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BOOK OF ABSTRACTS

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Catalytic wet air oxidation of olive mill wastewater

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Abstract The objective of this work was to study the suitability of catalytic wet air oxidation (CWAO) for the treatment of olive mill wastewater (OMW). Accordingly, experiments were performed in a high pressure reactor at 100ºC and 200ºC under an oxygen partial pressure of 6.9 bar, using carbon supported platinum (1wt.% Pt) and iridium (5 wt.% Ir) catalysts prepared by incipient wetness impregnation. Both catalytic systems showed a very high activity in the total organic carbon (TOC) removal of the effluent, an increase in TOC removal relatively to non-CWAO being observed. At 200ºC, complete TOC and colour removal was obtained with the Pt/C catalyst after 8 h of reaction. At 100ºC, the results indicate that a certain fraction of compounds in the effluent (low molecular weight recalcitrant carboxylic acids) could not be removed even after prolonged reaction time. A kinetic model was developed taking into account catalytic and non-catalytic reaction, formation of refractory compounds and catalyst deactivation. A very good agreement between the model results and the CWAO experimental data at 200ºC was found. The results obtained in this work indicate that Pt/C is a promising catalyst for the CWAO of OMW.

Keywords carbon supported catalysts; catalytic wet air oxidation; olive mill wastewater; platinum and iridium catalysts; wastewater treatment

Introduction

In the Mediterranean countries, mainly in Spain, Italy, Greece and Portugal, olive oil production is an activity with a strong economic impact. Olive processing is mainly carried out in widespread small to medium sized facilities, using the traditional press method or the continuous three phase centrifugation process, which generate large amounts of wastewater (3.25 m^3/t of olive oil produced in the traditional mills and 5 m^3/t of olive oil produced in the centrifugal mills (Kapellakis et al., 2006)), characterized by high loads of chemical oxygen demand (above 40 g/L) and strong dark brown color (Azbar et al., 2004). In the last years, the average annual olive mill wastewater (OMW) production rose to more than 7 Mt/year in the Mediterranean countries, accounting for more than 95% of world OMW generation (Kapellakis et al., 2006). OMW contain a large diversity of organic compounds (including phenols, polyphenols and polyalcohols) with low biodegradability and toxicity (Aktas et al., 2001; Ben Sassi et al., 2006). Recently, the Mediterranean countries faced changes in their national legislation regarding treatment and disposal of OMW. In Portugal, governmental legislation was issued in 2000, obliging all olive oil processing plants to treat their effluents before discharge (Despacho Conjunto nº 118/2000, 2000), otherwise they were not allowed to operate. As a result, in the last few years, there has been a great effort to develop efficient treatment solutions for OMW. Biological treatments are ineffective in practice, but when combined with chemical or physical processes the reduction of the OMW pollution parameters can be drastically improved (Bressan et al., 2004; Fiorentino et al., 2004). Other solutions, such as advanced oxidation processes and/or physico-chemical processes, have also been developed. Some examples include Fenton treatment (Nasr et al., 2004; Vlyssides et al., 2004), ozonation (Ahmed et al., 2005), ultra-filtration and photo-peroxidation techniques (Drouiche et al., 2004), electrochemical oxidation (Panizza and Cerisola, 2006), electrocoagulation (Adhoum and Monser, 2004) and electro-Fenton oxidation (Khoufi et al., 2004). To our knowledge, there are only a few studies which involve wet air oxidation technologies (catalytic (CWAO) or non-catalytic (WAO)) to treat OMW (Rivas et al., 2001; Minh et al., 2006), although they seem to be very good options, because the concentrations of OMW are too high for biological treatment and too diluted for incineration.

WAO consists in the total oxidation of the organic species present in the effluent to CO_2 and H_2O at relatively high temperatures and pressures (220-320ºC, 50-200 bar), using oxygen or air as the oxidising source. WAO has been used previously for the treatment of several types of wastewater (Chen et al., 2000; Verenich et al., 2000; Hu et al., 2001; Verenich et al., 2004). Although very efficient, WAO implies high capital costs and safety issues, mainly due to material corrosion, which requires the construction of WAO units with high nickel content alloys, much more expensive than common stainless steel, and high thickness, in order to support the high pressures involved. To reduce process conditions to more amenable values (125-220ºC, 5-50 bar), suitable catalysts can be introduced. Several catalysts were studied in the last decades. Copper salts are very efficient homogeneous catalysts for the oxidation of organic model compounds (Imamura et al., 1982; Imamura, 1999), but their use in wastewater treatment requires a further step in the process, such as precipitation or membrane separation, in order to remove them from the treated effluents. As they can be easily removed by filtration from the treated solution, heterogeneous catalysts presenting a very high activity and stability has been sought over the last years (An et al., 2001; Liu et al., 2001; Lin et al., 2002; Cao et al., 2003; Pintar et al., 2004; Yang et al., 2004). Good catalytic systems were found and used for the oxidation of model compounds (mainly phenol and carboxylic acids) as well for the oxidation of wastewater. In this work we used Pt/C and Ir/C catalysts to study the degradation of an OMW by CWAO, because we have previously demonstrated their excellent activity and stability in the oxidation of low molecular weight carboxylic acids (Gomes et al., 2000, 2002a, b, 2004), organic compounds which are very refractory to oxidation, and normally found as end products of the oxidative degradation of several types of wastewater (Belkacemi et al., 2000; Zhu et al., 2002).

The catalytic results obtained were fitted with a kinetic model which takes into consideration catalytic and non-catalytic oxidation, catalyst deactivation and formation of inhibitory organic compounds. The heterogeneous contribution was included considering a Langmuir-Hinshelwood approach and the oxidation reactions taking place in the adsorbed state between the organic compounds present in the OMW and dissociatively adsorbed oxygen.

Methods

Olive Mill Wastewater

The OMW used in this work was collected from an olive oil processing plant near Vila Real in the North of Portugal, operating with the traditional press method. It has a strong orange color and a TOC of 15 g/L. Before performing WAO/CWAO tests, the OMW was filtered, diluted 10 times with distilled water and stored at -15ºC in several plastic cans. For each reaction, a new frozen sample was used in order to avoid initial composition discrepancies between them.

Oxidation Procedure

The oxidation reactions were performed in a 160 mL, 316 stainless steel high pressure reactor (model 4564, Parr Instrument Co. Ltd., Illinois, USA) equipped with a magnetically driven stirrer and a thermocouple. The reactor was heated by an electrical heating mantle controlled by a temperature controller unit (model PID 4842, Parr Instrument Co. Ltd., Illinois, USA).

Typically, in an oxidation run, 70 mL of the wastewater and 1 g of catalyst (for CWAO runs) were placed inside the reactor. After flushing with N_2 in order to remove dissolved oxygen, the reactor was heated to the desired reaction temperature (100ºC or 200ºC). Pressurization with air was then completed (6.9 bar of oxygen partial pressure) and time zero of reaction was considered. Periodically, samples of 1 mL were withdrawn from the reactor to be further analyzed for TOC determination in a TOC analyzer (Shimadzu 5500A). This equipment determines in separate runs the sample total carbon (TC) by combustion over a Pt catalyst bed at 700ºC and the total inorganic carbon (TIC) by sample treatment with phosphoric acid. TOC is obtained by subtracting TIC from TC. Three reproducible runs (< 2%) were considered.

Catalyst Preparation

For catalyst preparation, the commercial activated carbon Norit ROX 0.8 in pellet form, washed with hot hydrochloric acid in order to remove mineral impurities, was used as support (ROX). The BET surface area (S_{BET}), the microporous volume (V_{μ}) and the mesoporous surface area (S_{Meso}) of ROX were calculated by analysis of the corresponding N_2 adsorption isotherm at 77 K, measured in a Coulter Omnisorp 100CX and shown in Table 1.1.

Platinum (1 wt.% Pt) and iridium (5 wt.% Ir) catalysts supported on ROX were prepared by incipient wetness impregnation, using aqueous solutions of the metal precursors H_2PtCl_6 and $(NH_4)_3IrCl_6$, respectively. After impregnation, the materials were dried overnight at 110ºC. Prior to reaction the catalysts were heat treated under helium flow at 400ºC for 2 h, reduced in hydrogen/helium flow at 350ºC for 3 h and flushed in helium flow at 350ºC for 30 min in order to remove physisorbed hydrogen. The textural characterization of the prepared catalysts is also shown in Table 1.1. More detailed characterization was published elsewhere (Gomes et al., 2000, 2002a, b, 2004). Analysis of Table 1.1 shows that the materials have similar texture.

Table 1.1 Textural characterization of the prepared catalysts and of the corresponding support

	S_{BET} (m^2/g)	S_{Meso} (m^2/g)	V_μ (cm^3/g)
Support (ROX)	1053	113	0.405
Pt/C	1064	125	0.409
Ir/C	1007	104	0.385

Results and discussion

Oxidation Reactions

The oxidation studies carried out with the OMW samples were performed at two different temperatures, 100ºC and 200ºC, at an oxygen partial pressure of 6.9 bar. The results obtained are shown in Figure 1.1 and Table 1.2.

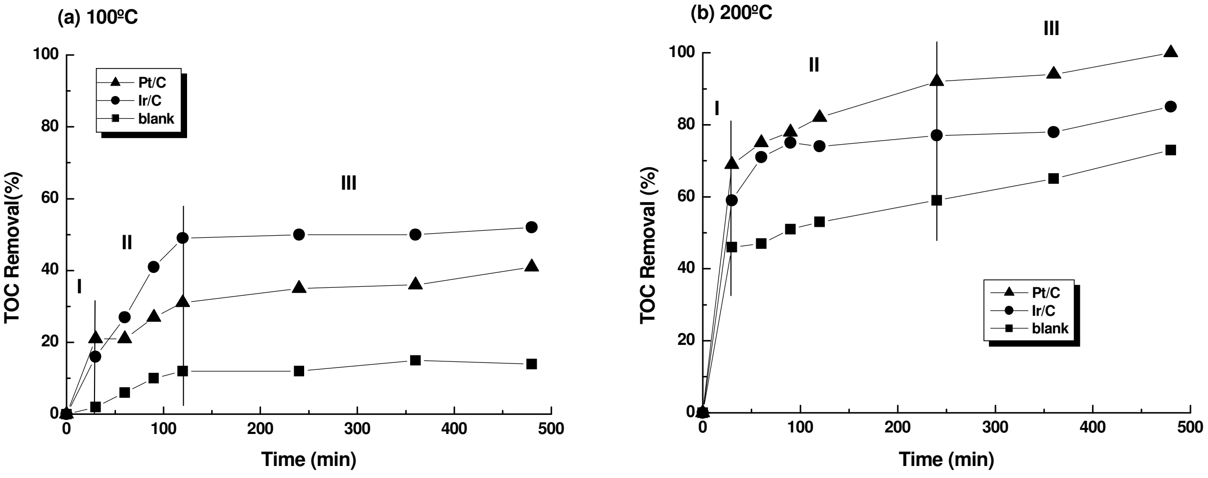

Figure 1.1 TOC removal curves for the WAO/CWAO of OMW samples at 6.9 bar of oxygen partial pressure and (a) 100ºC (b) 200ºC

It can be observed from Figure 1.1 and Table 1.2 that the non catalytic wet air oxidation of the OMW cannot be neglected. TOC removal increases with temperature, as expected, values of 12% and 53% being obtained after 2 h of reaction (14% and 73% after 8 h) for the experiments performed at 100ºC and 200ºC, respectively. The significant removal of organic matter observed in the experiments performed without any catalyst indicates that the OMW contains a large fraction of organic compounds which are easily mineralized to non-organic compounds, such as CO_2 and H_2O. However, the most recalcitrant and non-biodegradable compounds are expected to still remain in the treated solution, even after 8 h of reaction at 200ºC, thus requiring the use of suitable catalysts to promote their degradation.

With the introduction of Pt/C or Ir/C catalysts in the system (1 g), the TOC removal observed at 100ºC and 200ºC is increased when compared to the non catalytic values, thus proving their good catalytic efficiency and suitability to degrade OMW by CWAO. It is also observed that the sequence in catalyst activity is reversed depending on the reaction temperature. At 100ºC, the Ir/C catalyst is more active than the Pt/C catalyst, whilst at 200ºC the reverse occurs. The oxygen solubility at 100ºC is 40% lower than the oxygen solubility at 200ºC (Mathias, 1993; Belkacemi et al., 1999). The explanation for the reversal in relative activity with temperature resides in the reduction potential of the metals. As the reduction potential of iridium is lower than the reduction potential of platinum, iridium has more propensity for oxygen adsorption. In previous work (Gomes et al., 2004) dealing with the CWAO of butyric acid solutions, it was shown that this higher affinity leads to higher deactivation on Ir/C catalysts in contact with an excess of oxygen, when compared with the deactivation observed on Pt/C catalysts at 200ºC. Although the activity observed for both catalysts at 100ºC is lower than at 200ºC, the iridium catalyst has higher activity than platinum, because less oxygen is available in solution to deactivate the metal by over-oxidation. This leads to the conclusion that iridium catalysts have higher intrinsic activity than platinum catalysts, but that Ir is affected by deactivation due to oxygen poisoning, when high reaction temperatures and excess oxygen concentration are used. Accordingly, choosing between iridium or platinum catalysts for CWAO treatment should also take into consideration the reaction conditions to be employed.

Table 1.2 Results obtained in the WAO/CWAO of OMW samples

Temperature (ºC)	Catalyst	TOC removal (%) after 2 h	TOC removal (%) after 8 h
100	Pt/C	31	41
	Ir/C	49	52
	blank	12	14
200	Pt/C	82	100
	Ir/C	74	85
	blank	53	73

The TOC removal values obtained with the platinum and with the iridium catalysts after 2 h of reaction are, respectively, 31% and 49% at 100ºC (41% and 52% after 8 h) and 82% and 74% at 200ºC (100% and 85% after 8 h). Complete TOC removal was obtained at 200ºC after 8 h of reaction with the Pt/C catalyst. During the catalytic experiments at 200ºC, the initial strong orange color observed in the OMW disappeared, non coloured solutions being obtained after 8 h of reaction, contrarily to what was observed in the experiments performed without any catalyst. Therefore, it may be concluded that the organic compounds responsible for the OMW colour can only be destroyed by chemical oxidation at the given conditions, if suitable catalysts are used.

Taking a closer look at the TOC removal curves of Figure 1.1 we can divide them into three distinct regions. In the first region (first 30 minutes of reaction), there is a sharp TOC removal, particularly noticed at 200ºC (between 45% and 70% TOC removal), corresponding to the decomposition of large organic molecules, either directly to the final mineralization products, CO_2 and H_2O, or into smaller intermediates, also easily oxidizable to CO_2 and H_2O. In the second region (30 to 120-240 minutes of reaction), the TOC decrease is very slight, due to degradation of smaller intermediates into refractory compounds, such as carboxylic acids, which cause an inhibition effect on the reaction. Depending on the reaction conditions, the TOC removal in this stage is around 10-20% of the original value, a residual TOC which is not significantly changed (third region) being observed. In the third region (above 120-240 minutes of reaction), there are only refractory organic compounds, like low molecular weight carboxylic acids which are not further oxidized (Mantzavinos et al., 1996; Hu et al., 2001), a plateau being observed. This inhibition effect is particularly evidenced at 100ºC, because at this temperature, the catalysts used are expected to be completely inactive for carboxylic acids degradation (Gomes et al., 2000, 2002b). A possible mechanism involving the above mentioned steps is that presented in Figure 1.2.

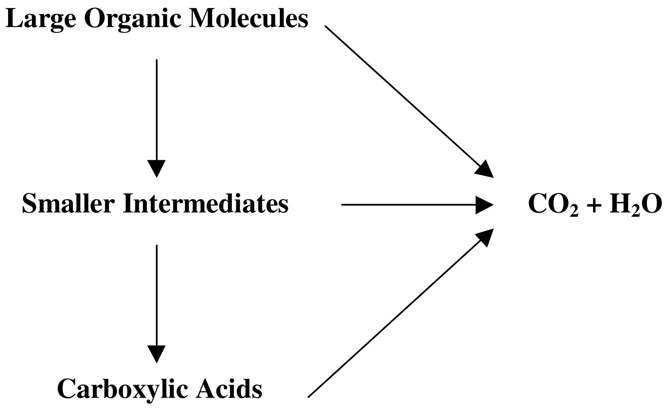

Figure 1.2 Reaction mechanism expected for OMW oxidation

Kinetic Model

Based in the above mentioned observations, a kinetic model was developed to fit the catalytic results obtained in the degradation of the OMW at 200ºC and 6.9 bar of oxygen partial pressure, these being the reaction conditions with more practical interest due to the excellent performance obtained with the platinum and iridium catalyts, which can be further explored to evaluate the CWAO technological implementation viability. Due to the complex wastewater composition, a lumped parameter TOC was used in order to describe the organic compounds concentration evolution during the reaction. The detailed mechanism for the process is extremely difficult to obtain and in practice it has little utility (Rostrup-Nielsen, 2000). As observed in Figure 1.1, the effluent TOC reduction, which is high at the beginning of reaction, decreases strongly due to the formation of organic compounds which are very refractory to further oxidation, a plateau being observed in the TOC removal curves after 240 minutes of reaction time. The proposed model takes into consideration catalyst deactivation and the TOC removal rate reduction due to the increasing inhibition due to the formation of refractory compounds, such as low molecular weight carboxylic acids. The inhibition character of these compounds was described by an inhibition function τ (Belkacemi et al., 1999).

Since it was observed that the non-catalytic organic matter content removal cannot be neglected, it was considered that the organic compounds present in the effluent were degraded by non catalytic oxidation (rate constant k_{hom}) and by catalytic oxidation (rate constant k_{het}), final products CO_2, H_2O and refractory organic compounds, being obtained.

A Langmuir-Hinshelwood approach was adopted to describe the proposed reaction-deactivation scheme. It was considered that the reaction occurs in the adsorbed state between the organic compounds present in the effluent and oxygen dissociatively adsorbed, characterized by adsorption constants K_{TOC} and K_{O2}, respectively. Catalyst deactivation is introduced considering an empirical deactivation function α, defined as the ratio between the number of active sites available on the catalyst at time t of reaction and the number of active sites available before the reaction starts. With these assumptions, the effluent oxidation reactions can be described by the following set of equations:

$$-\frac{d[TOC]}{dt} = k_{hom}[TOC]\tau + \frac{W.k_{het}K_{TOC}[TOC]\sqrt{K_{O_2}[O_2]}}{\left(1+K_{TOC}[TOC]+\sqrt{K_{O_2}[O_2]}\right)^2}\alpha \qquad (1)$$

$$\tau = 1 - [TOC]_\infty/[TOC] \qquad (2)$$

$$\alpha = e^{-kt} \qquad (3)$$

where

K_{TOC} – global equilibrium adsorption constant of the organic compounds found in the effluent ($L.mg^{-1}$)
K_{O2} – O_2 adsorption equilibrium constant ($L.mmol^{-1}$)
k_{hom} – homogeneous reaction rate constant (h^{-1})
k_{het} – heterogeneous reaction rate constant ($mg.h^{-1}.g_M^{-1}$)
$[TOC]$ – total organic carbon ($mg.L^{-1}$)
$[TOC]_\infty$ - residual total organic carbon ($mg.L^{-1}$)
$[O_2]$ – liquid phase oxygen concentration ($mmol.L^{-1}$)
k – catalyst deactivation constant (h^{-1})
W – metal concentration ($g_M.L^{-1}$)
τ - inhibition function
α - deactivation function
t – reaction time (h)

The oxygen concentration in the liquid phase at 200ºC is expressed as a function of the oxygen partial pressure (in bar) by equation (4) as deduced from results taken from the literature (Belkacemi et al., 2000). Considering ideal behavior for the gas phase we can obtain a relationship between the oxygen concentration in liquid and gas phases (equation (5)). The concentration in the gaseous phase is obtained from the oxygen mass balance, equation (7), considering a total oxidation stoichiometry of one mole of O_2 to one mole of organic carbon present in the effluent (equation (6)).

$$[O_2] = 1.34314P_{O2} \qquad (4)$$

$$[O_2] = 0.0521[O_2]_g \qquad (5)$$

$$C + O_2 \rightarrow CO_2 \qquad (6)$$

$$[O_2]_g V_g = [O_2]_{g0} V_g - ([TOC]_0 - [TOC])V_l/12 \qquad (7)$$

In the above equations, P_{O2}, $[O_2]_g$, and $[O_2]_{g0}$, represent the oxygen partial pressure (in bar), concentration and initial concentration (in $mmol.L^{-1}$) in the gas phase, respectively, V_g, the gas phase volume (in L) and V_l, the liquid phase volume (in L). Based in equations (1) to (7) a numeric model was formulated and solved with the program MATLAB, defining as objective function $fobj = \sum_t \left([TOC]_t - \overline{[TOC]}_t\right)^2$, where $[TOC]_t$ and $\overline{[TOC]}_t$ represent the experimental and calculated total organic carbon concentrations of the reaction mixture at instant t, respectively. The optimization was performed by using the routine fmins, which uses a Nelder-Mead type simplex search method. To solve the rate law equation (1), the routine ODE23 was implemented, a 2nd and 3rd order Runge-Kutta method being applied. Fitting the experimental data with the model, the results shown in Figure 1.3 were obtained. A good agreement between model and the catalytic experimental results at 200ºC was observed.

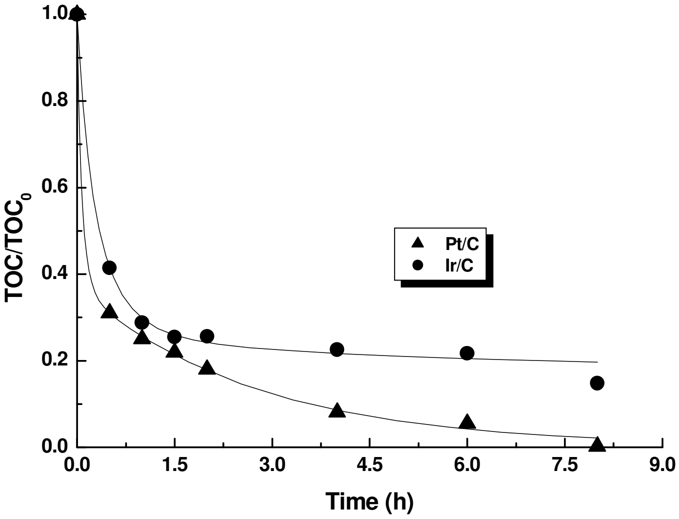

Figure 1.3 Results obtained with the developed model fitting to the CWAO experimental data at 200ºC and 6.9 bar of oxygen partial pressure

From the fitting procedure, the parameters involved in the model were obtained, which are collected in Table 1.3. The 95% confidence interval, estimated numerically by a mathematical routine of MATLAB software named nlparci, is also given for all the calculated parameters.

Table 1.3 Model parameters obtained in the CWAO of an OMW with Pt/C and Ir/C catalysts at 200ºC and 6.9 bar of oxygen partial pressure

Catalyst	k_{hom} (h^{-1})	k_{het} (mg.h^{-1}.g$_M^{-1}$)	K_{TOC} (L.mg^{-1})	K_{O2} (L.mmol^{-1})
Pt/C	0.37±0.02	(2.20±0.06)x10^{9}	(1.10±0.03)x10^{-5}	(6.7±0.3)x10^{-8}
Ir/C	0.3±0.1	(2±2)x10^{8}	(2.0±0.1)x10^{-5}	(2.4±0.1)x10^{-7}

Analyzing the magnitude of the parameters obtained we can conclude that the Pt/C catalyst is more active than the Ir/C catalyst at 200ºC and 6.9 bar of oxygen partial pressure, based on the heterogeneous reaction rate constants (2.20x10^{9} mg.h^{-1}.g$_{Pt}^{-1}$ for the Pt/C catalyst and 2x10^{8} mg.h^{-1}.g$_{Ir}^{-1}$ for the Ir/C catalyst). Observing the oxygen adsorption equilibrium constants we can conclude that O_2 adsorption has a very important role in the mechanism of oxidation when using Ir/C, relatively to catalyst Pt/C (6.7x10^{-8} L.mmol^{-1} in the Pt/C catalyst and 2.4x10^{-7} L.mmol^{-1} in the Ir/C catalyst). This result was expected, taking into account the high reduction potential of platinum, which make it less prone to oxygen adsorption. In previous work on the CWAO of butyric acid at the same reaction conditions, the Pt/C catalyst was shown to have higher long term deactivation resistance than the Ir/C catalyst (Gomes et al., 2004). The deactivation of the latter was attributed to over-oxidation of iridium by oxygen.

The results obtained in this work show that CWAO is a promising technology to treat OMW and encourage future research studies on this subject. This type of effluent contains organic compounds of high toxicity and low biodegradability, such as phenols, polyphenols and polyalcohols, which explains the lack of a well stablished technology for their treatment. Complete removal of the organic matter was obtained with the Pt/C catalyst. The kinetic results can be used to design CWAO reactors for the specified conditions and to study the economical viability of this technology in the treatment of OMW, an issue of great importance in Mediterranean countries.

Conclusions

The Pt/C and Ir/C catalysts prepared by incipient wetness impregnation showed a very high efficiency for the catalytic wet air oxidation of an olive mill wastewater. Complete removal of the organic matter and colour present in the effluent was obtained at 200ºC and 6.9 bar of oxygen partial pressure with the Pt/C catalyst after 8 h of reaction. As the degradation rate obtained with the Pt/C catalyst under these conditions is very high, the CWAO of olive mill wastewater seems environmentally attractive. The low concentration of organics in the final treated effluents allows their reuse in the process, with a better process waters management and better environmental impact. A kinetic model was developed considering the contribution of homogeneous and heterogeneous reactions, oxidation reaction inhibition due to refractory organic compounds formation and catalyst deactivation due to oxygen poisoning. The model fits very well the experimental data at 200ºC, and should allow further studies on the economical viability of this technology in the treatment of olive mill wastewater.

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