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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). Experiments were performed in a high pressure reactor at 100 and 200 °C under an oxygen partial pressure of 6.9 bar, using carbon supported platinum (1 wt.% Pt) and iridium (5 wt.% Ir) catalysts prepared by incipient wetness impregnation. At 100 °C, refractory organic compounds persisted even after prolonged reaction time (8 h). At 200 °C, complete total organic carbon and colour removal was obtained with the Pt/C catalyst after 8 h of reaction. A kinetic model was developed taking into account catalytic and non-catalytic reactions, formation of refractory compounds and catalyst deactivation. Very good agreement between the proposed model and CWAO experimental data at 200 °C 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

1. 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 primarily 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 $m^3\ t^{-1}$ of olive oil produced in the traditional mills and 5 $m^3\ t^{-1}$ of olive oil produced in the centrifugal mills [1]), characterized by high loads of chemical oxygen demand (above 40 $g\ L^{-1}$) and strong dark brown colour [2]. In recent years, the average annual olive mill wastewater (OMW) production rose to more than 7 Mt $year^{-1}$ in the Mediterranean countries, accounting for more than 95% of world OMW generation [1]. OMW contain a large diversity of organic compounds (including phenols, polyphenols and polyalcohols) with low biodegradability and high toxicity [3,4], which may explain the lack of a well-established technology for their treatment. However, recently, the Mediterranean countries faced changes in their national legislation regarding treatment and disposal of OMW. After year 2000, some countries (like Portugal [5]) issued new legislation forcing all olive oil processing plants to treat their effluents before discharge, in order to be allowed to operate. As a result, in the last few years, there has been a great effort to develop efficient solutions for the treatment of 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 [6,7]. Other solutions, such as advanced oxidation processes and/or physico-chemical processes, have also been developed. Some examples include Fenton treatment [8,9], ozonation [10], ultra-filtration and photo-peroxidation techniques [11], electrochemical oxidation [12], electrocoagulation [13] and electro-Fenton oxidation [14]. To our knowledge, there are only a few studies which involve wet air oxidation technologies (catalytic or non-catalytic) to treat OMW [15,16], although they seem to be very promising, given the stream concentrations, which are too high for biological treatment and too low for incineration.

Wet air oxidation (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 (220–320 °C, 50–200 bar), using oxygen or air as the oxidising source. WAO has

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been used previously for the treatment of several types of wastewater [17–20]. 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 large thickness, in order to support the high pressures involved. To reduce process conditions to more amenable values (125–220 °C, 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 [21,22], 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. Heterogeneous catalysts presenting very high activity and stability have been developed over the last years [23–28], since they can be easily removed by filtration from the treated solution. Good catalytic systems were found and used for the oxidation of model compounds (mainly phenol and carboxylic acids) as well for the degradation of wastewater. In this work we used Pt/C and Ir/C catalysts to study the degradation of an OMW by catalytic wet air oxidation (CWAO), because we have previously demonstrated their excellent activity and stability in the oxidation of low molecular weight carboxylic acids [29–32], organic compounds which are very refractory to oxidation, and normally found as end products of the oxidative degradation of several types of wastewater [33,34].

The catalytic results obtained were fitted with a kinetic model which takes into consideration catalytic and non-catalytic oxidation, catalyst deactivation and formation of inhibiting organic compounds. The heterogeneous contribution was included by 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.

2. Experimental

2.1. 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 a continuous three-phase centrifugation process. The detailed characterization of the OMW (which presents a strong orange colour) was published elsewhere [35] and reproduced in Table 1 for the readers' convenience. Before performing WAO/CWAO tests, the OMW was filtered, diluted 10 times with distilled water and stored at −15 °C in plastic cans. After these procedures, the OMW chemical oxygen demand was reduced to 2.8 g L^{-1} [35]. For each reaction, a new frozen sample was used in order to avoid initial composition discrepancies between them.

Table 1
Physico-chemical characterization of the studied OMW (reproduced from Ref. [35])

Parameter	Value
pH	4.3
BOD	10.2 g L^{-1}
COD	60.5 g L^{-1}
Suspended solids	6.8 g L^{-1}
Phenols	0.56 g L^{-1}
BOD/COD	0.17

2.2. 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, 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 (100 or 200 °C). 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 the sample total carbon (TC) by combustion over a Pt catalyst bed at 700 °C and, in a separate run, 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.

2.3. 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 are shown in Table 2.

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 110 °C. Prior to reaction, the catalysts were heat treated under helium flow at 400 °C for 2 h, reduced in hydrogen/helium flow at 350 °C for 3 h and flushed in helium flow at 350 °C for 30 min in order to remove physisorbed hydrogen. The textural properties of the prepared

Table 2
Textural characterization of the prepared catalysts and of the corresponding support

	S_{BET} ($m^2\,g^{-1}$)	S_{Meso} ($m^2\,g^{-1}$)	V_{μ} ($cm^3\,g^{-1}$)
Support (ROX)	1053	113	0.405
Pt/C	1064	125	0.409
Ir/C	1007	104	0.385

catalysts are also shown in Table 2. More detailed characterization was published elsewhere [29–32]. Analysis of Table 2 shows that the materials have similar texture.

3. Results and discussion

3.1. Oxidation reactions

The oxidation studies carried out with the OMW samples were performed at two different temperatures, 100 and 200 °C, at an oxygen partial pressure of 6.9 bar. The percentage of TOC removal as a function of time is shown in Fig. 1 for the non-catalytic process and in the presence of different catalysts.

From Fig. 1 it is clear that the non-catalytic wet air oxidation of the OMW cannot be neglected. As expected, TOC removal increases with temperature when going from 100 to 200 °C: an increase from 12% to 53% is observed after 2 h of reaction and from 14% to 73% after 8 h. 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, mainly CO_2 and H_2O. However, the most recalcitrant compounds are expected to remain in the treated solution, even after 8 h of reaction at 200 °C, thus requiring the use of suitable catalysts to promote their degradation.

With the introduction of Pt/C or Ir/C catalysts in the system, the TOC removal observed at 100 and 200 °C is increased when compared to the non-catalytic values, thus proving the catalysts good efficiency and suitability to treat OMW by CWAO. It may also be observed that the sequence in catalyst activity is reversed depending on the reaction temperature. At 100 °C, the Ir/C catalyst is more active than the Pt/C catalyst, while the reverse occurs at 200 °C. The explanation for this reversal in relative activity with temperature resides in the reduction potential of the metals ($E^0_{\mathrm{IrO_2/Ir}} = 0.926\,\mathrm{V}$, $E^0_{\mathrm{Ir_2O_3/Ir}} = 0.926\,\mathrm{V}$ and $E^0_{\mathrm{PtO/Pt}} = 0.980\,\mathrm{V}$) [36]. As the reduction potential of iridium is lower than the reduction potential of platinum, iridium has more propensity for surface oxygen adsorption. In previous work [32] dealing with the CWAO of butyric acid solutions, it was shown that this higher affinity to oxygen leads to higher deactivation of Ir/C catalysts in contact with an excess of oxygen, when compared to the deactivation observed with Pt/C catalysts at 200 °C. Taking into consideration that the oxygen solubility at 100 °C is 40% lower than the oxygen solubility at 200 °C [37,38], in spite of the activity observed for both catalysts at 100 °C being lower than at 200 °C, the iridium catalyst is more active than platinum, because less oxygen is available in solution to deactivate the metal by over-oxidation (irreversible oxygen adsorption at the metal surface). 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 concentrations are used. Accordingly, the choice between iridium and platinum catalysts for CWAO treatment should also take into consideration the reaction conditions to be employed.

The TOC removal values obtained with the platinum and with the iridium catalysts after 2 h of reaction are, respectively, 31% and 49% at 100 °C (41% and 52% after 8 h) and 82% and 74% at 200 °C (100% and 85% after 8 h). Complete TOC removal was obtained at 200 °C after 8 h of reaction with the Pt/C catalyst. During the catalytic experiments at 200 °C, the initial strong orange colour observed in the OMW disappeared, colourless 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 Fig. 1, they can be divided into three distinct regions, each corresponding to predominant reaction steps (although occurring simultaneously with other reaction steps), as shown in Fig. 2. In the first region (first 30 min of reaction), there is a sharp TOC removal, more pronounced at 200 °C (between 45% and 70% TOC removal), corresponding to the decomposition of large organic molecules (maybe aromatic compounds), either directly to the final mineralization products, CO_2 and H_2O, or into smaller intermediates, some of them also easily oxidizable to CO_2 and H_2O. In the second region (30–120 min at 100 °C or to

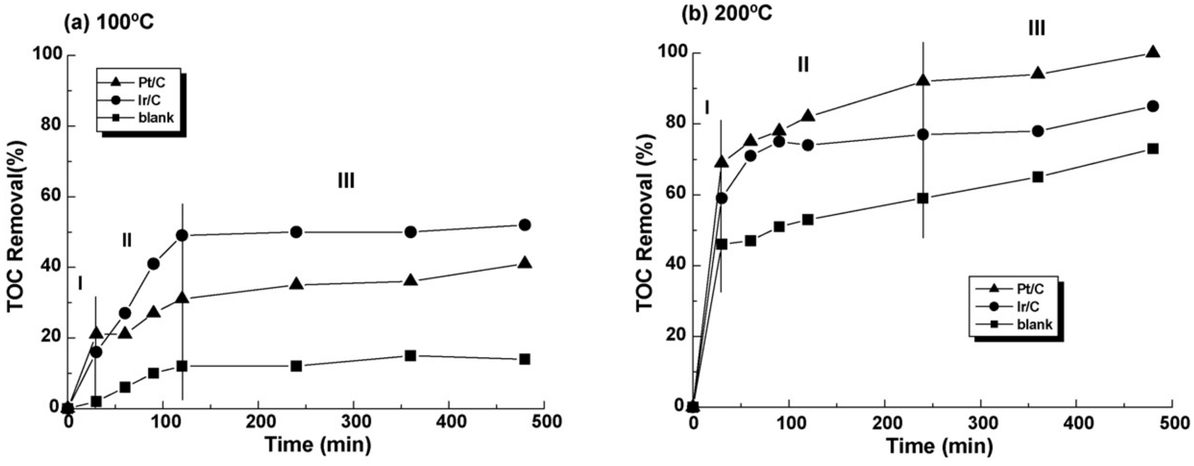

Fig. 1. TOC removal curves for the WAO/CWAO of OMW samples at 6.9 bar of oxygen partial pressure: (a) 100 °C; (b) 200 °C.

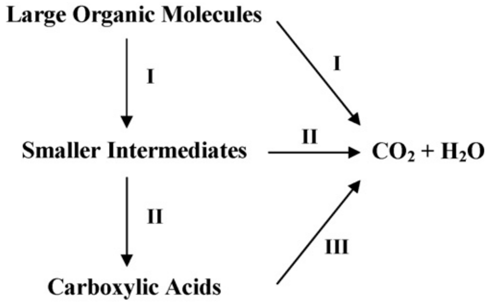

Fig. 2. Reaction scheme for OMW oxidation.

240 min at 200 °C), the TOC decrease is very slight, due to degradation of more refractory smaller intermediates into very refractory compounds (such as carboxylic acids), or directly to CO_2 and H_2O. Depending on the reaction conditions, the TOC removal at this stage is around 10–20% of the original value. In the third region (above 120 or 240 min of reaction), there is a residual TOC originating a plateau due to refractory organic compounds, like low molecular weight carboxylic acids which are not further oxidized [19,39]. This inhibition effect is particularly evident at 100 °C, because the catalysts used are expected to be completely inactive for carboxylic acids degradation at this temperature [29,31]. In fact, the third region considered in Fig. 1 at 100 °C may be extensively overlapped by the second region, since it is expected that, at this temperature, some refractory smaller intermediates are not oxidized or are only partly oxidized, thus with no effect on TOC removal.

3.2. Kinetic model

Based on the above mentioned observations, a kinetic model was developed to explain the catalytic results obtained in the degradation of the OMW at 200 °C 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 catalysts, which can be further explored to evaluate the CWAO technological implementation viability. Due to the complex composition of the wastewater, 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 [40]. As observed in Fig. 1, the effluent TOC reduction, which is large at the beginning of reaction, decreases strongly due to the formation of organic compounds, such as low molecular weight carboxylic acids, which are very refractory to further oxidation, a plateau being observed in the TOC removal curves after 240 min of reaction time. The proposed model takes into consideration catalyst deactivation and the TOC removal rate reduction due to the increasing inhibition caused by the formation of refractory compounds. The inhibition character was described by an inhibition function τ [38]. Catalyst deactivation was 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.

Since the non-catalytic homogeneous oxidation was found to be relevant, a rate constant k_{hom} was considered in addition to the heterogeneous oxidation rate constant k_{het}. The final products were assumed to be CO_2, H_2O and refractory lightweight organic compounds.

A Langmuir–Hinshelwood approach was adopted to describe the proposed reaction-deactivation scheme. It was considered that the reaction occurs in the adsorbed phase between the organic compounds present in the effluent and dissociatively adsorbed oxygen. The corresponding adsorption equilibria are characterized by the constants K_{TOC} and $K_{\mathrm{O_2}}$, respectively. With these assumptions, the effluent oxidation reactions can be described by the following set of equations:

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

$$\tau = 1 - \frac{[\mathrm{TOC}]_\infty}{[\mathrm{TOC}]} \tag{2}$$

$$\alpha = \mathrm{e}^{-kt} \tag{3}$$

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

The oxygen concentration in the liquid phase at 200 °C is expressed as a function of the oxygen partial pressure (in bar) by Eq. (4) as deduced from results taken from the literature [33]. Considering ideal behaviour for the gas phase we can obtain a relationship between the oxygen concentration in liquid and gas phases (Eq. (5)). The concentration in the gaseous phase is obtained from the oxygen mass balance, Eq. (7), given the total oxidation stoichiometry of n moles of O_2 to one mole of organic carbon present in the effluent (Eq. (6)). In fact, due to the complex composition of the OMW and of the resulting reaction samples, the theoretical total oxidation stoichiometry cannot be determined. Accordingly, the results reported here were obtained considering $n = 1$ for which we obtained the best agreement between model and experimental results (simulations using other n values up to 2 led greater deviations):

$$[\mathrm{O_2}] = 1.3431 P_{\mathrm{O_2}} \tag{4}$$

$$[\mathrm{O_2}] = 0.0521[\mathrm{O_2}]_{\mathrm{g}} \tag{5}$$

$$\mathrm{C} + n\mathrm{O_2} + \cdots \rightarrow \mathrm{CO_2} + m\mathrm{H_2O} + \cdots \tag{6}$$

$$[\mathrm{O_2}]_{\mathrm{g}} V_{\mathrm{g}} = [\mathrm{O_2}]_{\mathrm{g0}} V_{\mathrm{g}} - n([\mathrm{TOC}]_0 - [\mathrm{TOC}])\frac{V_1}{12} \tag{7}$$

Table 3
Model parameters obtained in the CWAO of an OMW with Pt/C and Ir/C catalysts at 200 °C and 6.9 bar of oxygen partial pressure

Catalyst	k_{hom} (h^{-1})	k_{het} (10^9 mg h^{-1} g_M^{-1})	K_{TOC} (10^{-5} L mg^{-1})	K_{O_2} (10^{-7} L $mmol^{-1}$)
Pt/C	0.37 ± 0.02	2.20 ± 0.06	1.10 ± 0.03	0.67 ± 0.03
Ir/C	0.3 ± 0.1	0.2 ± 0.2	2.0 ± 0.1	2.4 ± 0.1

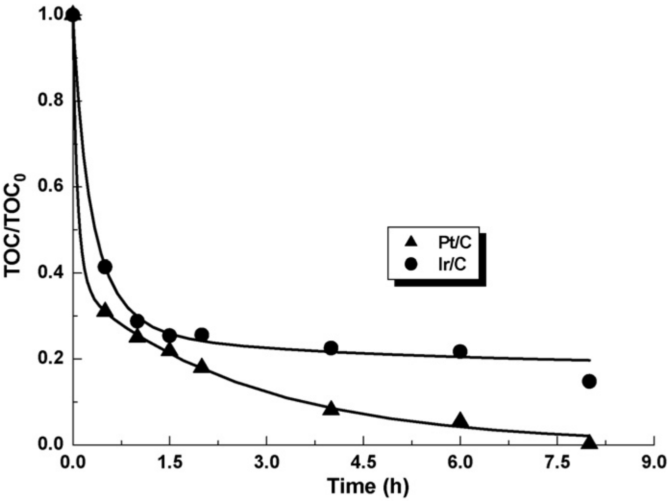

Fig. 3. Model fitting to the CWAO experimental data obtained at 200 °C and 6.9 bar of oxygen partial pressure.

In the above equations, P_{O_2}, $[O_2]_g$, and $[O_2]_{g0}$, represent the oxygen partial pressure (in bar), concentration and initial concentration (in mmol L^{-1}) in the gas phase, respectively, n and m, the stoichiometric coefficients for oxygen consumption and water production, respectively, V_g, the gas phase volume (in L) and V_l, the liquid phase volume (in L). Based in Eqs. (1)–(7) a numerical model was built and solved using MATLAB, defining as objective function $\text{fobj} = \sum_t \left([\text{TOC}]_t - \overline{[\text{TOC}]}_t\right)^2$, where $[\text{TOC}]_t$ and $\overline{[\text{TOC}]}_t$ represent the experimental and calculated total organic carbon concentrations of the reaction mixture at instant t, respectively. The optimization was carried out using the routine fmins, which uses a Nelder–Mead type simplex search method. To solve the rate law Eq. (1), the routine ODE23 was implemented, a second and third order Runge-Kutta method being applied. Fitting the experimental data with the model, the results shown in Fig. 3 were obtained. A good agreement between the model and the catalytic experimental results at 200 °C was observed.

From the fitting procedure, the parameters involved in the model were obtained, which are collected in Table 3. The 95% confidence interval, estimated numerically by a mathematical routine of MATLAB software named nlparci, is also given for all the calculated parameters.

Analyzing the magnitude of the parameters obtained we can conclude that the Pt/C catalyst is more active than the Ir/C catalyst at 200 °C and 6.9 bar of oxygen partial pressure, based on the heterogeneous reaction rate constants (2.20×10^9 mg h^{-1} g_{Pt}^{-1} for the Pt/C catalyst and 2×10^8 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 (6.7×10^{-8} L $mmol^{-1}$ in the Pt/C catalyst and 2.4×10^{-7} L $mmol^{-1}$ in the Ir/C catalyst). This result was expected, taking into account the higher reduction potential of platinum, which makes it less prone to oxygen adsorption. In previous work on the CWAO of butyric acid under the same reaction conditions, the Pt/C catalyst was shown to have higher long term deactivation resistance than the Ir/C catalyst [32]. The deactivation of the latter was attributed to over-oxidation of iridium by oxygen.

4. 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 200 °C and 6.9 bar of oxygen partial pressure with the Pt/C catalyst after 8 h of reaction. This result proves that CWAO is a promising technology to treat OMW and encourages further research studies on this subject. Since the degradation rate obtained with the Pt/C catalyst is very high, the CWAO of olive mill wastewater seems environmentally attractive. The low concentrations of organic compounds in the final treated effluents allows for their reuse in the process, leading to a more efficient process water management and better environmental impact.

A kinetic model was developed, which takes into account 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 200 °C, therefore can be used to design CWAO reactors for the specified conditions and to study the economical viability of this technology for the treatment of OMW, an issue of great importance in Mediterranean countries.

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