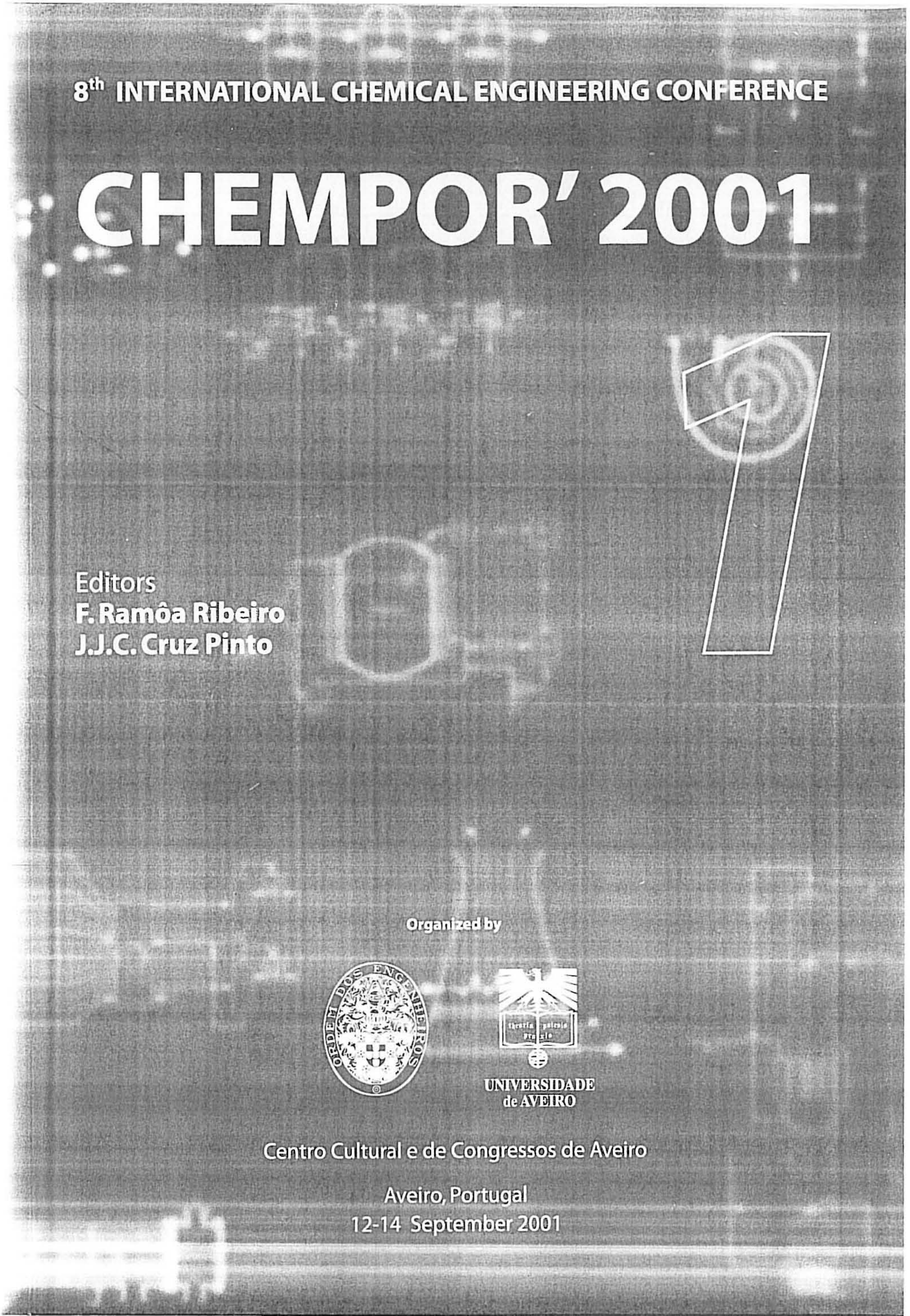

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Catalytic Wet Air Oxidation of Organic Pollutants in Waste Waters

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Introduction

Organic compounds are involved in the manufacture of a wide variety of chemical products, generating in the process different kinds of liquid effluents with high chemical oxygen demand (COD) and high toxicity. Discharge of these waters without treatment into a river course is unacceptable, due to the toxic potential of some organic compounds or to depletion of the dissolved oxygen level, which can decrease below the level considered necessary to support aquatic life. These are serious problems, mainly in liquid effluents of petrochemical, chemical and pharmaceutical industries and constitute one of the major concerns of our society. More stringent laws in the industrialized countries, increasing environmental worries and the pressure of the environmental groups impose the reduction of effluent COD values to very low levels.

The available industrial wastewater processes are mainly chemical, physical, biological treatments, or any combination of those, and include incineration and wet air oxidation (WAO, non catalytic and CWAO, catalytic). These treatments can be applied individually or in combination with other treatments, depending on the nature of the effluent to be oxidized. There is also a set of recent technologies named advanced oxidation processes (AOP), which involve the generation of reactive intermediate species, such as the hydroxyl radical. Some examples are supercritical oxidation, ozonation, peroxidation and the Fenton reaction.

In Figure 1 we can observe a technology map, where the most suitable technology for specified effluent treatment parameters in terms of COD and effluent flow rate is represented (adapted from [1]).

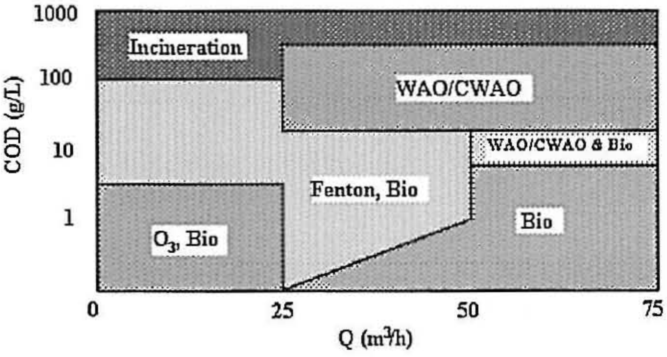

Figure 1 – Technology map for treatment of liquid effluents

The map boundaries should not be interpreted as rigid limits, because in practice some technology overlapping may occur.

WAO is well suited for effluents with a COD too high to be treated by biological processes [2] and too diluted to be incinerated (10 g/L <CQO< 100 g/L) [3]. The process involves mineralization of organic or oxidizable inorganic compounds in solution to carbon dioxide and water at high pressures and temperatures (50-200 bar P_T, 125-320 °C), by means of an appropriate oxidation source (air or oxygen) [4]:

$$\text{Organic Compound} + O_2 \xrightarrow{T,P} CO_2 + H_2O \quad (1)$$

Aiming at the reduction of operational and investment costs of WAO units [5] and minimization of corrosion problems in the reactors favored by the severe reaction conditions [6], there is a current interest in the development of new catalysts, capable of bringing the oxidation reaction conditions to more amenable values (5-50 bar P_T, 125-220 °C) and possessing an efficiency comparable to WAO processes. The first studies on CWAO of organic compounds date from mid 70's, beginning of 80's [5, 7-9], using transition metal salts dissolved in the reaction medium [10, 11], iron salts [10] and copper oxide supported catalysts [7]. Although very efficient, homogeneous processes had the disadvantage of introducing toxic ions in solution, which implies the existence of an additional step for eliminating these species [12], such as precipitation or membrane separation. On the other hand heterogeneous catalysts could avoid the need for this separation step. Indeed, some very active heterogeneous catalysts were developed, such as copper oxide supported in $ZnO\text{-}Al_2O_3$ [13] and the composite oxides of Mn-Ce [12] and Co-Bi [5]. The first heterogeneous catalysts were not stable enough and the active species were lixiviated from the support [13], implying an additional separation step.

The development of heterogeneous catalysts highly active and stable became a challenge. More recent studies indicate that noble metal catalysts supported on stable materials, resistant to acid corrosion, can be applied successfully in the CWAO process [14-17]. Among such materials we may find carbon, titanium oxides, alumina and silica.

The increasing interest in the CWAO process is followed by the need to adopt a rational approach and to establish reaction mechanisms and adequate kinetic models. Normally, real effluents have a very complex composition that is difficult to characterize completely [18]. In order to reduce complexity and to enhance process efficiency by laboratorial studies, it is necessary to adopt representative model systems such as mixtures of compounds normally found in effluents, or study individual species [5, 12, 13, 19]. Low molecular weight carboxylic acids (ex. formic, acetic, propionic, butyric, isobutyric) were used as model systems in several WAO and CWAO investigations [4, 20-23], because they are very refractory to oxidation, being found as final products of the gradual degradation of the majority of organic compounds [2, 24]. The oxidation mechanism of organic compounds usually accepted for this process [25] is depicted in Figure 2.

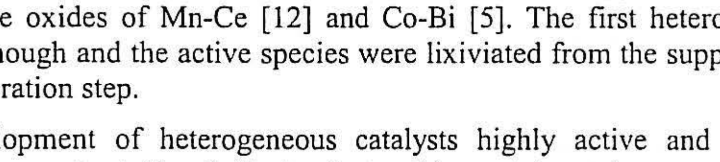

Figure 2 – Simplified Scheme of WAO of an organic compound

In this work some carbon supported noble metal catalysts were developed and used in a model reaction - butyric acid oxidation. The catalysts developed were then used in the oxidation of an olive mill wastewater.

Experimental

Catalyst Preparation

Activated carbon pellets (Norit ROX 0.8) were used as support in the preparation of platinum and iridium catalysts. Prior to any use, the supports were washed with hot hydrochloric acid during 12 h in order to remove some impurities and afterwards washed with water until the pH of rinsing water reached the value of 6. Textural characterization based on the N_2 adsorption isotherm at 77 K, gives a BET surface area and a micropore volume of 1053 m^2g^{-1} and 0.405 cm^3g^{-1}, respectively.

The catalysts were prepared by incipient wetness impregnation. In the case of the platinum catalyst, an aqueous solution of hexachloroplatinic acid was used with the concentration needed to obtain 1 wt.% metal load in a single step (Pt/C). The iridium catalyst was prepared using an aqueous solution of ammonium hexachloroiridate in order to obtain a 5 wt.% metal load in two impregnation steps (Ir/C). After each impregnation step, the catalysts were dried overnight at 110°C. Prior to reaction the catalysts were reduced under flowing hydrogen during 3 h at 350°C.

The catalyst loads, before and after reaction, were determined by a thermogravimetric method, burning away the carbon support and measuring the weight of metal.

Oxidation Procedure

CWAO reactions were carried out in a 160 cm^3 high pressure reactor (Parr 4564) described in detail elsewhere [16]. In each experiment, the reactor was loaded with 70 cm^3 of the solution to be oxidized and with the desired amount of catalyst. After the heating period under continuous stirring (500 rpm), air was added to the reactor until the operating pressure was attained (time zero of the reaction). Periodically, liquid samples where withdrawn from the reactor and analyzed either by gas chromatography (Dani GC1000) or with a TOC analyzer (Shimadzu TOC 5000A).

Results and Discussion

Butyric Acid

Low molecular weight carboxylic acids are known to be very refractory to oxidation, and appear as end products in the oxidative degradation of the majority of the organic compounds. In order to find the most active carbon supported metal catalysts for this class of compounds, a series of catalysts with different metal phases (5 wt.% metal load) were prepared by the incipient wetness impregnation method and tested in the model reaction of butyric acid oxidation at 200°C and 6.9 bar of oxygen partial pressure. From the results (Figure 3), we can conclude that platinum and iridium catalysts are very efficient systems in the removal of butyric acid. It was also verified that either without catalyst or with just the bare support without metal, butyric acid conversion was negligible.

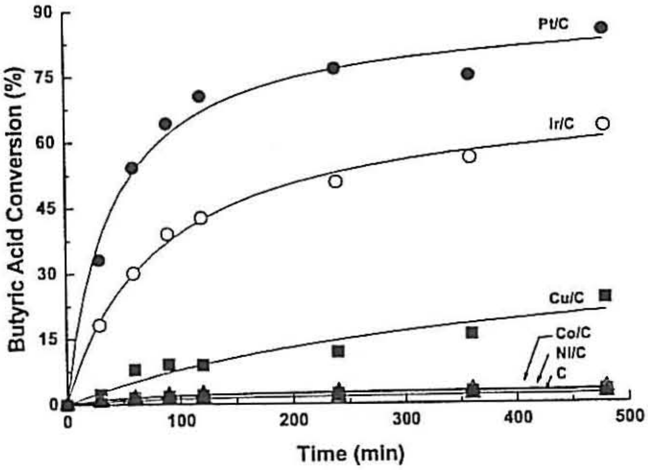

Figure 3 – Conversion curves of butyric acid oxidation in the presence of several metal catalysts

The activity of metal catalysts increased in the order 0<Ni≈Co<Cu<Ir<Pt, similar to the reduction potential series of these elements. This correlation indicates that oxygen adsorption ability of a given metal strongly affects the catalyst activity. A metal with higher reduction potential (such as platinum) has less ability to adsorb oxygen molecules, leaving more available active sites for organic molecules, increasing the catalyst activity. From the results of the preliminary study, Pt/C and Ir/C catalysts were chosen for further work.

The catalytic oxidation of butyric acid was performed using the Pt/C and Ir/C catalysts at different temperatures and 6.9 bar of oxygen partial pressure (Figure 4).

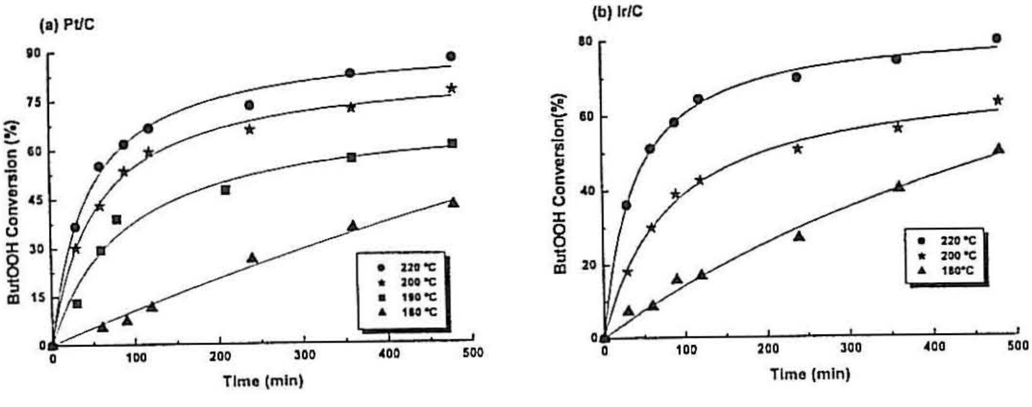

Figure 4 – Catalytic oxidation of butyric acid, using (a) Pt/C and (b) Ir/C catalysts

The initial specific rates of butyric acid disappearance calculated for each reaction are presented in Table 1. From the data, we observe that the activity of Pt/C catalysts decreases more rapidly with temperature than the activity of the Ir/C catalyst. Using the Pt/C catalyst, the butyric acid conversions after 2 h of reaction were 11.4 and 59.4% at 180 and 200 °C, respectively, while for the Ir/C catalyst, the conversions obtained were 16.8 and 42.6%.

Table 1 – Temperature dependence on the catalytic wet air oxidation reaction

Catalyst	**T (°C)**	**Conversion after 2h (%)**	**r_i (mmol.h^{-1}.g$_M$$^{-1}$)**
Pt/C	180	11.4	20
	190	38.9[a]	115
	200	59.4	184
	220	66.6	291
Ir/C	180	16.8	14.3
	200	42.6	29.8
	220	64.2	51.9

[a] After 80 min

The apparent activation energies of butyric acid oxidation over the different catalysts were determined from an Arrhenius-like plot of ln(r_i) vs 1/T. The values of 56.9 and 59.0 kJ/mol were obtained for the Pt/C and Ir/C catalyst, respectively. Although these apparent activation energies are comparable to an homogeneous process, the conversions obtained with blank experiments (support without metal or without any material) are negligible, eliminating the possibility of a pure thermally homogeneous mechanism.

It was found experimentally that the main intermediates are propionic and acetic acids. No other detectable intermediates were found, ruling out other possible oxidation routes (via alcohol, ester or aldheydes).

The experimental observations and the results reported in the literature suggest the following conceptual mechanism (Figure 5):

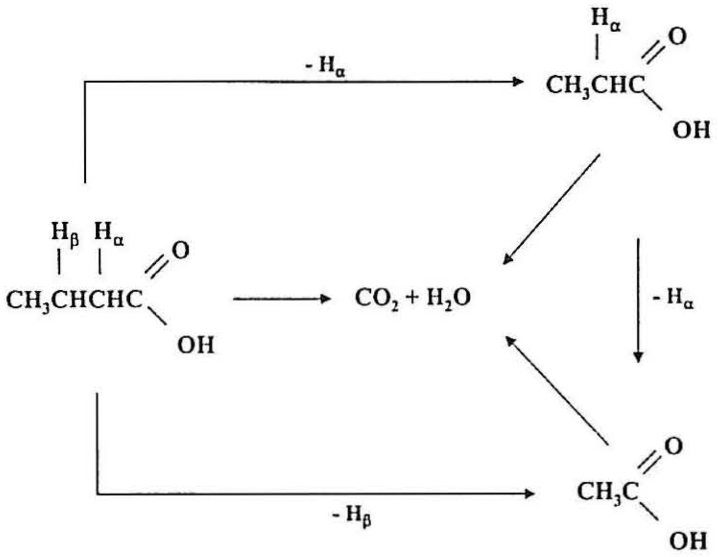

Figure 5 – Butyric acid oxidation mechanism

After adsorption of the organic substrate at the metal surface, hydrogen abstraction from the α– or β– position on the carboxylic acid group occurs. After this step the radical formed is desorbed into solution and reaction proceeds by a radical pathway until the desired end products $CO_2 + H_2O$. The involvement of a radical species was confirmed by selective scavenging experiments.

Metal catalyst surfaces easily chemisorb oxygen [26], lowering the accessibility of the organic substrate to the metal active sites. But metals with a higher reduction potential (such as platinum) in the presence of organic molecules with some affinity to metal are less prone to oxygen chemisorption. This type of metal-oxygen-organic substrate interaction explains the observed activity differences between Ir/C and Pt/C catalysts, because Ir has a lower reduction potential than Pt, and consequently has higher surface oxygen chemisorption coverage, leading to lower accessibility of the butyric acid molecules to the active sites.

The catalytic systems developed are very stable in solution, with no metal leaching detected in all cases. Consecutive runs with the same catalyst showed that Pt/C catalysts are more resistant to deactivation than Ir/C (Figure 6), the observed deactivation of the latter being attributed to the metal over-oxidation.

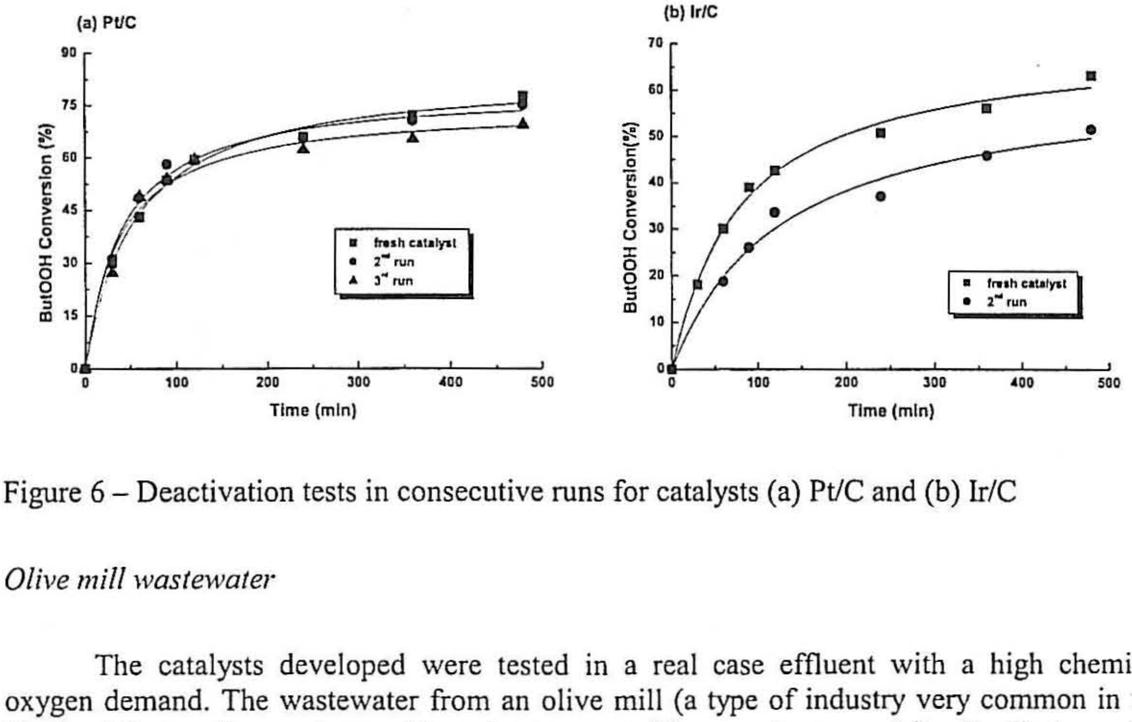

Figure 6 – Deactivation tests in consecutive runs for catalysts (a) Pt/C and (b) Ir/C

Olive mill wastewater

The catalysts developed were tested in a real case effluent with a high chemical oxygen demand. The wastewater from an olive mill (a type of industry very common in the North of Portugal) was chosen. Nowadays, some of these waters are arbitrarily discharged in the rivers, causing a very negative environmental and social impact.

The degradation profiles of an olive mill effluent diluted 10 times (TOC_0 = 1500 mg/L) are presented in Figure 7. The reaction was carried out at 6.9 bar of oxygen partial pressure, at two different temperatures in the presence and absence of two different catalysts.

Observing the degradation curves, we can conclude that the catalytic systems developed do improve TOC removal of this effluent. Although at 200°C there is a significant decrease in organic concentration in non-catalytic wet air oxidation, Pt/C catalyst showed to be very active. After 2 h of reaction the TOC removal observed with this catalyst was 55%

higher than the non-catalytic run. It should be pointed out that complete removal is achieved with this catalyst after 8 h of reaction.

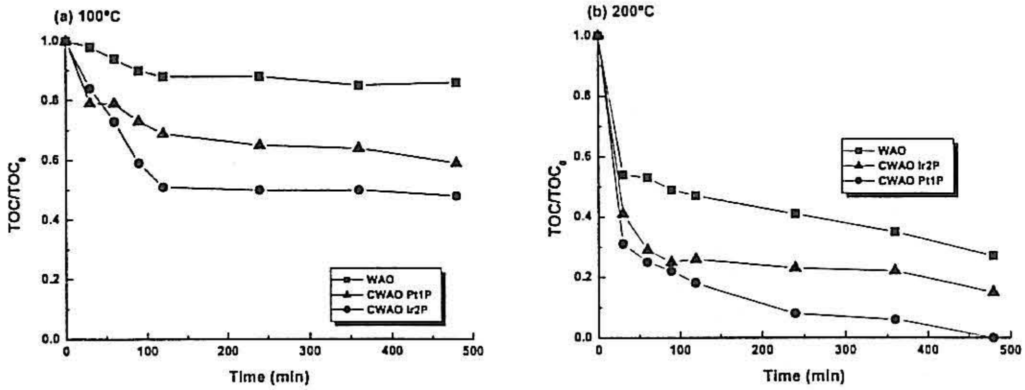

Figure 7 – Temperature and catalyst effects on the catalytic wet air oxidation of an olive mill effluent (diluted 10 times).

At 100°C, the most active catalyst was Ir/C. As observed in the study of butyric acid oxidation, the decrease in activity with the temperature obtained with this catalyst in not so strong as observed for the Pt/C catalyst. Under these conditions, TOC removal in the non-catalytic wet air oxidation run, although not negligible, is very low compared with the results obtained with the catalytic systems. After 2 h of reaction, the TOC removal observed was 12, 31 and 49% for non-catalytic wet air oxidation, Pt/C and Ir/C runs, respectively.

Conclusions

Catalytic wet air oxidation as an emerging wastewater treatment technology proved to be very efficient for the elimination of the chemical oxygen demand of effluents. Pt/C and Ir/C catalysts were found to be suitable catalysts for the oxidation of butyric acid, a low molecular weight carboxylic acid refractory to oxidation. The organic substrate degradation may proceed via a free radical mechanism, after adsorption at the metallic surface and hydrogen abstraction. The catalysts developed are very stable in solution at the reaction conditions, but Pt/C catalyst is more resistant to long-term deactivation than Ir/C catalyst.

The study carried out with an olive mill diluted wastewater (1:10) confirmed the very good efficiency of these catalysts for catalytic wet air oxidation processes. With Pt/C at 200°C, complete removal of the initial organic matter was attained.

Acknowledgments

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