, nm; ϵ_λ: L/(cm·mg O_2).

Values of ε_λ were calculated from samples of wastewater while those of f_λ have been obtained from the manufacturer. Table 1 gives the results for both types of wastewater.

Given the fact that absorption of radiation above 400 nm is negligible and that the exponential term of eq. [3] for any value of wavelength, exp(-2.303L ε_λ COD), is lower than 10^{-2}, equation [3] becomes:

$$-\frac{dDQO}{dt} = \sum_{\lambda} \left\{ \Phi_\lambda I_0 f_\lambda \right\} \qquad [4]$$

Equation [4] represents a zero order kinetics for the photolytic process of wastewater. Integration of eq. [4] yields:

$$DQO = DQO_0 - \sum_{\lambda} \left\{ \Phi_\lambda I_0 f_\lambda \right\} t \qquad [5]$$

According to eq. [5], the COD profile with time should yield a straight line whose slope allows us to determine the quantum yield, provided this can be taken as an average value in the case of polychromatic radiation. These plots are given in Figure 1. It is observed that eq [5] is only valid for the first hour of reaction. At more advanced times, however, this equation does not hold since COD remains unchanged and UV radiation is inefficient to further reduce the COD.

Table 2. Quantum yields of several organic compounds at 254 nm			
COMPOUND	Φ_{254}, mol/Einst	Reference	$^{1}\Phi_{254}$, mg O_2/Einst
Phenol	0.05	Dulin et al. 1986	11200
Chlorobenzene	0.37	Dulin et al. 1986	82800
Naphtalene	0.019	Tuhkanen, 1994	7296
Acenaphthene	0.052	Beltrán et al. 1995b	24128
Fluorene	0.0075	Beltrán et al. 1995b	3722
Phenanthrene	0.0069	Beltrán et al. 1995b	3643
Atrazine	0.05	Beltrán et al. 1993	28000
Simazine	0.06	Beltrán et al. 2000	30720
Debittering wastewater			4595
Washing wastewater			14865
[1]For organic compounds expressed as total oxygen demand, TOD. For the estimation of TOD, chlorine is considered to remain as Cl^-, and nitrogen is oxidised to NO_3^-.			

From the least squares analysis of experimental results the following values were obtained for the quantum yield:

For debittering wastewater:

Monochromatic radiation at 254 nm: 4595±540 mgO_2/Einstein
Polychromatic radiation (200-600 nm): 529±59 mgO_2/Einstein

For washing wastewater:

Monochromatic radiation at 254 nm: 14865±1540 mgO_2/Einstein
Polychromatic radiation (200-600 nm): 1647±88 mgO_2/Einstein

It can be observed that the quantum yield of washing wastewater are approximately three times higher than that of debittering wastewater, which suggests the presence of compounds more easily photodegraded. Also, it is seen that average quantum yields for Polychromatic radiation are about nine times lower than those corresponding to the Monochromatic radiation at 254 nm regardless of the wastewater type. This also suggests that contribution of wavelengths different than 254 nm to the photolysis of wastewater is low. This can be confirmed by calculating the average quantum yield due to radiation of any wavelength except that at 254 nm. Thus, from eq. [5] this quantum yield was found to be 250±26 and 738±57 mgO_2/Einstein for debittering and washing wastewater, respectively. According to these results, it can be concluded that UV/visible radiation different from that at 254 nm absorbed by wastewater is inefficient to yield photolysis reactions that lead to reduction of COD. Hence, when

using a photolytic processes to treat this wastewater, low pressure UV lamps that emit radiation at 254 nm are recommended.

In addition, quantum yields at 254 nm are of the same order of magnitude found in different works for model compounds like aromatic hydrocarbons, herbicides, etc. Thus, if quantum yields at 254 nm of these compounds are expressed as mg of theoretical oxygen demand (TOD) per Einstein the resulting values are similar to those obtained for the wastewater studied as shown in Table 2. This means that photolytic processes of these wastewaters theoretically provides degradation rates similar to those of model compounds.

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