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Detoxification of Phenolic Wastewaters by Catalytic Wet Oxidation in Batch and Continuous Mode

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Catalytic wet oxidation of simulated olive oil wastewaters has been investigated in batch and trickle-bed reactors. The comparison between two operating reactor systems is presented querying the effect of temperature and pressure. The higher decontamination rates of organic matter were obtained in the batch reactor, which has promoted the complete mineralization of liquid pollutants after 60 min at 200°C and 30 bar. At equivalent operation times, the batch reactor exhibited higher decontamination efficiencies when compared to the continuous flow trickle-bed reactor. Additionally, the effect of pressure on TOC removal became less significant when compared to the influence of oxidation temperature for both reactor configurations.

Keywords batch; catalytic wet oxidation; phenolic wastewaters; trickle-bed reactor

INTRODUCTION

Multiphase reactors have been retained for the oxidation of organic and hazardous chemical species from industrial effluents which represents an imperative area of contemporary environmental research. Focusing mainly on hydric resources, treatments such as biological nitrification, activated carbon adsorption, and ion exchange processing are only able to achieve phase transformations and may yield contaminated sludge and adsorbent, both of which require further disposal (1). Mainly due to a large amount of phenolic wastewaters generated in petro-, electro-, or agro-chemical industries, advanced environmental technologies were being investigated during the last decades to accomplish the rigorous environmental regulations.

A significant production of phenolic wastewater arises from the olive oil extraction industries in the Mediterranean countries that generate each year an increasing volume of olive mill wastewater heavily contaminated with biological-recalcitrant behaviour (2,3). Generally, for each ton of olive oil, 15 cubic meters of olive oil wastewater are produced, which is a severe environmental problem due to its high organic fraction including not only sugars, tannins, acids, pectins, lipids but also phenols and polyphenols which are known to be bio-refractory (4,5). Apart from the total organic carbon content, olive oil wastewater is often characterized by a high chemical oxygen demand that require advanced treatment technologies for a proper management and secure disposal. Chemical oxygen demand lies typically in the range of 25–300 gO_2L^{-1} (6) that arise eminent and severe risks enabling irreversible environmental problems due to the high fraction of toxic and hazardous compounds to fauna and flora.

Traditionally, biological treatments for the decontamination of olive oil wastewater are focused on aerobic (7) or anaerobic digestion (8,9). Notwithstanding, the high toxicity and the biodegradability of the effluents have been identified during these anaerobic treatments (10) as the root issues since satisfactory results are only achievable when they are conducted on a highly dilute substrate once the aromatic and phenolic compounds are toxic for methanogenic bacteria (11,12). Recently, advanced oxidation processes have emerged as an interesting alternative for the destruction of organic pollutants in industrial wastewater. The core technology involves basically the generation of reactive hydroxyl radicals with high oxidation potential that promote an efficient mineralization of refractory compounds (13). These chemical oxidations apply oxygen, hydrogen peroxide, and ozone which are promising treatment technologies that reduce significantly the chemical and biological oxygen demand. An overview of advanced oxidation processes for the treatment of olive oil wastewater is given in (14). To list a few examples of oxidation processes that rely on the generation of free hydroxyl radicals include ozone, UV radiation, hydrogen peroxide, Fenton reagent, photocatalysis, or various combinations. Fenton's reagent has been identified as a

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powerful source of oxidative radicals (15,16) and it is based on the reaction of H_2O_2 with Fe(II)/Fe(III) ions. Among the oxidation technologies, wet air oxidation is also increasingly used for the decontamination of a variety of organic contaminants in wastewaters from different sources (17–19).

Conversely, wet oxidation transforms organic substances into intermediate compounds more amenable to biological treatments with small molecular weights or final end products (carbon dioxide and water) at temperatures up to 400°C and pressures up to 200 bar. Aiming to accelerate the industrial application, catalytic wet oxidation demonstrated how to improve wet oxidation technology if committed catalysts are used in order to promote oxidation with shorter reaction times under milder operating conditions (1,20,21). Supercritical wet air oxidation has been used to degrade diluted olive oil wastewaters with an initial chemical oxygen demand of $3.3\,gO_2/L$ giving a 99.9% removal for this lumped parameter and 98% phenol removal after 3 min (22). Municipal wastewater with a total organic carbon concentration of $4.9\,gL^{-1}$ has been also diluted in order to study subcritical conditions with $2\,gL^{-1}$ CuO/C or Pt/Al_2O_3 catalysts with or without H_2O_2 at 180°C and 70 bar pressure, exhibiting 50% chemical oxygen demand removal and 80% phenol removal after 6 h (23). Wet air oxidation of olive oil wastewaters catalyzed by Pt/C and Ir/C showed a high efficiency in the from a continuous three-phase centrifugation process with a initial chemical oxygen demand of $60.5\,gL^{-1}$ after dilution to $2.8\,gL^{-1}$ at 200°C and 6.9 bar of oxygen partial pressure (24).

To the best of our knowledge, the catalytic wet oxidation has been investigated mostly for the catalyst screening and the determination of kinetic parameters in batch mode (17–21,23,24). In fact, to obtain kinetic information laboratory three-phase reactors are required for the design of commercial reactors, as well as for the evaluation of newly developed catalysts so that it allows to establish kinetic parameters without any external effects such as mass, heat transfer resistances, and axial dispersion. In this realm, batch reactors can be effectively used to measure the kinetics with stable catalytic activity without the external effects. Among several advantages over flow-type reactors, one can mainly point out the short span of experimental data and batch stirred reactors confer also a better control on the accurate reaction starting time as reported by Ishigaki and Goto (25), at high temperature and pressure for pelletized catalysts and a reactant injection type batch reactor for powdered catalysts (26). However, multiphase reaction systems such as the catalytic oxidation of phenol-like compounds exhibited gradually changes on the catalyst activity so that the reaction mechanism and the catalyst deactivation cannot be decoupled in batch-wise experiments. Trickle-bed reactors disclose themselves as a feasible alternative to accomplish kinetic measurements. Indeed, gas and liquid velocities in laboratory scale trickle-bed reactors are usually up to three orders of magnitude lower than those in commercial reactors that may result in the incorporation and coupling of external effects on the kinetic data. Therefore, the catalytic bed of laboratory trickle-bed reactors are often diluted with fine inert particles allowing substantially the attenuation of axial dispersion to the extent where plug flow can be attained and much higher liquid hold-up are established to improve both the overall reaction rate and the catalyst wetting efficiency at lower gas and liquid velocities (27–29).

Given the above-mentioned differences between batch and flow-type multiphase reactors for the catalytic wet oxidation, in this paper, experiments were carried out to evaluate the trickle-bed reactor diluted with fine particles in where the effects of the catalyst bed dilution were quantitatively evaluated by measuring dynamic liquid holdup, pressure drop, and mostly the reaction rate in terms of total organic carbon depletion for the catalytic wet oxidation of phenolic compounds typically found in olive oil wastewaters. Hence, olive oil mill wastewaters were mimicked by a six-acid phenolic mixture (30,31) and the catalytic wet oxidation was then accomplished comparatively in batch and continuous mode in a batch stirred tank reactor and a pilot trickle-bed reactor, respectively, addressing the catalyst deactivation after long-term experiments.

EXPERIMENTAL

Materials

Low- to moderate-molecular weight phenolic compounds are known to be the major contributors to the toxicity and the antibacterial activity of olive oil wastewater. Hence, six phenolic-like compounds were obtained from Sigma-Aldrich to mimic the bactericide behaviour of olive oil processing wastwaters, namely: syringic, vanillic, *3,4,5*-trimethoxybenzoic, veratric, protocatechuic, and *trans*-cinnamic acid. The simulated effluent was prepared through an aqueous solution with 200 ppm for each phenolic acid. Following the screening studies performed in batch mode, a commercial catalyst CuO-MnO_x (N-140: CuO-22%; MnO_x–50%) available from the Süd-Chemie Group, Munich was employed throughout the trickle-bed reactor studies. N-140 catalyst was provided as cylindrical pellets with regular dimensions 4.8 × 4.8 mm and bulk density 0.9 kg/L.

Equipment

The batch oxidation experiments were carried out in a 316-SS high-pressure 1 L autoclave (Parr Instrument Company, model 4531 M) equipped with two six-bladed mechanically driven turbine agitators and a PID temperature controller (4842 Parr model) described elsewhere (20). The trickle-bed reactor studies have been carried out in a pilot plant comprising of a cylindrical reactor in stainless steel (SS-316) with 50 mm of internal diameter and 1.0 m length as illustrated in Fig. 1. A gas-liquid distributor is attached at the top of the vertical column to promote a better multiphase flow distribution at the reactor inlet. In order to maintain the flux of both phases approximately uniform over the cross-sectional area, the liquid distributor was designed with 60 capillary tubes (0.12 mm internal diameter). The capillaries are held between two plates 1 cm apart. The bottom plate has circular holes around the capillaries: the holes are slightly larger in diameter than the outer diameter of the capillary tubes. The gas phase was introduced into the chamber formed between the plates, and it exited the distributor through these holes. The top of the packing was 0.5 cm below the distributor, while the packing itself was kept in place by a stainless steel mesh placed at the bottom of the column. A gas-liquid separator is connected to the bottom of the trickle-bed reactor.

An upstream electronic mass flow controller and a downstream electronic backpressure controller (*Brooks* 5866 series with maximum pressure operation of 100 bar) were used to obtain and maintain the desired flow of gas and operating pressure. The pressure drop across the packed bed was measured with a high-pressure differential transducer, which was connected to the top and the bottom of the reactor bed. The liquid phase was delivered to the reactor by a high-pressure *Dosapro Milton Roy* (model XB140K5A100 – SS 316) and can work up to 100 bar and 114 L/h, while the gas phase was delivered to the reactor from high-pressure gas cylinders. The liquid feed was preheated by an external oven from *Carbolite Peak Series* PN120 1500 W equipped with a PID controller for temperature stability ±0.5 K and 7 electrical heating jackets (800 W) were attached to the trickle-bed reactor wall.

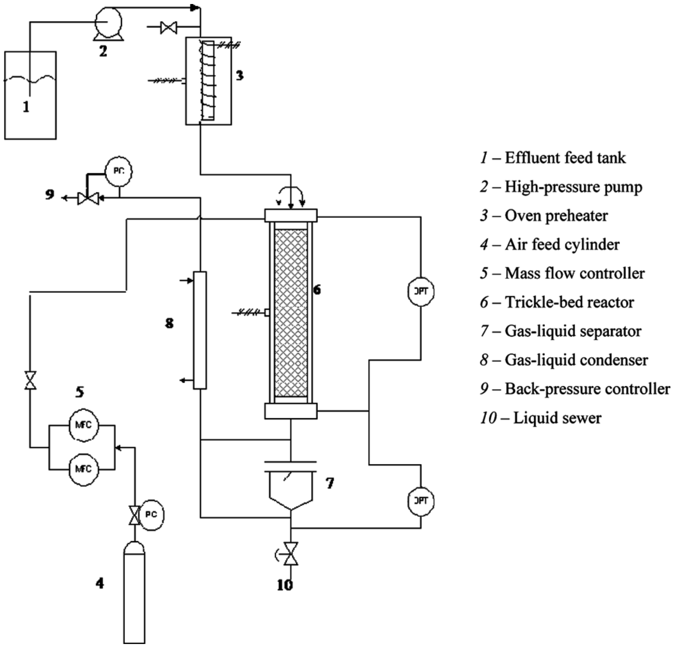

FIG. 1. Schematic diagram of trickle-bed reactor experimental setup.

Experimental Procedure and Analytical Techniques

The liquid feed was preheated at the temperature set-point and pure air (99.999%) was used as the oxygen source and flowed from the rack of gas cylinders through the mass flow controller into the top of the reactor where it was mixed with the phenolic acids solution feed at the gas-liquid distributor before entering the reactor. The trickle-bed reactor configuration was such that the feed passed over a short bed (length: 5 cm) of inert glass beads before entering the catalyst zone. After exiting the reactor the effluent was cooled and depressurized. The reactor was loaded with 990 g of N-140 catalyst and run continuously until the completion of the flow reactor studies. Liquid flow rate was maintained constant in the range 1–15 kg/m^{2}s and the air inlet flow rate was maintained in the range 0.1–0.7 kg/m^{2}s which allows one to operate in the trickling flow conditions (32). For a single run, the flow rates were kept constant throughout the trickle bed studies in order to maintain consistent hydrodynamics (liquid holdup and two-phase pressure drop) in the reactor to eliminate side effects such as natural pulsing flow that would exist at the upper values for the gas and liquid flow rates. Pressure was maintained at approximately 30 bar while the temperature range studied was from 160°C to 200°C. The temperature along the different axial points of the reactor is monitored by means of six *Omega* thermocouples (*K-type*) inserted in one single rod in the radial center of the reactor and with the following located distances from the bottom: 5, 20, 40, 55, 70, and 90 cm. The trickle-bed reactor has five equidistant sample points disposed axially. Total organic carbon was measured with a *Shimadzu 5000 TOC Analyser*, which operates based on the combustion/nondispersive infrared gas analysis method. The parameter uncertainty in TOC measurement, quoted as the deviation of three separate measurements, was never larger than 2% for the range of the TOC concentrations. *Atomic absorption* was used to measure the leaching of manganese and copper metals to the liquid phase and the analysis was performed in a spectrometer *Perkin-Elmer 3300*.

RESULTS AND DISCUSSION

Trickle-Bed Reactor

Total organic carbon (TOC) conversion is plotted in Fig. 2 as a function of mean bed temperature for different liquid mass fluxes at G = 0.5 kg/m^{2}s and P = 30 bar. The increase of temperature from 160 to 220°C led to higher

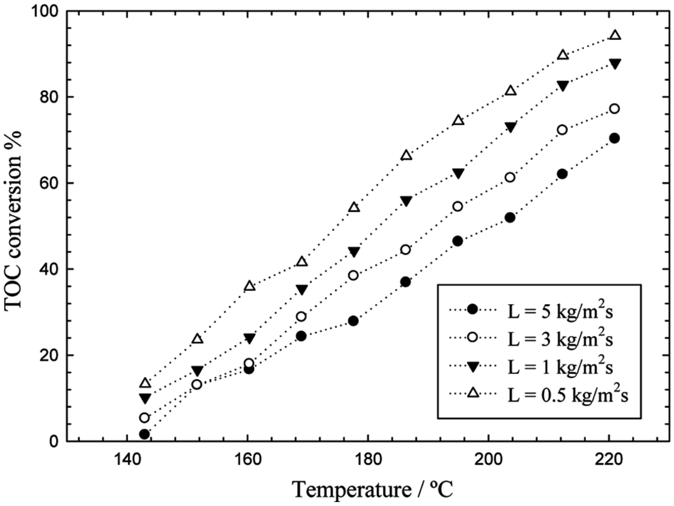

FIG. 2. TOC conversion as a function of mean bed temperature for different liquid mass fluxes ($G = 0.5\,kg/m^2s$; $P = 30$ bar).

decontamination rates of the organic fraction in liquid phase from 18 to 71% of conversion at the higher liquid flow rate $L = 5\,kg/m^2s$, respectively. In fact, given the exothermic nature of catalytic wet oxidation, one should expect that a further increase of temperature is responsible for higher mineralization rates total organic carbon due to thermodynamic considerations. Additionally, from Fig. 2 one can also observe that the conversion increase to 36 and 96% when the temperature increase from 160 to 220°C at the lower liquid flow rate $L = 0.5\,kg/m^2s$, respectively. This behavior can be explained by the high residence times achieved in such conditions that allows one to obtain higher TOC conversions.

Figure 3 plots the effect of operating pressure on TOC conversion for different temperatures at $L = 0.5\,kg/m^2s$. Therefore, for the maximum liquid residence time and as one operates the trickle-bed reactor at the lower interaction regime for gas and liquid phases (trickling flow regime), one can identify that the influence of pressure in the range 10 to 30 bar seems almost inexistent. In fact, at P = 10 bar the TOC conversions are 64 and 75% for 170 and 200°C, respectively. Moreover, a threefold increase of the total operating pressure to 30 bar led only to a increase of TOC conversions to 69 and 80% at 170 and 200°C, respectively. Therefore, comparing Figs. 2 and 3 a slight increase on temperature led to sizeable TOC decontamination rates whereas a major increase on pressure seems practically negligible. According to these concentration profiles, the total organic carbon conversion is higher when the catalytic wet air oxidation is carried out at higher temperatures because the oxidation reaction is exothermic and follows Arrhenius dependences, therefore, the reaction rate increases with increasing temperature. One should also bear in mind that an increase in temperature also increases the equilibrium water vapor pressure so that an increase in operating temperature requires an increase in total operating pressure in order to maintain the oxygen partial pressure. Since the catalytic wet air oxidation of phenolic acids is exothermic it releases energy which raises the temperature of the liquid and gas streams leading to further water evaporation. This fact can be advantageous because water will act as a heat sink, preventing the reaction from running away.

Figure 4 plots the effect of liquid mass flux on TOC conversion for different pressures at $G = 0.5\,kg/m^2s$. If one recalls the main effect of liquid flow rate on the depletion rate of organic carbon from Fig. 2 that was explained by the intrinsic liquid residence time of pollutant, one should anticipate a strong dependence of TOC conversion on it. Indeed, according to Fig. 4 there is virtually no effect of

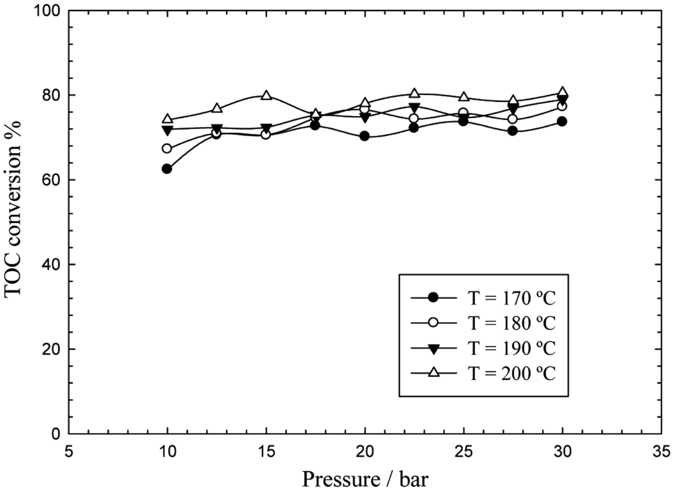

FIG. 3. TOC conversion as a function of operating pressure for different temperatures ($L = 0.5\,kg/m^2s$).

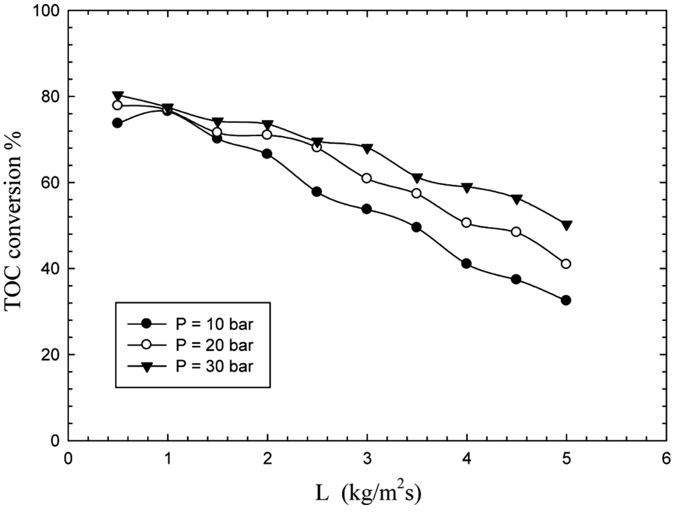

FIG. 4. TOC conversion as a function of liquid mass flux for different pressures ($G = 0.5\,kg/m^2s$).

pressure on TOC mineralization at the higher residence time given by the lower liquid flow rate ($L = 0.5\,kg/m^2s$) but the same is not true for the lower liquid residence time ($L = 5\,kg/m^2s$) which enables a differentiation of TOC conversion from 32 to 41% at P = 10 and 30 bar, respectively. This fact allows one to conclude that the higher interaction regimes attained by liquid and gas phases at $L = 0.5\,kg/m^2s$ when coupled with the variation of operating pressure, it promotes positively the TOC depletion rate as it can be observed from Fig. 4.

In order to investigate the effect of the gas flow rate on TOC conversion, Fig. 5 plots this reaction parameter for different temperatures at the lower liquid flow rate ($L = 0.5\,kg/m^2s$) and P = 30 bar. Once again, in the whole range of gas flow rate there is only a slight influence of oxidant flow rate on TOC conversion. In fact, at the lower gas flow rate ($G = 0.1\,kg/m^2s$) the TOC conversion increases from 57 to 78% at T = 170 and 200°C, whereas it increased from 65 to 81% for the same temperatures at the higher gas flow rate ($G = 0.7\,kg/m^2s$), respectively. Consequently, the gas flow rate seems to have an identical effect that was observed for operating pressure as discussed for Fig. 3. A sevenfold increase on the gas flow rate had an insignificant effect on TOC conversion when compared to a minor increase on temperature. Therefore, temperature plays a primordial role on the reaction behavior of the trickle-bed reactor when one balances it with major and integral hydrodynamic parameters that govern the multiphase flow regime.

Figure 6 plots the influence of liquid flow rate on TOC conversion for different initial TOC values (TOC_0) at $G = 0.5\,kg/m^2s$ and P = 30 bar. According to Fig. 6, one can observe the remarkable effect of the liquid flow rate already advanced in the discussion of Fig. 4, but now it can then be correlated as a function of initial concentration of organic carbon in the liquid phase. At the lower liquid flow rate ($L = 0.5\,kg/m^2s$), the TOC conversion increases from 64 to 81% for $TOC_0 = 200$ and 1200 mg/L whereas it increases from 39 to 53% at the higher liquid flow rate ($L = 5\,kg/m^2s$) for the same initial concentrations total organic carbon, respectively. As expected, the increase of TOC_0 led to higher mineralization rates in the whole range of liquid flow rate and can be explained by the kinetics and thermodynamic considerations systematized before that manage the catalytic wet air oxidation of phenol-like compounds.

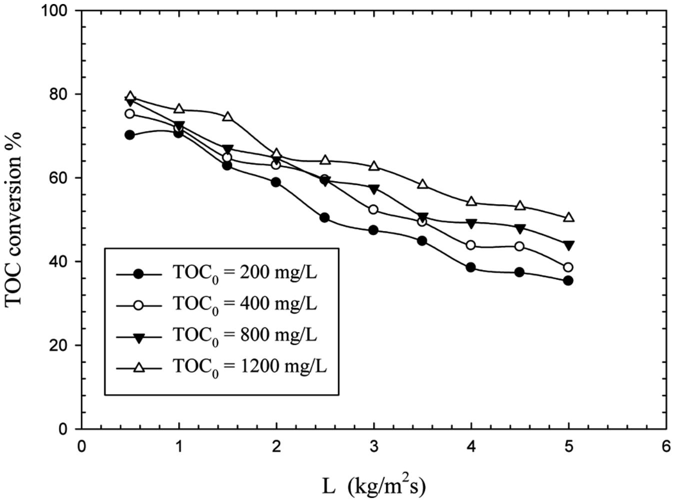

FIG. 6. TOC conversion as a function of liquid mass flux for different initial TOC values (TOC_0) ($G = 0.5\,kg/m^2s$; P = 30 bar).

Batch and Trickle-Bed Reactor

Total organic carbon conversions obtained from the batch experiments are plotted in Fig. 7 at different

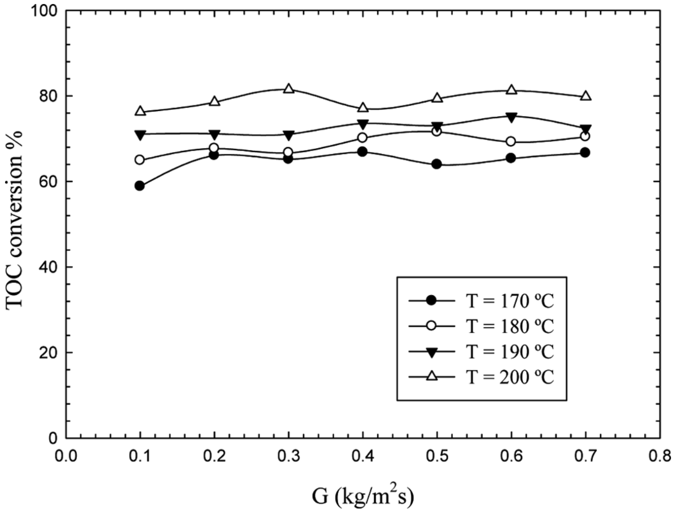

FIG. 5. TOC conversion as a function of gas mass flux for different temperatures ($L = 0.5\,kg/m^2s$; P = 30 bar).

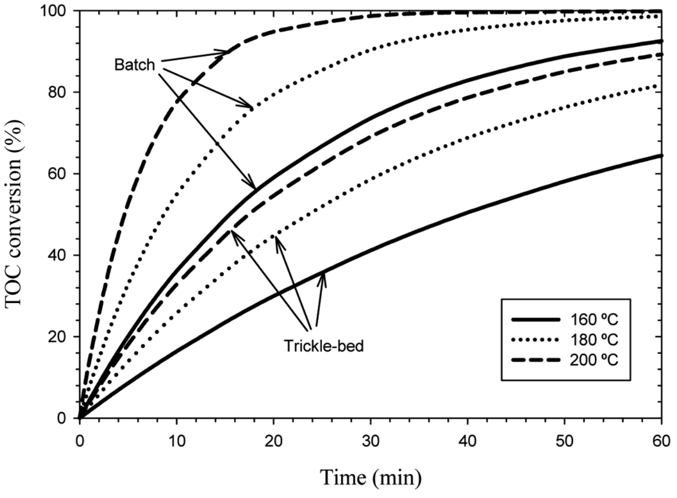

FIG. 7. TOC conversion for the BSTR and TBR at different temperatures ($L = 0.25\,kg/m^2s$, $G = 0.1\,kg/m^2s$, P = 30 bar).

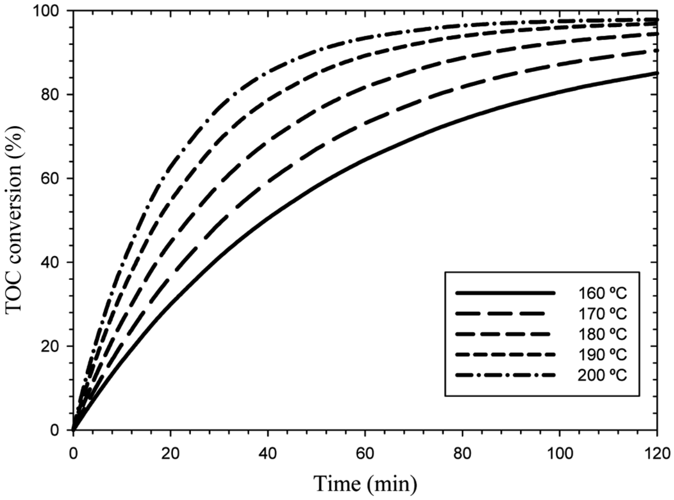

FIG. 8. TOC conversion for the TBR at different temperatures ($L = 1\,kg/m^2s$, $G = 0.3\,kg/m^2s$, $P = 30$ bar).

temperatures with the TOC conversion axial profiles along the trickle-bed reactor. After 30 min in the batch reactor, the TOC conversions were 73.6, 90.4, and 98.7 at 160, 180, and 200°C, respectively, whereas the corresponding TOC conversions attained along the TBR were 41.2, 58.6, and 69.0%. The detoxification was almost complete after 60 min in batch mode so that the TOC conversions were 92.6, 98.6, and 99.8% at 160, 180, and 200°C, respectively, while the continuous reactor exhibited lower TOC conversions: 64.5, 81.7, and 89.2%. Figure 8 plots the TOC conversion for the trickle-bed reactor for different temperatures at $L = 1\,kg/m^2s$, $G = 0.3\,kg/m^2s$, and $P = 30$ bar. As one should expect, the temperature had a strong effect on the decontamination efficiencies for a single operation mode as one can see in Fig. 8. Concerning the oxidation experiments that were carried out at the same temperature, the batch mode presented the higher TOC conversions when compared to the oxidations performed at trickling flow conditions. These differences can be explained by the hydrodynamic regime that characterizes the continuous operation mode which gave rise to mass transfer resistances that were practically inexistent at batch mode as opposed to the experimental findings reported for carbon-based catalysts (33).

Figure 9 plots the TOC conversion as a function of temperature at different reaction times for the batch reactor and at different liquid flow rates or different residence times for the trickle-bed reactor making use of splines to smoothen experimental data. The liquid flow rates used to build the TOC profiles for the trickle-bed reactor correspond to the times used to create the TOC profiles for the batch reactor. At 200°C, the TOC conversions were 73.6, 80.7, 85.7 and 94.3% after 3.3, 5.4, 16.4, and 32.7 min at batch mode. If the trickle-bed reactor is operated at the same temperature and residence times as stated before, the TOC conversions were 53.0, 61.3, 72.6, and 82.1% for the corresponding liquid flow rates that are 0.5, 1, 3, and $5\,kg/m^2s$. Therefore, temperature had a strong influence on TOC degradation in the range 160 to 220°C. Since the oxidation reaction is exothermic and follows Arrhenius dependence, the reaction rate increased with increasing temperature. From the comparison between the batch and integral profiles plotted in Figs. 7 and 9, it can be seen that the reaction rates in the integral reactor were always lower than those obtained for the batch reactor. This fact can be explained by the partial catalyst wetting achieved in trickling flow conditions. In addition, external mass transfer effects must also be considered as influencing the

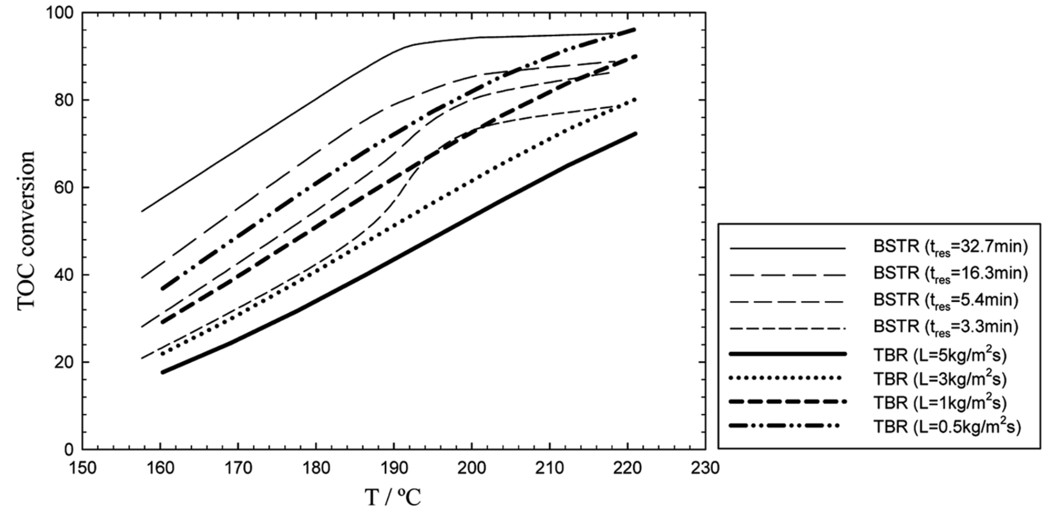

FIG. 9. TOC conversion as a function of mean bed temperature for different liquid mass fluxes ($G = 0.5\,kg/m^2s$; $P = 30$ bar).

observed rates in this reactor. Both of these effects are expected to diminish with increasing gas and liquid flow rates. One should mention that the dilution of catalytic bed have been performed uniformly so that it does not affect the residence time distribution of liquid phase in the trickle-bed flow regimes. Hence, the dilution should be carefully carried out to obtain reproducible data.

Figure 10 shows the TOC conversion profiles as a function of liquid flow rate for the trickle-bed reactor and the corresponding reaction times for the batch reactor. At 200°C, the TOC conversions in batch mode were 69.8 and 78.4% at 15 and 30 bar after 16.3 min, respectively, whereas at the lowest temperature (160°C) for the same residence time the TOC conversions were 19.8 and 37.4% at 15 and 30 bar in batch mode. Therefore, the double increase of pressure had less effect on TOC removal rather than the increase of 40°C. In what concerns the TOC conversions attained for the trickle-bed reactor, the effect of operating pressure is even smaller which allows one to conclude that the influence of temperature is predominant over the oxidant pressure.

Long-Term Stability

In order to evaluate the leaching of active species to the liquid phase that may become a second pollution source and an important catalytic deactivation factor that has to be avoided, the manganese and copper metals were measured in terms of leaching for the batch and trickle-bed reactor experiments. Applying the same catalyst sample, the reusability of the powder catalysts in batchwise experiments was investigated in the oxidation of phenolic acids with five consecutive experiments. After each experimental run, the catalyst was removed from the batch stirred reactor and then was washed with water, dried at atmospheric condition, and submitted for another oxidation run. The temperature used to dry the catalyst between the different consecutive experiments of the stability study was 105°C. The loss of catalyst mass was detected with an extent of 3 to 5% of the catalyst mass that was measured during the assembly of each recycling procedure. Leaching of active metals such as manganese and copper were then monitored for each consecutive run leading to a loss of 8% (*w*/*w*) of initial mass of active metals loaded into the batch reactor.

Adsorption of phenolic acids and other organic compounds that are generated during the oxidation on the catalyst surface is also an important parameter. Less than 3–5% conversion of organic carbon was identified in the first cycle at the starting reaction time. As long as the recycling pathway was underway, there is no quantifiable organic carbon due to adsorption meaning that phenol-like pollutants could not be eliminated during the washing procedure so that it linger on the recycled manganese-copper catalyst. However, it should be stressed out that a loss of catalytic activity measured in terms of TOC abatement was observed after three successive experimental runs and languish if one proceeds further with the recycling process. TOC conversion decreased after the first three successive runs but next, in the fourth and fifth runs, the TOC conversion remained practically constant, this fact being explained by structural stabilization of manganese-copper catalysts. According to the literature (34), one may also advance that a reasonable explanation for the catalyst deactivation might be some modification of the active manganese-copper oxides that occurred due to the oxidizing medium. Since the catalytic activity strongly

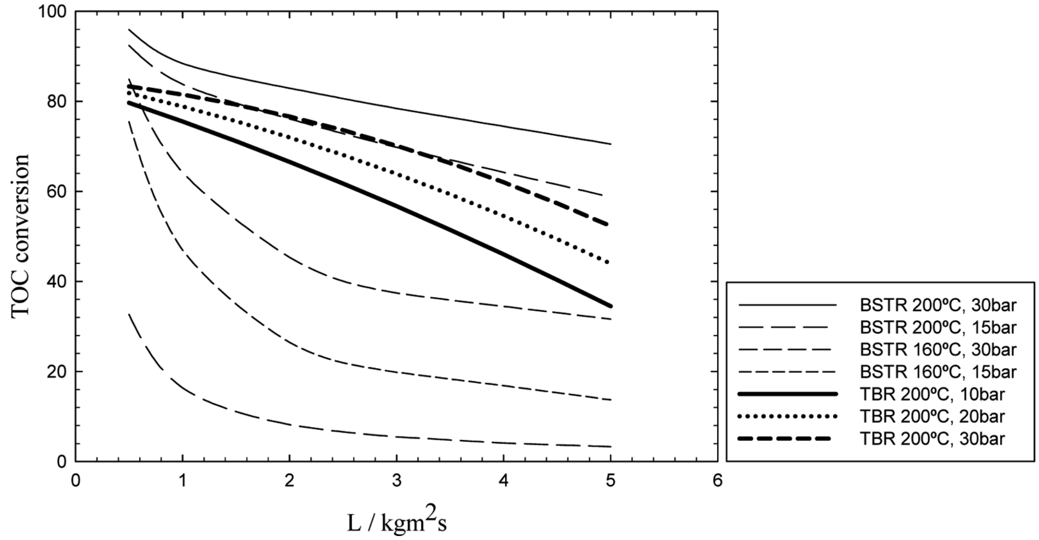

FIG. 10. TOC conversion as a function of liquid mass flux for different pressures (G = 0.5 kg/m^{2}s).

depends upon the reduction/oxidation treatment of the catalyst, the loss of catalytic activity after three consecutive experimental runs was due to over-oxidation of the surface of catalyst particles and could be minimized when submitting the manganese-copper catalyst to a reduction environment. As a final point on batchwise experiments, the above-mentioned facts warned good catalytic properties which suggest that long-term stability can be attained with a manganese-copper oxide framework.

The catalytic stability in trickle-bed reactor experiments was checked by analysing TOC concentration under standard operational conditions at trickling flow conditions. On the evolution of the TOC with time, different stages were monitored at the starting reaction time. After the initial period of reaction of gas-liquid equilibrium, it was identified as a transient stage during which the TOC conversion increased slowly to an asymptotic value which lasts up to 300 h of operation before the steady state was reached. This behavior can be explained by the time required to achieve a stable equilibrium of the oxygen coverage on the manganese-copper catalyst surface. Afterwards, as long as a stable equilibrium of the oxygen coverage of the catalyst surface was attained, it exhibited a stable activity up to 600 h. Repeating the reaction process, after a few weeks on operations in such a way that the outlet solution was collected during the steady state operation and reused over the catalytic bed, the same behavior was recognized in the presence of manganese-copper oxides being noticeable that the catalytic activity remains stable during each oxidation step. TOC concentration in the outlet stream kept invariable at each commencement of the experimental run with insignificant loss of catalytic activity.

CONCLUSIONS

High-strength phenolic wastewaters can be successfully treated by catalytic wet oxidation either in batch or trickle-bed reactors. However, considerable differences on TOC conversion were attained in the whole temperature range. Whereas at 200°C and 30 bar, the detoxification can be successfully accomplished in batch mode after 60 min, the TOC conversion achieved with the trickle-bed reactor was 89.2%. The oxidation temperature has a major effect on decontamination efficiencies rather than the oxidant pressure. Also, the total organic carbon conversion profiles were evaluated at equivalent reaction times both for the batch and trickle-bed reactors. In the whole investigated range of temperature and pressure, the batch reactor exhibited the highest detoxification rates compared to the trickle-bed ones. Notwithstanding, a demerit of the batch reactor was linked with the loss of catalytic activity in the long-term operation.

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NOMENCLATURE

G	Gas mass flux, kg/m^{2}s
L	Liquid mass flux, kg/m^{2}s
p	Pressure, bar
$-r$	Oxidation rate
t	Time, s
T	Temperature, $^\circ C$
TOC	Total organic carbon, ppm

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