

# Ozone and membrane filtration based strategies for the treatment of cork processing wastewaters

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## Abstract

The degradation of the pollutant organic matter present in the cork processing wastewater was studied by combining chemical treatments, which used ozone and some Advanced Oxidation Processes, and membrane filtration procedures. Two schemes were conducted: firstly, a single ozonation stage followed by an UF stage; and secondly, a membrane filtration stage, using different MF and UF membranes, followed by a chemical oxidation stage, where ozone, UV radiation, and the AOPs constituted by ozone plus UV radiation and ozone plus hydrogen peroxide, were used. The membrane filtration stages were carried out in tangential filtration laboratory equipment, and the membranes used were two MF membranes with pores sizes of 0.65 and 0.1  $\mu\text{m}$ , and three UF membranes with molecular weights cut-off of 300, 10, and 5 kDa.

The effectiveness of the different stages (conversions in the chemical procedures and rejection coefficients in the membrane processes) were evaluated in terms of several parameters which measure the global pollutant content of the wastewater: COD, absorbance at 254 nm, tannins content, color, and ellagic acid. In the ozonation/UF combined process the following removals were achieved: 100% for ellagic acid and color, 90% for absorbance at 254 nm, more than 80% for tannins, and 42–57% for COD reduction. In the filtration/chemical oxidation combined process, 100% elimination of ellagic acid, more than 90% elimination in color, absorbance at 254 nm and tannins, and removal higher than 80% in COD were reached, which indicates a greater purification power of this combination.

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## 1. Introduction

The amount of discharged pollutant effluents into the environment can be reduced by using several chemical and physical techniques, which lead to waters with enough quality for its discharge or reuse. Thus, chemical oxidation procedures degrade organic compounds and do not produce any additional wastes. In this kind of oxidation, the most common oxidants are ozone, hydrogen peroxide, UV radiation, etc. or the so-called advanced oxidation processes (AOPs), which are constituted by the simultaneous combinations of the above mentioned oxidants, and are based on the generation of very reactive and oxidizing radicals, mainly hydroxyl radicals [1,2].

More specifically, ozone is a very powerful oxidant for water and wastewater treatments, and once dissolved in the water,

reacts with a high number of organic compounds in two different ways: by direct oxidation, as molecular ozone, or by indirect reaction, through the formation of secondary oxidants such as free radicals, specially hydroxyl radicals [3]. By means of ozonation, it is expected to achieve great color and COD eliminations and an increase of the biodegradable organic carbon for later physical or biological stages [4]. In the same way, the AOPs have shown to be effective for the treatment of industrial wastewaters, especially for the elimination of organic pollutant compounds [5].

Physical treatments are also frequently used for the purification of surface waters and wastewaters, due their low costs and small environmental impacts. Among them, the application of membrane technologies to wastewater treatments has increased in the last times, with continuous reduction of their costs and extension of the application possibilities [6]. These membrane-driven processes are suitable to remove organic matter of different sizes, from small solutes (through nanofiltration) to macromolecules (through ultrafiltration) or suspended matter

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(through the use of microfiltration) [7]. Moreover, the obtained permeate after membrane techniques has in many cases enough quality to be reused in different stages (rinsing, washing, etc.) of the same industrial plant [8].

However, a clear limitation of filtration processes through membranes lies in the membrane fouling, this effect being associated with a decline in the permeate flux with processing time [9]. In order to minimize this undesirable effect and to reach more elimination levels in the purification of wastewaters with high organic pollutant contents, it has recently been proposed the use of sequences of treatments, which frequently start with a chemical oxidation stage followed by a membrane treatment stage [10,11], although the opposite sequence has also been tested with effectiveness [12].

The largest production of cork takes place in Portugal, followed by other Mediterranean countries such as Spain and Algeria. Inside Spain, around 30% of this production is generated in Extremadura Region (in the border with Portugal). The cork is useful for many practical applications, one of the most important being the manufacture of cork wine stoppers. The processing of the raw cork from *Quercus suber* to obtain the final material includes some industrial steps such as cleaning, disinfecting and moistening of the raw material. In its first step, the corkwood is immersed in boiling water during an hour and as result, a dark liquor which contains some corkwood extracts, such as phenolic acids, tannic fraction, 2,4,6-trichloroanisole and pentachlorophenol, is generated [13]. Specifically, the following acids have been identified by HPLC in this phenolic fraction: gallic, protocatechuic, vanillic, syringic, ferulic and ellagic, the last one in a major extent. The resulting effluent has an accumulation of these undesirable compounds, and therefore, it is obliged a frequent evacuation of the water (usually, 6–8 cork loads for each load of water). Consequently, some treatment of this effluent before its discharge into public courses is obliged, with the aim to observe the legislation on discharges imposed by the environmental authorities, which is established in 0.5 g of COD l<sup>-1</sup>; or more interesting, for its reuse in other applications in the same industrial process.

By taking into account these considerations, a research program was designed by us for the study of the removal of the organic pollutant matter present in cork processing wastewater by the use of membranes, in order to obtain an effluent useful for discharge or reuse in the same process. This program started with previous works focused on the elimination by UF membranes of some specific compounds, selected as model pollutants of the phenolic fraction, which were dissolved in ultra-pure and synthetic waters [14,15]; and continued with a research based on the application of MF and UF processes for the purification of this effluent [16]. In the present work, the overall objective was the reduction of the organic matter present in the cork processing wastewater by the combination of chemical procedures (ozonation and AOPs) and membrane processes (MF and UF), by taking advantages of both systems.

Specifically, two schemes were explored: the first one started with a single ozonation stage, and the effluent obtained was the feed for an UF process. In the second one, the first membrane filtration stage was carried out by using different MF and UF mem-

branes; and the effluent obtained was subjected to several chemical oxidation stages, by using mainly ozone, but also, UV radiation and the AOPs constituted by ozone plus UV radiation, and ozone plus hydrogen peroxide. In all the mentioned treatments, the removals of the oxidation stages and the rejection coefficients of the filtration stages were assessed on the basis of a decrease in various pollution indices of the wastewater. These selected indices were: chemical oxygen demand (COD), absorbance at 254 nm, tannins content, color, and ellagic acid. This last compound is a major pollutant in cork processing wastewater, and it was selected as a model of the numerous contaminants which are present in the phenolic fraction of this effluent.

## 2. Materials and methods

The studied wastewater was generated in a cork process industry located in the Extremadura Community (south-west of Spain). Its main physico-chemical parameters were evaluated by following the procedures described in the Standard Methods [17] and the values obtained were: pH=4.7; COD=4.40 g l<sup>-1</sup>; BOD<sub>5</sub>=1.75 g l<sup>-1</sup>; tannins content=0.897 g l<sup>-1</sup>; Absorbance at 254 nm=0.516 (after a dilution 1:100), color at 580 nm=0.157 (after a dilution 1:10), ellagic acid concentration=4.7 × 10<sup>-5</sup> M, and total suspended solids concentration=0.28 g l<sup>-1</sup>. Prior to any experiment, the wastewater was filtered through 11 μm nylon filters in order to remove suspended solids.

The chemical ozonation experiments, with and without H<sub>2</sub>O<sub>2</sub> or UV radiation, were conducted in a batch reactor which consisted of a 700 cm<sup>3</sup> cylindrical glass vessel. It was provided with a cover containing inlets for introducing the gas feed and stirring, and outlets for sampling and venting. For the ozone generation, oxygen taken from a commercial cylinder was dried with silica gel traps and introduced into an ozone generator (Sander, model 301.7). This ozone-oxygen gas stream, with a pO<sub>3</sub>=4.7 kPa (equivalent to a specific ozone dose of 0.05 mg ozone mg TOC<sup>-1</sup>), was fed to the reacting medium through a bubble gas sparger with a constant flow rate of 40 l h<sup>-1</sup> at room conditions. The ozone transfer coefficient at the working temperature was 12.3 × 10<sup>-5</sup> m s<sup>-1</sup>. All experiments were carried out at the natural pH of the wastewater, and a selected temperature of 20 °C. Once the process started, the experiment lasted around 6 h, and several samples were taken periodically to analyze the selected pollutant indices in the reacting mass: chemical oxygen demand (COD), absorbance at 254 nm (A), tannins (T), color (C), and concentration of ellagic acid (E).

In the experiments where the UV radiation was used (that is, single photochemical experiment and the AOP O<sub>3</sub>/UV), the reactor was also equipped with a radiation source located in axial position: it was a Hanau TQ150 high pressure mercury vapor lamp (nominal power 150 W) which emitted a polychromatic radiation in the range from 185 to 436 nm. Finally, in the experiment with hydrogen peroxide combined with ozone, an amount of concentrated H<sub>2</sub>O<sub>2</sub> was added to the wastewater in order to obtain the desired initial concentration of 1 × 10<sup>-3</sup> M.

On the other hand, the membrane filtration process was carried out in a tangential filtration Labscale™ TFF System

unit, manufactured by Millipore Corporation (USA), that was described in detail in previous publications [14,15]. Basically consisted of a 500 cm<sup>3</sup> acrylic feed reservoir with two pressure gauges (for the measuring of the inlet and outlet pressures), a device docking manifold, a retentate back pressure valve, and a diaphragm pump. Five commercial membranes were used in this work, which were supplied by Millipore Corporation (USA). Two of them were microfiltration Durapore™ membranes with pore sizes of 0.65 and 0.1 μm (DUR-0.65 and DUR-0.1, respectively). The three remaining membranes were ultrafiltration Biomax™ membranes, with molecular weight cut-off of 300,000 Da (BIO-300K), 10,000 Da (BIO-10K) and 5000 Da (BIO-5K). According to the manufacturer, the Durapore™ membranes were made of PVDF (polyvinylidene fluoride), and the Biomax™ membranes were made of polyethersulfone, all of them with an active surface area of 50 cm<sup>2</sup>. In these experiments, permeate and retentate streams were collected separately, and their flow rates were measured. In the permeate stream, the parameters selected (COD, A, T, C, and E) for the evaluation of the pollutant content of the effluent were also measured.

These quality parameters were analyzed as follows: the COD was determined in a Lange photometer, the absorbance and color were measured as the absorbance values at 254 and 580 nm, respectively, in a Unicam Helios β spectrometer; and the tannins content was measured by following the procedure also described in the Standard Methods [17]. On the other hand, ellagic acid was analyzed by HPLC, according to the procedure described in detail in a previous research [16]. Finally, the concentration of ozone in the gas phase was determined iodometrically [18].

### 3. Results and discussion

The efficiencies of both different treatments conducted in this study, chemical oxidations or filtration membrane processes, were established by determining the removals obtained for the following selected parameters that measured the pollutant content of the cork processing wastewater: COD, absorbance at 254 nm, tannins, color, and the model pollutant ellagic acid. Specifically for the COD, these removals were quantified in the chemical oxidation processes by the conversions  $X_{\text{COD}}$ :

$$X_{\text{COD}} = \frac{\text{COD}_0 - \text{COD}_f}{\text{COD}_0} \times 100 \quad (1)$$

where  $\text{COD}_0$  and  $\text{COD}_f$  represent the measured initial and final values of COD in any oxidation stage. Similarly, in the membrane filtration processes, the removal evaluation was made by measuring the corresponding rejection coefficient, which can be defined for the COD in the form:

$$f_{\text{COD}} = \frac{\text{COD}_F - \text{COD}_P}{\text{COD}_F} \times 100 \quad (2)$$

where  $\text{COD}_F$  and  $\text{COD}_P$  represent the COD values measured in the feed and permeate streams, respectively, in any filtration stage. Similar definition equations were applied for the remaining conversions and rejection coefficients ( $X_A$  and  $f_A$  for absorbance at 254 nm,  $X_T$  and  $f_T$  for the tannins content,  $X_C$  and  $f_C$  for color, and  $X_E$  and  $f_E$  for the model pollutant ellagic acid).

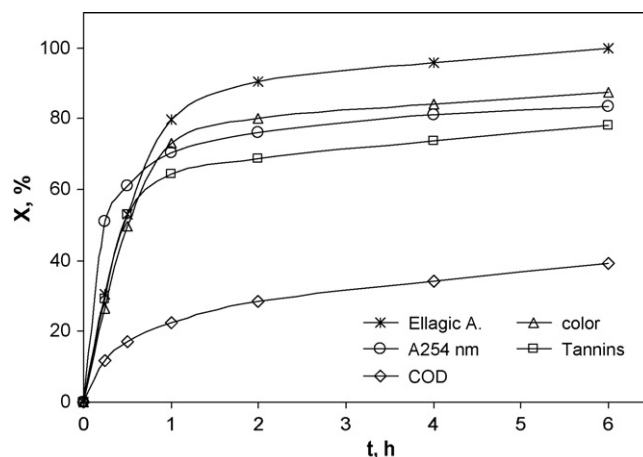


Fig. 1. Evolution of the conversions obtained during the ozonation of cork processing wastewater.

#### 3.1. Ozonation pretreatment followed by ultra-filtration membrane processes

The first stage of this combined treatment consisted in an ozonation process of the raw wastewater, during around 6 h, time enough to obtain a significant removal of the pollutant load present in this effluent. Fig. 1 shows the evolution of the conversions for the selected pollutant indices with reaction time: it is clearly observed that these conversions increased continuously with ozonation time, due to the oxidation of the organic substances by ozone. On the other hand, Table 1 summarizes the initial and final pollutant contents in this process, and the corresponding removals obtained. With the exception of the COD, most of the parameters reached a removal higher than 80%; even more, ellagic acid was almost totally eliminated from the wastewater. These generally high removal values are a consequence of the great reactivity of molecular ozone with unsaturated organic compounds, such as tannic, aromatic, and phenolic compounds [3]. Therefore, it can be concluded that ozone is an excellent oxidizing agent in the specific destruction of aromatic and tannic compounds, as well as color.

The removal for COD was 39.3% which can be considered as moderate. It is probably due to the presence of refractory substances which are oxidized but not mineralized. In effect, the organic compounds are very reactive towards ozone in general, and an ozonation process leads to oxidation products constituted by smaller molecules with less pollutant character; however, they still would need more ozone to complete their oxidation,

Table 1

Conversions obtained in the ozonation stage within the ozonation/UF combined process ( $p\text{O}_3 = 4.7 \text{ kPa}$ )

	Initial value	Final value	X (%)
COD (g l <sup>-1</sup> )	4.40	2.67	39.3
Absorbance at 254 nm	0.516	0.085	83.5
Tannins (g l <sup>-1</sup> )	0.897	0.197	78.1
Color at 580 nm	0.157	0.020	87.5
Ellagic acid (M)	$4.69 \times 10^{-5}$	D.L.	100

D.L. = concentration below the detection limit.

Table 2  
Experimental conditions applied and rejection coefficients obtained in the filtration stage within the ozonation/UF combined process

Experiment	$Q_F$ ( $l\ h^{-1}$ )	TMP (bars)	$f_{COD}$ (%)	$f_A$ (%)	$f_T$ (%)	$f_C$ (%)	$J_v$ ( $l\ h^{-1}\ m^{-2}$ )
O-BIO-5K	2.5	0.75	24.3	39.3	30.8	90.6	20.9
O-BIO-10K-1	2.5	0.75	18.2	31.4	19.4	88.9	85.9
O-BIO-10K-2	2.5	1.25	18.8	31.8	24.5	92.3	97.7
O-BIO-10K-3	2.5	1.8	19.8	33.3	25.5	93.3	107.4
O-BIO-10K-4	5.4	1.8	23.4	34.1	28.7	93.8	146.8
O-BIO-10K-5	6.8	1.8	29.4	34.5	41.3	94.7	170.8
O-BIO-300K	2.5	0.75	6.6	8.3	15.9	83.3	90.2

and therefore, they demand oxygen, leading to intermediate values of COD, as it has been observed in the treatment of other wastewater with high initial COD content [19].

The effluent of the preceding stage, with the pollutant contents depicted in Table 1, constituted the feed stream for the second stage of the process, which was based on the use of ultrafiltration membranes for the removal of the remaining organic pollutant load. In this stage, several experiments were carried out, by varying the nature of the UF membranes (BIO-300K, BIO-10K and BIO-5K, with 300, 10 and 5 kDa MWCO, respectively), the transmembrane pressures (0.75, 1.25 and 1.8 bars) and the feed flow rates (2.5, 5.4 and  $6.8\ l\ h^{-1}$ ). The experimental conditions of this group of experiments are summarized in Table 2, as well as the results obtained after 20 min of process, time enough to reach the steady state conditions in each experiment. As a result of the first stage, with total elimination of ellagic acid, this pollutant compound was not measured in this second stage.

It is interesting to establish the effect of the different operating conditions on the permeate flux  $J_v$  obtained in the experiments. Thus, the transmembrane pressure exerts a positive influence on  $J_v$ : thus, an increase in the permeate flux is observed when the transmembrane pressure is increased (Expts. O-BIO10K-1, O-BIO10K-2 and O-BIO10K-3 in Table 2). Even more, this variation of  $J_v$  with TMP seems to be almost linear, in the same way as previous researchers reported [20], which was attributed to a minor severe fouling phenomena. In effect, in the present work an important hazardous content has been eliminated in the pre-ozonation stage and compounds with lower molecular weight have been formed. Therefore, the effluent fed to the UF membrane is less contaminated, with a lower fouling effect on the membrane.

Similarly, the effect of the feed flow rate on the permeate flux is also positive; that is, an increase in  $J_v$  is deduced with the increase in  $Q_F$  at a constant TMP = 1.8 bars (Expts. O-BIO-10K-3, O-BIO-10K-4, and O-BIO-10K-5). This improvement of the permeate flux is due to the increase in the turbulence, which removed part of the fouling layer formed on the membrane surface [21,22]. The removed components were returned to the bulk of the fluid, with the subsequent decrease of the membrane fouling.

The influence of the different MWCO of the membranes on the permeate flux can be also deduced from the results depicted in Table 2. It is seen a significant increase of the permeate flux with the increase in the MWCO as could be expected, due to the

fact that the 5 kDa membrane, with a lower MWCO, presents a higher resistance to the liquid flow than the 10 kDa membrane; and the 300 kDa membrane, with the higher MWCO, presents the lower resistance to the liquid flow, and subsequently, the higher permeate flux.

The values obtained for the rejection coefficients in this group of experiments are also detailed in Table 2. In general, it must be taken into account that ozone in the previous stage oxidized the organic matter to lower molecular weight compounds which can permeate more easily through the membranes. Therefore, the rejection coefficients for COD, tannins and absorbance were rather low. Only high molecular weight compounds causing color could be retained in a major extent.

The influence of the operating variables on these rejection coefficients can also be established from these  $f$  values in Table 2. Thus, the effect of the TMP on  $f$  (Expts. O-BIO-10K-1, O-BIO-10K-2, and O-BIO-10K-3) is slightly positive, with an increase in the rejection coefficients with increasing TMP, although this increase is very low for COD and absorbance at 254 nm (almost constant values are obtained), and moderate for color and tannins. This positive effect could be explained by considering that the increase in the TMP leads to some increase of the fouling layer onto the membrane, which at the same time, obstructs the permeation of the organic molecules and increases the rejection coefficients.

On the other hand, when the feed flow rate increases (Expts. O-BIO-10K-3, O-BIO-10K-4, and O-BIO-10K-5), slight increases are also observed in the  $f$  coefficients for absorbance at 254 nm and color, and more significant increases for COD and tannins. In effect, an increase in the feed flow rate leads to a decrease in the membrane surface concentration due to the sweeping action of cross-flow, and therefore, the permeate concentration decreases. In any case, it must be remarked the high removal of color obtained in this stage, with values around 90% and higher.

The effect of the MWCO of the membranes on the rejection coefficient for the pollutant parameters in experiments performed with the three membranes, at  $Q_F = 2.5\ l\ h^{-1}$  and TMP = 0.75 bars, can be also observed in Table 2 (Expts. O-BIO-5K, O-BIO-10K-1 and O-BIO-300K). From these results, it is easily deduced that the rejection coefficients obtained were higher in the BIO-5K membrane, intermediates in the BIO-10K membrane and lower in the BIO-300K membrane, as could be expected by considering their MWCO. In effect, the BIO-5K is a membrane with lower MWCO than BIO-10K membrane;

Table 3  
Total removals (%) obtained by the ozonation/UF combined process

Experiment	COD	Absorbance (254 nm)	Tannins	Color	Ellagic acid
O-BIO-5K	51.2	90.1	85.8	98.1	100
O-BIO-10K-1	48.0	88.6	82.0	98.7	100
O-BIO-10K-2	52.1	88.8	82.0	99.4	100
O-BIO-10K-3	53.2	89.1	82.1	99.4	100
O-BIO-10K-4	56.2	88.8	82.7	99.4	100
O-BIO-10K-5	57.5	89.3	86.2	99.4	100
O-BIO-300K	42.1	85.1	82.0	98.7	100

and much lower than the highest MWCO that corresponds to the BIO-300K membrane. Thus, it is expected that a membrane with small pores (the BIO-5K) rejects a larger amount of organic load than those with larger pores (BIO-10K and BIO-300K). In general, the minimum removals were obtained for COD, intermediates for tannins and absorbance at 254 nm, and the maximum elimination took place for color.

The total effectiveness of the combined process, globally considered, can be seen in Table 3 which depicts the final values obtained for the removals of the five pollutant parameters once both stages, ozonation and UF membrane, were completed. As it is seen, almost total reduction in ellagic acid and color; high removals in tannins and absorbance at 254 nm (in the range 82–90%), and moderate removal in COD (in the range 42–57%) were reached. Two aspects must be also remarked in these results: on one hand, the membrane with lower MWCO yielded higher removals, as was discussed previously. On the other hand, and focusing in the different experiments of the second stage which were performed with the BIO-10K membrane, it can be concluded that the operating variables, transmembrane pressure and feed flow rate, exerted almost no effect on the global removals, except for COD.

Finally, it is also interesting to establish the partial contribution of the two stages individually considered to the global effectiveness of the combined process. These contributions are represented in Fig. 2 for the Expt. O-BIO-10K-4 taken as example, with similar results obtained for the remaining experiments. Thus, the first ozonation stage provided a major contribution in

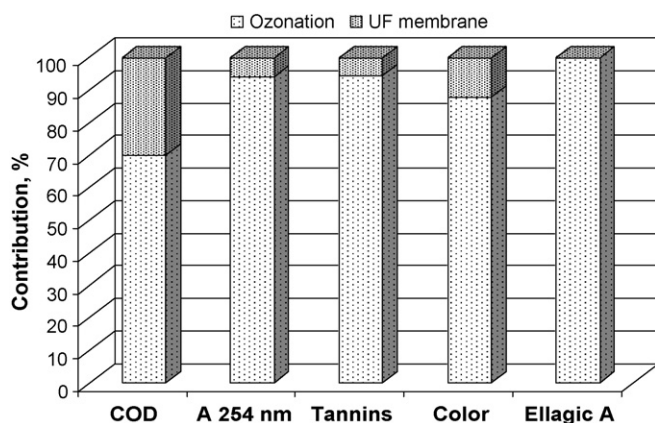


Fig. 2. Contributions of the individual stages to the global removal in the ozonation/UF membrane combined process. (Expt. O-BIO-10K-4).

the five pollutant parameters, being the only contribution in the case of ellagic acid; while the UF membrane process contributed in a less extent in the four remaining indices. Only the removal of COD during the UF stage was significant.

### 3.2. Membrane filtration pretreatment followed by chemical processes

This combined treatment started with a filtration stage that was followed by a chemical oxidation stage. In the first stage, different membranes were used: two MF membranes of 0.65 and 0.1  $\mu\text{m}$  (DUR-0.65 and DUR-0.1 membranes), and two UF membranes, which MWCO were 300 and 10 kDa (the previously used BIO-300K and BIO-10K membranes). In these experiments, the liquid feed flow rate was maintained constant at 2.5 l h<sup>-1</sup>. The effluent from these membranes filtration treatments were oxidized in a second chemical stage by using ozone. Other oxidation experiments with the effluent from the 300 kDa membrane were also conducted by using UV radiation alone, and by the Advanced Oxidation Processes constituted by ozone plus hydrogen peroxide, and ozone plus UV radiation.

Focusing in the first stage, Fig. 3 summarizes the results obtained for the rejection coefficients corresponding to the five pollutant parameters selected. Once again, the higher removals were obtained for ellagic acid and color, intermediates for absorbance at 254 nm and tannins, and lower removals for COD, with values varying from 30% for the DUR-0.65 membrane to 68% for the BIO-10K membrane. At the same time, it is clearly seen the influence of the membrane pore size on the rejection coefficients: an increase in the removal was obtained when the pore size was decreased, as it has been previously discussed in the UF stage of the previous combined process (ozonation followed by UF).

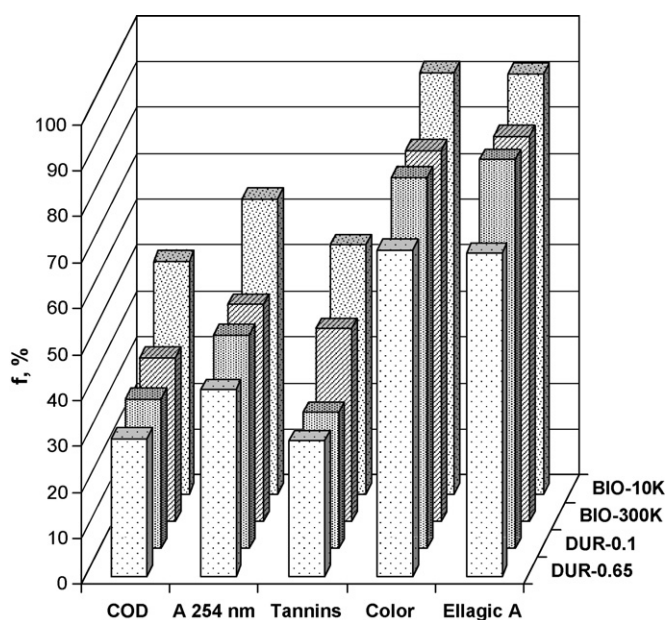


Fig. 3. Effect of the membrane MWCO on the rejection coefficients in the membrane filtration stage of the filtration/chemical oxidation combined process.

It is interesting to remark the decrease in the permeate flux in this UF stage in comparison to the filtration stage of the preozonated wastewater at the same operating conditions. In effect, the  $J_v$  obtained in Expt. BIO-10K-O (that is, filtration of the raw wastewater, without ozonation pretreatment) was  $65.71 \text{ h}^{-1} \text{ m}^{-2}$ , which is lower than the  $85.91 \text{ h}^{-1} \text{ m}^{-2}$  obtained in the filtration stage of the preozonated wastewater (see Expt. O-BIO-10K-1 in Table 2). These results demonstrate the benefits of a combined process, constituted by two successive treatments.

As was previously mentioned, the permeate stream of the preceding filtration stage, constituted the feed for the following chemical stage of the process, where several oxidation experiments were carried out by using ozone as oxidant agent, or by varying the nature of the oxidants in the effluent from the filtration process with the BIO-300K membrane. All these chemical oxidation experiments lasted 6 h.

Regarding to the experiments conducted with the permeate produced by the four membranes with ozone alone (Expts. DUR-0.65-O, DUR-0.1-O, BIO-300K-O and BIO-10K-O), it is expected a direct attack of the oxidant to the organic compounds in the form:



As Table 4 shows for these experiments, it is obtained a total removal of ellagic acid, removals higher than 90% for absorbance at 254 nm and tannins, and 78–94% for color, with almost no influence on those removals of the type of membrane used in the preceding stage. Once again, the lowest conversion values correspond to the COD content, although these removals are higher than 75% in the four experiments, which shows the high efficiency of the ozonation stage for the purification of the wastewater after the filtration stage. Even more, these removals are much higher than those obtained in the oxidation of wastewater without filtration pre-treatment (see Table 1).

An alternative chemical treatment to ozonation was proposed. For this purpose, another classic oxidant, such as UV radiation, was tested. In this case, the photochemical decomposition takes place by a direct attack of the radiation to the organic matter:



The results depicted in the Expt. BIO-300K-UV of Table 4 reveal the scarce removals obtained for the pollutant parameters in this photodecomposition stage. These low efficiency values clearly indicate that UV radiation alone is not a qualified oxidant

Table 4

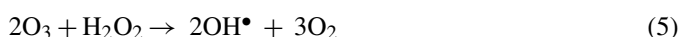
Conversions obtained in the chemical oxidation stage within the filtration/chemical oxidation combined process (ozonation time = 6 h)

Experiment	$X_{\text{COD}}$ (%)	$X_A$ (%)	$X_T$ (%)	$X_C$ (%)	$X_E$ (%)
DUR-0.65-O	74.9	96.2	90.8	93.9	100
DUR-0.1-O	74.8	95.9	95.8	78.3	100
BIO-300K-O	80.4	94.3	96.1	80.2	100
BIO-10K-O	79.3	96.1	96.5	90.9	100
BIO-300K-UV	7.5	4.7	2.2	1.0	22.0
BIO-300K-OUV	99.4	100	100	88.1	100
BIO-300K-OH	97.2	96.8	100	96.0	100

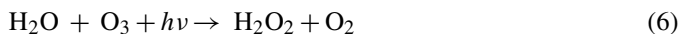
for organic matter removal, at least with the radiation source used in this research.

In order to enhance the efficiency of the ozonation treatment, the oxidation was conducted with the supplementary presence of  $\text{H}_2\text{O}_2$  or UV radiation in addition to ozone. These combinations constitute some of the Advanced Oxidation Processes mentioned in the Introduction, which generate the very reactive and oxidizing hydroxyl radicals that react with the organic matter and increase the efficiency of a single oxidant. In these cases, two reaction pathways must be taken into account [3]: a direct pathway with the attack of ozone to the organic compounds, and a radical pathway promoted by the hydroxyl radicals.

Thus, in the combination  $\text{O}_3/\text{H}_2\text{O}_2$  the hydroxyl radicals are generated by the attack of ozone to the hydrogen peroxide [23], according to the reaction:



However, in the combination  $\text{O}_3/\text{UV}$ , the OH radical generation reactions are different. Firstly, ozone absorbs UV radiation and produces hydrogen peroxide [24]:



Then, this reaction is followed by reaction (5) or by the photolysis of hydrogen peroxide which also generates hydroxyl radicals:



In any case, once the OH radicals are formed, they oxidize the organic matter through the mentioned radical pathway:



In the degradation experiments with these combinations, the evolution of the pollutant parameters with reaction time was quite similar to that of the single ozonation process as can be observed in Fig. 4 which depicts, as an example, the evolution of the COD concentration in the four chemical oxidation processes considered. The final removals obtained are

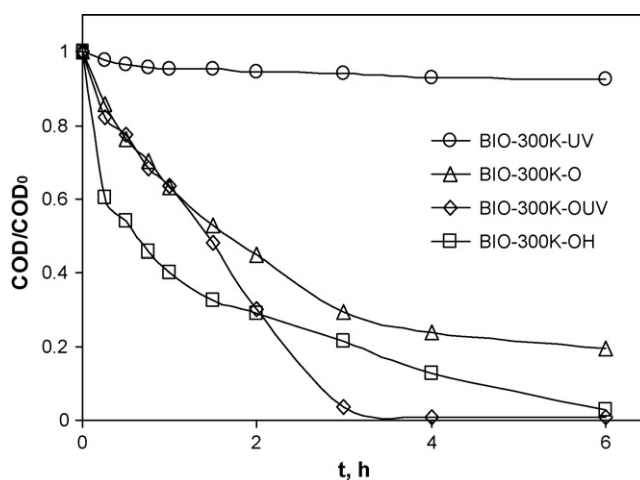


Fig. 4. Evolution of COD normalized concentration with processing time in some oxidation experiments of the filtration/chemical oxidation combined process.

Table 5  
Total removals (%) obtained by the filtration/chemical oxidation combined process

Experiment	COD	Absorbance (254 nm)	Tannins	Color	Ellagic acid
DUR-0.65-O	82.4	97.7	93.5	98.2	100
DUR-0.1-O	83.0	97.8	97.1	95.8	100
BIO-300K-O	87.4	97.0	97.8	96.2	100
BIO-10K-O	89.8	98.6	98.4	99.2	100
BIO-300K-UV	40.4	49.7	43.2	80.9	87.4
BIO-300K-OUV	99.6	100	100	97.7	100
BIO-300K-OH	98.2	98.3	100	99.2	100

also provided by Table 4, and it can be observed that the expected higher conversions of contaminants were achieved. Thus, from a  $X_{\text{COD}} = 80.4\%$  in Expt. BIO-300K-O, 99.4% and 97.2% removals were obtained in Expts. BIO-300K-OUV and BIO-300K-OH, respectively. These improvements were also obtained in the removals of the remaining pollutant parameters as Table 4 details, with total elimination in some cases. In conclusion, the generation of hydroxyl radicals due to the presence of hydrogen peroxide or UV radiation is a very effective coefficient in the elimination of organic matter pollutant present in wastewaters.

As it was explored in the previous combined process, the total effectiveness of the global combined process is shown in Table 5 which depicts the final removals obtained for the five pollutant parameters after the filtration and chemical oxidation stages were completed. The results reveal that, with the exception of the experiment conducted with UV radiation alone as oxidant agent, total elimination of ellagic acid, very high removals (more than 90%) of color, absorbance at 254 nm and tannins; and high removals (more than 80%) in COD were obtained. Additionally, the partial contribution to the global process of the two individual stages are also established and represented in Fig. 5 for the Expt. BIO-300K-O taken as example, with similar plots for the remaining experiments. As it is seen, the chemical stage provided slightly higher contributions in COD, absorbance at 254 nm and tannins elimination, while the previous UF mem-

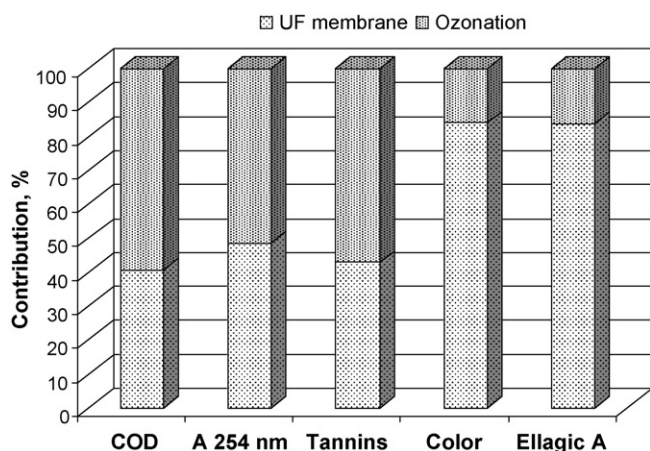


Fig. 5. Contributions of the individual stages to the global removal in the filtration/chemical oxidation combined process. (Expt. BIO-300K-O).

brane stage contributed in a major extent to the elimination of color and ellagic acid.

#### 4. Conclusions

The ozonation pre-treatment of the cork processing wastewater yielded a total removal of ellagic acid; elimination of absorbance at 254 nm, tannins and color in the range 80–90% and moderate removal of COD around 40%. The effluent from this ozonation stage was subjected to a filtration stage by means of UF membranes with different MWCO (5, 10 and 300 kDa), which yielded higher rejection coefficients with the decrease in the pore size of the membranes. In experiments with the same membrane (BIO-10K), the permeate flux increased with the increase in the transmembrane pressure and feed flow rate. At the same time, slight increases were observed in the rejection coefficients when both operating variables were increased. The global ozonation plus UF membranes combined process reached almost total reduction in ellagic acid and color, 90% reduction in absorbance at 254 nm, reduction higher than 80% in tannins, and COD reduction that varied from 42 to 57%.

In the opposite combination, the filtration pre-treatment with MF and UF membranes reached high rejection coefficients for ellagic acid and color, intermediates for absorbance and tannins, and lower for COD. Once again, an increase in these rejection coefficients was obtained when the pore size decreased. The following chemical stage individually considered, revealed a high efficiency in the removal of the several indices when ozone alone was used (100% for ellagic acid, higher removals than 90% for absorbance at 254 nm and tannins, higher than 80% reduction for color, and 75–80% removal for COD). These removal values were increased by the AOPs  $\text{O}_3/\text{UV}$  and  $\text{O}_3/\text{H}_2\text{O}_2$ , while very low efficiencies were reached in the case of UV radiation alone. The global combined process, with the exception of the photochemical experiment, reached total elimination of ellagic acid, more than 90% elimination in color, absorbance at 254 nm and tannins, and more than 80% removal in COD, which indicates a great destruction power of this combination. Moreover, the almost disappearance of the initial dark color of this wastewater improved the organoleptic characteristics of the final effluent. From the global results obtained (see Tables 3 and 5) it can be proposed that the combined process constituted by an UF pretreatment, followed by a chemical treatment based on the use of ozone plus UV radiation or hydrogen peroxide, seems to be the most effective process, with almost total removal of the five standard pollutant parameters considered. In conclusion, the application of membrane filtration procedures followed by conventional ozonation or ozone-related AOPs to the cork processing wastewater generates an effluent which can be discharged into public effluent or used in different applications in the same industrial plant. Even more, it could be reused in the boilers in conjunction with further treatment, targeted to tainted volatile compounds elimination.

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