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Highly effective oxide catalyst for the detoxification of oil mill wastewaters by the wet air oxidation process

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ABSTRACT

The performance of a model $MnCeO_x$ catalyst (Mn_{at}/Ce_{at}, 1) in the catalytic wet air oxidation of p-cumaric acid and a "real" Olive oil mill wastewater (OMW) has been thoroughly assessed. Experimental results in the temperature range of 383–433 K and pressure range of 1.0–1.5 MPa document a high purification efficiency of the $MnCeO_x$ system toward both p-cumaric acid and OMW, along with a high mineralization activity leading to CO_2 selectivity values of 60 and 50% (433 K) for p-cumaric acid and OMW, respectively. Stability tests indicate a high resistance of the catalyst against deactivation phenomena by fouling.

Keywords: Mineralization; Purification; p-cumaric acid; Olive mill wastewater; Abatement

1. Introduction

The environmental concern is nowadays expressed by more and more stringent regulations imposing even lower pollutant (organic and inorganic) discharge limits, the replacement of toxic substances/solvents and/or, in some cases, of the whole manufacturing processes. Consequently, industrial and civil wastewaters must be treated by appropriate methods, as physical, biological, chemical or combined treatments to reduce their toxicity before discharging in the environment [1]. Then, wastewaters purification is a major challenge of environmental technologies, since water is used as solvent or coolant in the majority of industrial processes, besides its major use for domestic and agricultural purposes [1,2].

In this context, Olive oil mill wastewaters (OMWs) represent an important class of wastewaters, due to the presence of high amounts of toxic and/or refractory organic compounds. OMWs are, then, very polluted aqueous streams, their disposal constituting a great environmental concern for olive oil manufacturing countries, mainly located in the Mediterranean Sea basin [2–9]. In fact, the production of Mediterranean

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countries amounts to 97% of the worldwide availability, with Spain (35%), Italy (24%) and Greece (16%) being the most important producers, followed by Turkey, Tunisia, Portugal, Morocco and Algeria [2].

Olive oil manufacturing involves high consumptions of water producing, then, large volumes of strongly polluted wastewaters that, depending on the milling process, range from about 0.6 m^3 t^{-1} olives for classical mills to about 1.7 m^3 t^{-1} olives for centrifugal mills [6]. Moreover, OMW is characterized by a very high chemical oxygen demand (up to 220 g L^{-1}), corresponding to biological oxygen demand values up to 100 g L^{-1}, a high content of recalcitrant compounds, such as lignins and tannins, (in the range of 0.5–2 g L^{-1}), which confers the characteristic brown colour, and a significant amount of phenolic compounds (in the range of 0.5–24 g L^{-1}) and fatty acids, toxic for the environment [2].

Being the majority of olive mills small enterprises, usually family businesses, and located nearby the olive production areas, current wastewater technologies are not economically feasible because of the small scale application [2]. Given the high phytotoxicity and strong antimicrobial properties [2,3,5,6], which make the classic biological treatment inapplicable, alternative methods, mostly physical and physicochemical techniques, such as precipitation, flocculation/clarification, coagulation, filtration, and evaporation in open ponds are applied, but they give only partial purification [2–6]. On the other hand, reverse osmosis or ultrafiltration techniques are highly costly, while anaerobic biological digestion producing biogas is increasingly being used, but it suffers of low yield, yet [2]. Then, a possible solution would be represented by an oxidative degradation of OMW. In this respect, among the various currently available options, the Catalytic wet air oxidation (CWAO) technology is one of the most promising processes, increasingly used for the abatement of organic pollutants in wastewaters, coming from different chemical plants [2–6].

Typical OMWs contain high concentrations of tyrosol, cinnamic and/or benzoic acid derivatives. For this reason, p-coumaric acid (trans-hydrocinnamic acid) is often taken as model compound of the phenolic fraction for the comprehension and the improvement of the CWAO of OMW [3,6,7].

The p-coumaric acid mineralization is a complicated process involving a great number of intermediates, ranging from p-hydroxybenzaldehyde and p-hydroxybenzoic acid, phenol, catechol and hydroquinone, and traces of hydroxylation products such as 3,4-dihydroxycinnamic acid (caffeic acid), 3,4-dihydroxybenzaldehyde and 3,4-dihydroxybenzoic acid, to progressively more recalcitrant products derived from the aromatic ring opening, such as maleic, fumaric, acetic, oxalic, and formic acids [6,7,10].

The CWAO of p-coumaric acid and other model organic compounds has been investigated by several authors with various homogeneous (Fe^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}) and heterogeneous, mostly noble-metals, catalysts [2,6–18]. However, $MnCeO_x$ catalysts present a very interesting CWAO performance toward a variety of organic pollutants under very mild operating conditions (T, 383–453 K; P, 0.6–2.0 MPa) [1,11], with samples prepared via the redox-precipitation route giving the better results [14–19].

Therefore, this work is aimed at assessing the performance of optimal *model* redox $MnCeO_x$ catalyst in the mineralization of both p-coumaric acid and a "real" OMW under mild conditions (T, 383–433 K; P, 0.6–1.5 MPa) for its application in the purification of toxic wastewaters at industrial scale.

2. Methods

2.1. Catalyst preparation

The $MnCeO_x$ catalyst was prepared by the "redox-precipitation" technique titrating a water solution of the $KMnO_4$ precursor (≈10 g/L) at a constant pH (8.0 ± 0.3) with a solution of Mn^{2+} and Ce^{3+} ions, in the appropriate amount to give a Mn_{at}/Ce_{at} equal to 1.0 [14]. After filtration and washing, the sample was dried at 373 K all night long and further calcined in air at 673 K for 6 h [14,15].

2.2. Catalyst characterization

The analytical composition of the investigated system was determined by XRF measurements, using a *Bruker AXS-S4 Explorer Spectrometer* by the emission value of Kα1 transitions of Mn (E = 5.9 keV), Ce (4.8 keV) and Fe (6.4 keV).

Surface area (SA_{BET}) values and pore size distribution were derived from the nitrogen absorption isotherm (77 K), using a *ASAP 2010* (*Micromeritics Instruments*). The isotherms were elaborated in the p/p^0 range of 0–0.2, according to the B.E.T. method, for surface area determination, while pore volume (PV) and average pore diameter (APD, $4PV/SA_{BET}$) were obtained using the H.K. and B.J.H. equations.

Temperature programmed reduction (TPR) was conducted using a 6% H_2/Ar mixture (60 STP mL min^{-1}) into a linear quartz microreactor (i.d., 4 mm) loaded with ca. 30 mg of catalyst. Measurements were performed in the 293–773 K temperature range at the heating rate of 12 K·min^{-1}.

X-ray diffraction (XRD) analysis was performed by means of a *Philips X-Pert diffractometer* operating with a Ni β-filtered Cu K_α radiation (40 kV; 30 mA) in the 2θ range of 20°–70° (scan step, 0.05 deg s^{-1}).

Thermogravimetric (TGA-DSC) analysis of the "used" samples (ca. 5 mg) was performed in static air atmosphere with a *Simultaneous Thermal Analysis Instrument* (*STA 409C, NETZSCH*) operating with a heating rate of 10 K min^{-1} in the temperature range of 373–773 K.

2.3. Catalytic tests

The CWAO of p-coumaric acid and OMW was performed using a PTF-lined autoclave (0.25 L), equipped with a magnetically driven turbine impeller (≈800 rpm) in the range of 383–433 K and a total pressure of 1.0–1.5 MPa (P_{O2}, 0.9 MPa). The reactor was loaded with an aqueous suspension (0.15 L) of powered catalyst (d_p, 5–10 μ), to avoid mass-transfer resistances, at a fixed concentration of 5.0 g L^{-1} and fed with a continuous oxygen flow at the rate of 0.1 STP L min^{-1}. When the reaction temperature was reached, a concentrated solution of the substrate was injected into the reactor by a pressurized loop to obtain an initial concentration of 1.0 g L^{-1} ($R=w_{cat}/w_{sub}$, 5). The reaction solution was periodically analyzed in terms of pH, substrate and intermediates concentration by HPLC (*UVD17OU, Dionex*) and TOC (*TOC-VCSN, Shimadzu*). The mineralization activity was probed by gravimetric analyses of the $BaCO_3$, formed by bubbling the reactor outlet into a saturated $Ba(OH)_2$ solution [15,18].

3. Results

The physico-chemical characterization data in Table 1 show the suitability of the "redox-precipitation" preparation method to give $MnCeO_x$ systems with the designed chemical composition and very high surface area, PV and APD, ensuring an easy surface accessibility and the consequent lack of significant internal diffusional resistances also to "heavy" organic pollutant species. Indeed, according to previous mechanistic evidences on the CWAO of phenol, indicating the occurrence of a typical Langmuir–Hinshelwood (L–H) reaction path involving adsorption as primary (*fast*) reaction step and the subsequent surface oxidation as *rate limiting step* [12], a Mn/Ce ratio of one ensures the best compromise between surface exposure and redox properties, enhancing the CWAO performance of the $MnCeO_x$ system [12,15,17–19].

The XRD pattern in Fig. 1(A) indicates that such textural characteristics depend on the peculiar structural arrangement of the oxide phases; namely, two broad peaks spanned in the ranges of 20°–38° and 40°–60° respectively, and none typical diffraction lines of crystalline phase(s) indicate that the redox-precipitation route leads to the growth of a completely amorphous structure, missing any *long-range* order [14,16]. This structural arrangement implies a very high dispersion of the active phase, reflecting in high catalyst reducibility, probed by the TPR pattern in Fig. 1(B). In particular, an onset temperature of ca. 323 K and a full reduction of the active phase ($MnO_2 \rightarrow MnO$) below 623 K document the enhanced oxidation strength of the studied catalyst at low temperature [14,16,19], favoring the oxidation of the adsorbed substrates on the catalyst surface (*r.d.s.*) [12,15,17,18,20].

The catalyst performance in the CWAO of the p-cumaric acid in the range of 383–433 K is shown in Fig. 2. The $MnCeO_x$ catalyst ensures a complete and almost instantaneous (5 min) abatement of the p-cumaric acid at any temperature, while the TOC abatement reaches a plateau of ca. 80% at 383 K (Fig. 2(A)) and 403 K (Fig. 2(B)) after 2 h, a total abatement being achieved only at 433 K after 3–4 h (Fig. 2(C)). Moreover, after a sudden growth due to the adsorption of the substrate on the catalyst surface, decreasing pH values match the ongoing release of acidic C1–C2 intermediates accounting for the incomplete TOC abatement at 383 and 403 K [10]. At variance, the continuous growth of pH up to a final value of 5.5 discloses a considerably higher purification efficiency at 433 K (Fig. 2(C)), further substantiated by CO_2 selectivity values rising from 17 to ca. 60% in the range of 383–433 K.

Table 1
Physico-chemical properties of the $MnCeO_x$ catalyst

Catalyst	Chemical composition			SA_{BET}	PV	APD
	$(Mn_{at}/Ce_{at})_{design}$	$(Mn_{at}/Ce_{at})_{exp.}$[a]	Mn (wt %)[a]	(m^2/g)	(cm^3/g)	(nm)
$MnCeO_x$	1.0	0.95	21.4	171	0.47	20

[a] From XRF analyses.

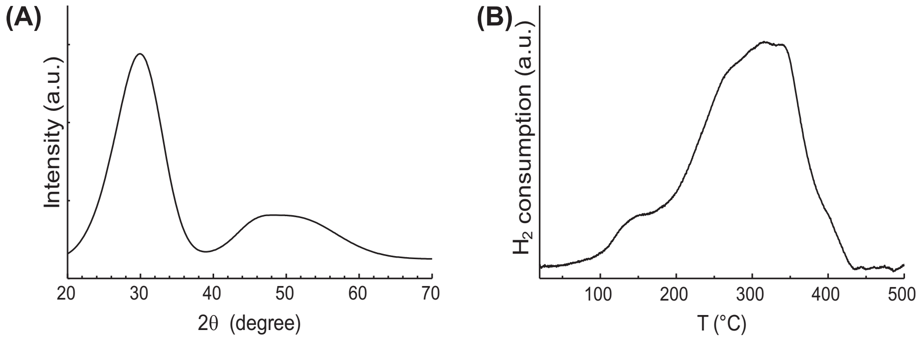

Fig. 1. XRD (A) and TPR (B) profile of the studied $MnCeO_x$ catalyst.

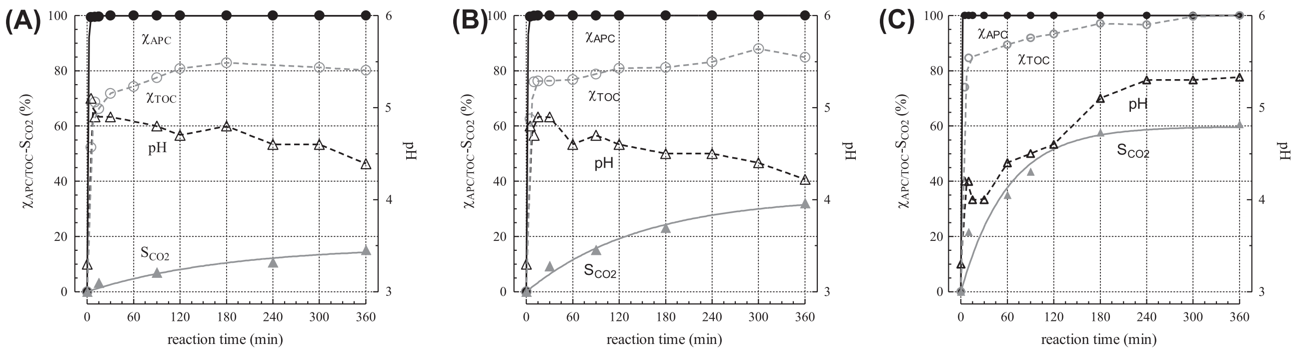

Fig. 2. Conversion, pH and CO_2 selectivity in the CWAO of p-cumaric acid at 383 (A), 403 (B) and 433 K (C).

Matching previous evidences on the CWAO of phenol [12,15,17,18,20], these findings confirm the occurrence of a typical L–H reaction mechanism [12,18,20], also supported by TGA-DSC characterization of the used samples (results not reported for the sake of brevity), showing a weight loss along with an exo DSC-peak in the range of 473–573 K [12,18], accounting for the gap between TOC conversion and CO_2 selectivity. Then, the effects of C-containing species accumulation on catalyst stability were probed by running 15 consecutive reaction cycles at 433 K (6 h) on the same catalyst sample (Fig. 3(A–B)). The catalyst ensures a complete removal of the substrate in the first 10 cycles (Fig. 3(A)), while the extent of TOC conversion decreases from 60 (1–10 cycle) to 26% (15th cycle) in the subsequent five cycles. Also, the mineralization activity keeps almost constant during the first 10 cycles, decreasing smoothly by ca. 50% in the last cycle (Fig. 3(B)), while neutral pH values at the end of each run account for total substrate adsorption on the cata-

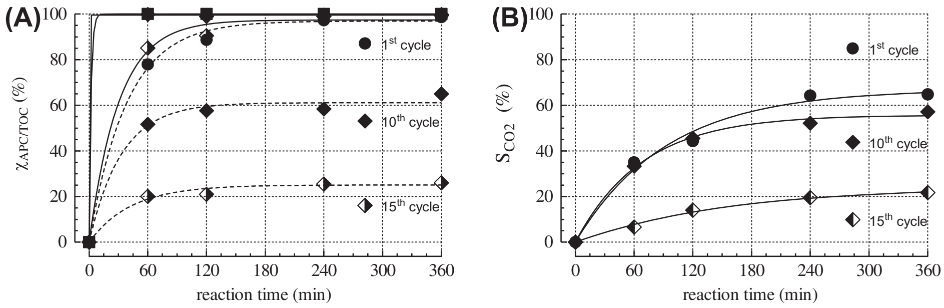

Fig. 3. (A) P-cumaric acid (continuous lines) and TOC (dotted lines) conversion and (B) CO_2 selectivity during 15 cycles of CWAO of p-cumaric acid (*T*, 433 K; *P*, 1.5 MPa).

Table 2
Main properties of the studied OMW as received and after CWAO treatment

As received			After treatment		
Color	pH	TOC	Color	pH	TOC[a]
Dark brawn	5.0	26,020	Transparent	8.0	397

[a]diluted 10 times.

lyst surface and consequent deactivation by fouling [18].

Such a good performance of the $MnCeO_x$ catalyst toward p-coumaric acid prompted us to inspect the efficiency toward a "real" OMW, typical of the Mediterranean area (Calabria, Italy).

The physico-chemical properties of the wastewater, before and after CWAO test are given in Table 2. Before test, the wastewater sample was centrifugated and filtered to set apart the suspended solids which could hinder the catalytic activity. Moreover, given the very high TOC value, the used sample was diluted (1/10, vol/vol) with distilled water, to operate in the same conditions of previous p-coumaric acid tests.

The results in Fig. 4 show that the $MnCeO_x$ catalyst features a promising performance also toward the real wastewater, with an extent of TOC abatement of ≈80% and a degree of mineralization (≈50%) only slightly lower than that of p-cumaric acid, while the treated solution appears colorless and almost neutral in pH. Therefore, all the reported experimental data point out the suitability of the studied catalyst in the CWAO of "real" oil-mills wastewaters, representing, thus, a potential solution to the issue of industrial wastewater purification.

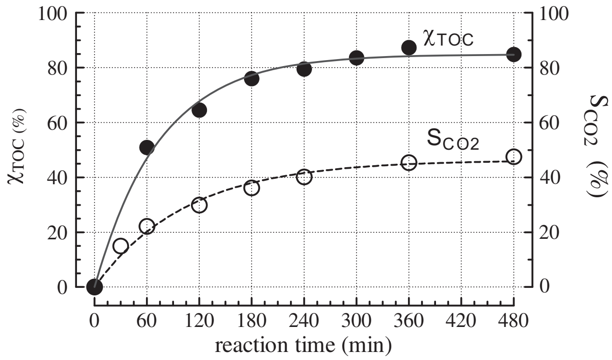

Fig. 4. TOC conversion and CO_2 selectivity in the CWAO of OMW (*T*, 433 K; *P*, 1.5 MPa).

4. Conclusion

The "redox-precipitated" $MnCeO_x$ catalyst is highly effective in the CWAO of p-cumaric acid in the range of 383–433 K, showing also a good resistance to deactivation phenomena by fouling.

The $MnCeO_x$ catalyst features a satisfactory performance in the CWAO of a "real" OMW, deserving potential application in the purification treatment of industrial wastewaters.

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