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Efficient mineralization of benzoic and phthalic acids in water by catalytic ozonation using a nickel oxide catalyst

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Abstract

Organic acids (OA) are usually used as a refractory model compounds that require prolonged reaction time for their mineralization by different treatments. In this study, benzoic and phthalic acids in aqueous solution, were significantly degraded and mineralized by catalytic ozonation in presence of nickel oxide (NiO). For instance, only 42% mineralization was obtained by direct reaction with molecular ozone, while by catalytic ozonation a 98% was achieved. These surprising results led to study in depth the role of NiO in the catalytic ozonation of both organic acids. With the aim of identifying the surface species responsible for the high activity of NiO, X-ray photoelectron spectroscopy (XPS) and High performance liquid chromatography (HPLC) were used as the main analytical tools. According to the results, the mineralization of both organic acids was directly influenced by the organic groups adsorbed onto NiO surface. Therefore, NiO plays a relevant role as a catalyst forming complex surface compounds which are subsequently decomposed increasing the mineralization efficiency. In addition, a simplified kinetic study was conducted to characterize the effect of NiO concentration on the removal efficiency of both organic acids and the main byproduct (oxalic acid) accumulation and degradation. These results were explained in terms of a combination of two reaction mechanism such as, conventional ozonation and indirect reaction based on •OH radicals.

Keywords: Catalytic ozonation, nickel oxide, benzoic acid, phthalic acid.

1. Introduction

The increasing worldwide contamination of freshwater with thousands of chemicals is a serious environmental problem facing humanity in the present century. Industrial and municipal wastewater containing numerous toxic and recalcitrant compounds seeps into rivers, lakes, groundwater and coastal seas [1,2]. Nowadays, a challenge in wastewater and drinking water treatment is to improve the existing processes and to design new ones, with the purpose of removing a larger number of pollutants from water matrices [3]. Therefore, various methods have been developed to capture, degrade or mineralize organic pollutants in wastewater, such as, ion-exchange, coagulation, flocculation, adsorption, chemical oxidation, ozone treatment, membrane filtration and photocatalysis [4]. Ozonation has been a successful method for degradation of organic pollutants and disinfection for several decades however, it is very difficult for this route to obtain a partial mineralization of organic compounds. Accordingly, several ozone-based advanced oxidation processes have emerged, for example to name a few, H_2O_2/O_3 , UV/ O_3 and catalytic ozonation [5].

Catalytic ozonation has been shown in many cases as an effective process to eliminate organic refractory compounds in wastewater [6,7]. This kind of treatment was developed to overcome the drawbacks of conventional ozonation such as, the accumulation of recalcitrant biodegradables byproducts and partial mineralization [8]. Commonly, activated carbons or metal oxides and supported metals have been the most studied catalysts in ozonation of toxic compounds in water [9,10].

However, until now, the mechanism of catalytic ozonation seems elusive and with a lot of contradictions [11]. The literature concerning catalytic ozonation has proposed several analytic techniques in order to establish and/or explain its reaction mechanism [5]. Recently, our research group has proposed X-ray photoelectron spectroscopy (XPS) as a basic tool to elucidate the reaction mechanism in the catalytic ozonation [10]. XPS can provide information related with the presence and nature of functional groups onto surface properties of spent catalyst during the organic compounds degradation. Our previous studies showed that 2,4-dichlorophenoxyacetic acid (2,4-D) elimination was possible due to surface complexes formation of organic compounds with active metal sites during catalytic ozonation [10]. XPS spectra revealed the presence of two important signals: nickel-oxalate complex and $NiCl_2$, this information was used to include these compounds in the reaction pathway.

Noble metals are efficient in the generation of surface carboxylate complexes in ozonation but a low pH condition is always necessary to achieve higher degree of contaminants degradation [12]. Nickel oxide (NiO) has many applications such as gas sensors [13], chemical catalysts [14], among others. NiO significantly increased the mineralization degree during the catalytic ozonation of 2,4-D at pH 3.1 and it also showed high stability [10]. On the other hand, in most of the reported works on catalytic ozonation, the effect of the reaction parameters on the degradation of different pollutants has been the main research topic [15-17]. Therefore, there is a lack of investigation of the reaction mechanism associated with the chemical structure of the contaminants, during the degradation and mineralization steps.

In general, the catalytic ozonation is considered as a non-selective process; however, the chemical structure of the initial compound is a primordial factor that defines the interactions with the catalyst during ozonation. Benzoic and phthalic acids were chosen as target compounds owing to its chemical structure are closely similar between them (the only difference being the number of carboxyl groups presented in each molecule). Both compounds are toxic and exhibit low

biodegradability [19,20]. Benzoic acid (BA) is found in wastewater from the pharmaceutical industry [21,22]. In the case of phthalic acid (PA), it has been used in the painting industries and the acylation - esterification in dyes. In consequence, it has been detected in different aqueous matrices, for instance: landfill leachate water, surface water, sediments and even in atmospheric aerosol [23,24]. With respect to the degradation of benzoic or phthalic acids by catalytic ozonation, the studies are scarce.

Some researchers have reported several details on the selectivity of the catalytic ozonation process over compounds with similar chemical structure. T. Zhang et al. [18] studied the selectivity of six carboxylic acids (acetic, citric, malonic, oxalic, pyruvic and succinic acids) that have relatively low reactivity with molecular ozone. Their results clearly showed that the catalytic ozonation in presence of CuO/CeO₂ cannot degrade all carboxylic acids. Acetic, malonic and succinic acids were removed less than 20% in comparison with the other acids. These authors employed IR spectroscopy (FTIR) to characterize the surface interaction of six carboxylates that were found as part of metal-carboxylate complex.

The aim of the present work is to investigate the catalytic ozonation of toxic organic acids (BA and PA) over NiO catalyst by using FTIR and XPS as characterization techniques. In particular, we are interested in studying the C1s and O1s regions, after catalytic ozonation of the organic acids, which provide useful information about the surface interactions on NiO catalyst.

2. Experimental section

2.1. Materials and reagents

The model solutions of both acids (BA or PA) were prepared with 80 mg L⁻¹ of the organic compound (Sigma Aldrich, 99%) and dissolved in distillate water. The initial pH was 3.2 and it was not controlled during the ozonation. All chemicals used in the experiments were analytic grade reagents. NiO (Sigma-Aldrich, 99%) was used in the experiments as catalyst.

2.2. Ozonation

Ozone was generated from dried oxygen by an ozone generator HTU500G (Azco Industries Limited, Canada) using the corona discharge effect. The ozone concentration in gas phase was measured by Ozone Analyzer BMT 946BT (BMT Messtechnik, Berlin). The catalysts and ozone concentrations were kept at constant values, 0.1 g L⁻¹ and 29±1 mg L⁻¹, respectively. The ozone-oxygen mixture flow was 0.5 L min⁻¹. All ozonation experiments were carried out in a semi-batch type reactor (0.5 L) at 21°C. Details of analytic conditions and ozonation procedure can be consulted in [10].

2.3. Analytical methods

The concentration of BA and PA were determined by high performance liquid chromatography (HPLC) using a Perkin Elmer Flexar instrument equipped with a DAD detector and "Prevail Organic Acid" 5μ Grace column. In the case of PA, the mobile phase was acetonitrile and 25 mM KH₂PO₄ buffer, previously adjusted at a 2.6 pH with H₃PO₄ (60:40 v/v), solution. The flow rate was set to 1 mL min⁻¹. While BA, the mobile phase was acetonitrile: water (70:30 v/v), mixture using C18 (Grace) column. External standard method and KH₂PO₄ buffer mobile phase, at a 210 nm wavelength, were used to identify presence of products and byproducts during BA and PA degradation. The mineralization degree of

organic acids was monitored with a Torch instrument (Teledyne, Tekmar). All results are presented as the mean for triplicate determinations of each sample.

The pH_{PZC} was determined by Malvern Zetasizer at 25°C and HCl titration was used to adjust the NaOH values for each sample. FTIR spectra were recorded using LabRna HR800 model with lens of Attenuated Total Reflection (ATR) operating on infrared middle range, with diamond crystal tip and magnification of 36X in a reflection configuration. XPS analyses were performed using ThermoFisher Scientific K-Alpha X-ray photoelectron spectrometer with a monochromatized $\text{AlK}\alpha$ X-ray source (1487 eV). The base pressure of the system was 10^{-9} mbar. Prior to XPS analysis, all samples were dried at 100°C for 24 h. Subsequently, each of the specimens powders were dispersed and embedded in a 5x5 mm indium foil, after these were fixed with Cu double side tape to the sample holder. The position of the C1s peak at 284.5 eV was monitored on each sample to ensure that no binding energy shift due to charging had occurred. Narrow scans were collected at 60 eV analyzer pass energy and a 400 μm spot size.

2.4. Kinetic model

The model of the organic acids (OA) decomposition was proposed to obey the so-called pseudo-monomolecular dynamics. This approach does not take into account some aspects of the reaction nature. However, the complexity of parallel-series reactions and the presence of catalyst in the reactor limited the application of more complicated and realistic model where all the byproducts variation (accumulation and degradation) are considered.

The modelling strategy consider two different types of reactions: the first one was the decomposition of the initial OA while the second one describes the accumulation of the main byproduct (oxalic acid or OXA) generated as consequence of decomposition of the initial OA. The first type of reaction was modeled using a decaying exponential function defined as:

$$OA(t) = OA(0)e^{-kt} \quad (1)$$

where $OA(t)$ is the concentration of OA measured during the reaction, $OA(0)$ is the initial concentration of the same organic acid and k is the pseudomonomolecular reaction rate constant. For the second reaction, the model selected to characterize the accumulation of byproducts was:

$$OXA(t) = OXA(t^*) \left(1 - e^{-k_f t}\right) \quad (2)$$

where $OXA(t)$ is the concentration of the oxalic acid measured during the reaction. The term refers to $OXA(t^*)$ that is the concentration of the same byproduct at the time t^* that coincides with the time where the maximum level of this organic was detected. The parameter k_f is the corresponding pseudomonomolecular accumulation reaction rate constant. Finally, the third type of reaction was modeled using the same decaying exponential function defined as:

$$OXA(t) = OXA(t^*) e^{-k_d(t^*-t)} \quad (3)$$

where $OXA(t)$ is the concentration of the byproduct to be decomposed and $OXA(t^*)$ is the maximum concentration of oxalic acid. The parameter k_d is the pseudomonomolecular decomposition reaction rate constant corresponding to this selected byproduct.

3. Results and discussion

3.1 Degradation and mineralization of BA and PA by conventional and catalytic ozonation

As mentioned before, in the last decade, there has been a growing interest in the study of the heterogeneous catalytic ozonation as a new and efficient method for the removal of contaminants from drinking water and wastewater. Several studies have indicated that metal oxides and supported metal oxides are effective catalysts for ozonation (e.g. Al_2O_3 , MnO_2 , TiO_2 , among others) [7]. In particular, nickel oxide (NiO) is an important transition metal widely used as a catalyst for its extraordinary electrical, thermal, catalytic and redox properties, and its application in catalytic ozonation is scarce [10].

Fig. 1 shows the degradation profiles of both aromatic organic acids (BA and PA) during direct reaction with molecular ozone and in presence of catalyst. By the first route (Fig 1A), it is clearly noticed that the degradation rate of benzoic acid was higher than that obtained for the PA, since 50% of BA degradation was reached after 3.5 min of reaction time, while PA degradation required a double of reaction time. These results indicate that benzoic acid is easily eliminated with ozone, which agree with the reaction rate constant ($k=1.2 \text{ M}^{-1} \text{ s}^{-1}$) reported by P. Neta et al. [25], in the case of phthalic acid, G. Wen et al. [26] determined a value of $0.092 \pm 0.042 \text{ M}^{-1} \text{ s}^{-1}$. Hence, the degradation efficiency is dependent on the organic acid chemical structure as well as the reaction time. It is worth noting, that direct reaction with molecular ozone was a feasible method to decompose BA and PA, achieving up to 95% removal of both compounds in 20 min. Fig. 1A also displays the elimination of BA and PA in combination of ozone and NiO as catalyst. The integrated treatment did not present a significant difference in the degradation profiles of two acids. This result has been also observed by Q. Dai et al. [27] in the degradation of acetylsalicylic acid using unsupported Fe_3O_4 and supported on SiO_2 , as catalysts. The total organic carbon (TOC) measurements showed that the mineralization degree was significantly improved in the catalytic ozonation mode compared to the conventional ozonation (Fig. 1B). By using this late route, a 35% and 42% of mineralization degree was reached for BA and PA at 60 min, respectively. Despite the fact that ozone is a strong oxidant agent but it is also selective, it does not remove the recalcitrant organic compounds in a reasonable time [28]. In contrast, by the catalytic ozonation process, a significant improves of TOC removal (around 95%) was attained at 60 min for both acids. On the contrary to the fact observed in the degradation of organic acids (Fig. 1A), the mineralization rate of PA was higher than that of BA, probably due to an increase of the generated oxidant species.

3.2 Effect of catalyst concentration

The heterogeneous catalytic ozonation is a complex process which involves gas, liquid and solid phases where the catalyst plays a relevant role. Therefore, some experiments were carried out to study the effect of catalyst concentration on the elimination degree of model compounds and to find out the optimal catalyst dose. Fig. 2A shows the degradation profiles of BA as a function of catalyst concentration (0.1, 0.5 and 1.0 g L^{-1}). According to these results, it can be observed that there was not a significant effect on the degradation profiles by varying the catalyst concentration.

Concerning the degradation profiles of PA (Fig. 2B), it was detected that PA degradation increased 30% at 1.0 g L^{-1} catalysts concentration compared to the direct reaction with molecular ozone during the first 2 min. This fact is in agreement with the results obtained by other researchers which have also reported that at increasing the catalyst

concentration, a better degradation rate of organic pollutants is obtained [29,30]. Note that the effect of catalyst concentration in both model compounds was quite similar at long reaction times (> 10 min, see Figs. 2A and B).

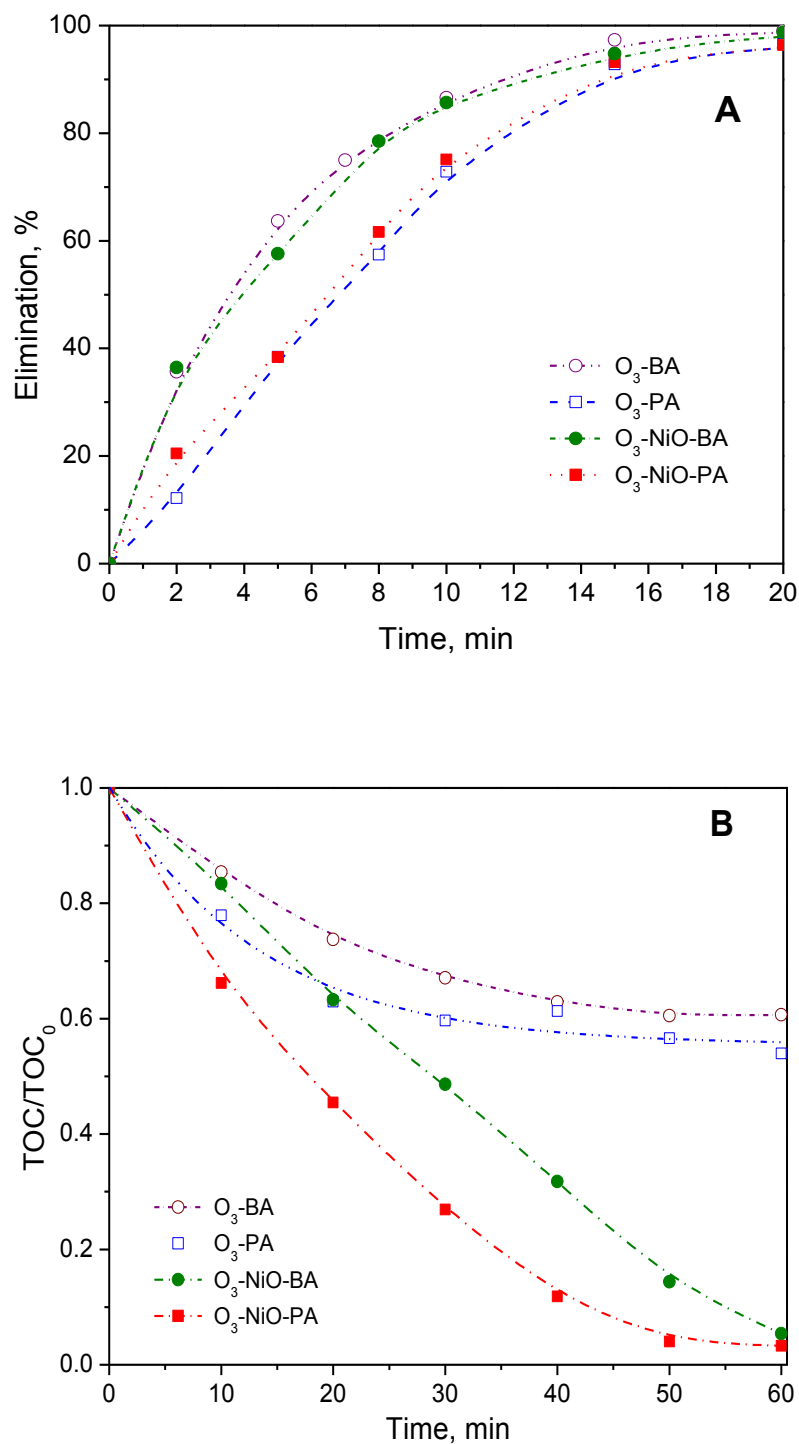


Figure 1 (A) Removal of BA and PA as a function of ozonation time, (B) TOC decay during conventional and catalytic ozonation with NiO.

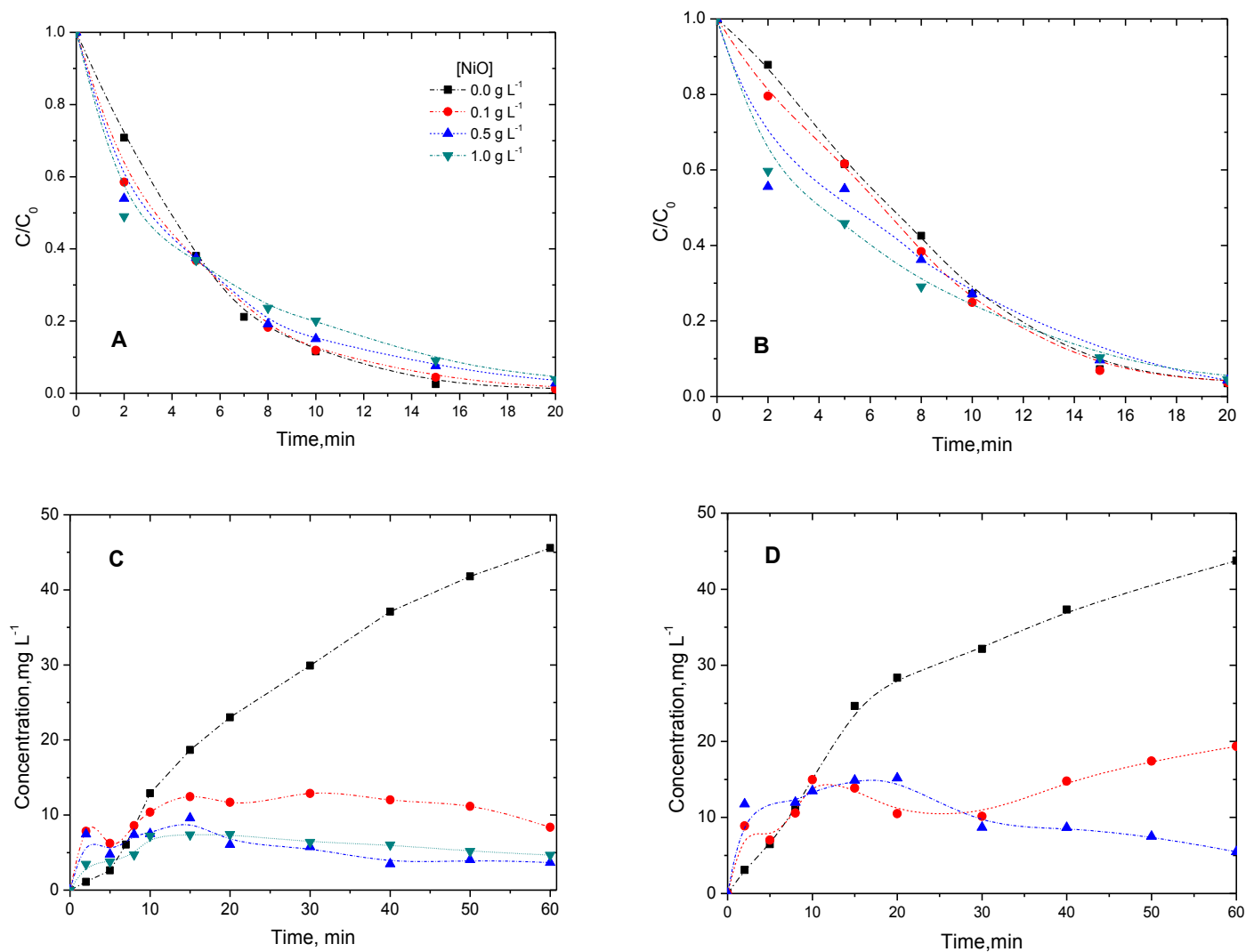


Figure 2 Effect of catalyst concentration on (A) elimination profiles of BA and (B) PA and (C-D) oxalic acid concentration coming from the degradation of BA and PA, respectively.

This result suggests that the reaction path for degrading BA and PA could be forming the similar byproducts before leading to the mineralization step, which it was not dependent of catalyst dose. For this reason, after a careful analysis of the byproducts generated in all experiments, we found that oxalic acid (OXA) was the main recalcitrant byproduct and it was chosen to continue the study of catalyst concentration influence.

Fig. 2C displays the effect of catalyst dose on the concentration profiles of oxalic acid generated by BA degradation. In the direct reaction with molecular ozone, OXA was accumulated during the whole reaction time reaching up a concentration of 45 mg L⁻¹. When NiO was introduced in the ozonation process, the concentration profile of OXA changed significantly. At the catalyst dose of 0.1 g L⁻¹, the OXA concentration was about 9 mg L⁻¹ which means almost 6 times lesser amount than conventional ozonation, after 60 min of reaction time. Further increase of the NiO loading (0.1 to 0.5 g L⁻¹) produced a minor amount of OXA (≈ 4 mg L⁻¹). However, catalyst dose in the range 0.5 to 1 g L⁻¹ slightly increased the OXA concentration (≈ 5 mg L⁻¹). These results exhibit that an optimum of NiO content (0.5 g L⁻¹) occurs

in the catalytic ozonation for organic acid. Therefore, due to the OXA concentration was lower in the degradation of BA compared to the degradation of PA at the same catalyst concentration, this means that the amount of formed OXA will depend on the chemical structure of the pollutants (Fig. 2C and D).

Our previous results clearly indicated that in the presence of NiO as catalyst, a significant reduction of the concentration of OXA was observed, which did not happen in the conventional ozonation. The kinetic study of the BA and PA decomposition yields to a better characterization regarding the effect of catalyst concentration. Table 1 enlists the reaction rate constants for BA and PA decomposition, the OXA formation–decomposition constants calculated on the basis of the proposed kinetic models. According to the results, at increasing the catalyst concentration, there was no effect in the rate constants for BA degradation, whereas, PA rate constants were slightly increased. With respect to the OXA reaction constants, k_f (formation) and k_d (decomposition), coming from BA and PA degradation, an optimal catalyst concentration of 0.5 g L^{-1} was found.

Table 1. Reaction rate constants of BA and PA decomposition, oxalic acid formation-decomposition for each model compound as a function of catalyst concentration.

[NiO], g L^{-1}	Benzoic acid k, min^{-1}	Oxalic acid		Phthalic acid k', min^{-1}	Oxalic acid	
		k_f, min^{-1}	k_d, min^{-1}		k_f, min^{-1}	k_d, min^{-1}
0	0.2069	0.03851	NA	0.1256	0.04856	NA
0.1	0.1909	0.1721	0.009172	0.1328	0.04717	0.006173
0.5	0.1847	0.2146	0.03182	0.1421	0.4299	0.02859
1.0	0.1759	0.03182	0.01177	0.161	-	-

3.3 Effect of hydroxyl radical scavenger

As is well known, tert-butyl alcohol (TBA) is a hydroxyl radical scavenger that is usually used to distinguish molecular ozone oxidation from hydroxyl radical oxidation in ozonation processes [31,32]. As shown in Fig. 3, the presence of TBA (200 mg L^{-1}) significantly depressed the TOC profile of both organic acids. In the case of BA it was observed a reduction in comparison without TBA, while PA retards mineralization degree from 95 to 22%, during the 60 min of ozonation. These results showed that TBA had a negative influence of the global efficiency of BA and PA elimination, which means that the catalytic ozonation is followed by a concerted series of reactions including, very importantly, hydroxyl radical generation in aqueous phase. On the other hand, it is feasible that the inhibition could be ascribed to the adsorption of TBA on the catalytic surface. This fact was confirmed by a surface chemical composition study of the spent catalyst carried out in the presence of TBA during the BA and PA degradation by XPS.

3.4 FTIR and XPS of fresh and ozonated NiO

Previous publications have reported that the study of catalyst in different stages of evaluation, helps to explain the mechanism of the catalytic ozonation [10,18,33]. Based on the latter and with the intention to conduct a careful analysis of the NiO, FTIR and XPS techniques were used as analytical tools to provide information about functional groups, the oxidation state and the chemical environment of the elements present on the catalyst surface.

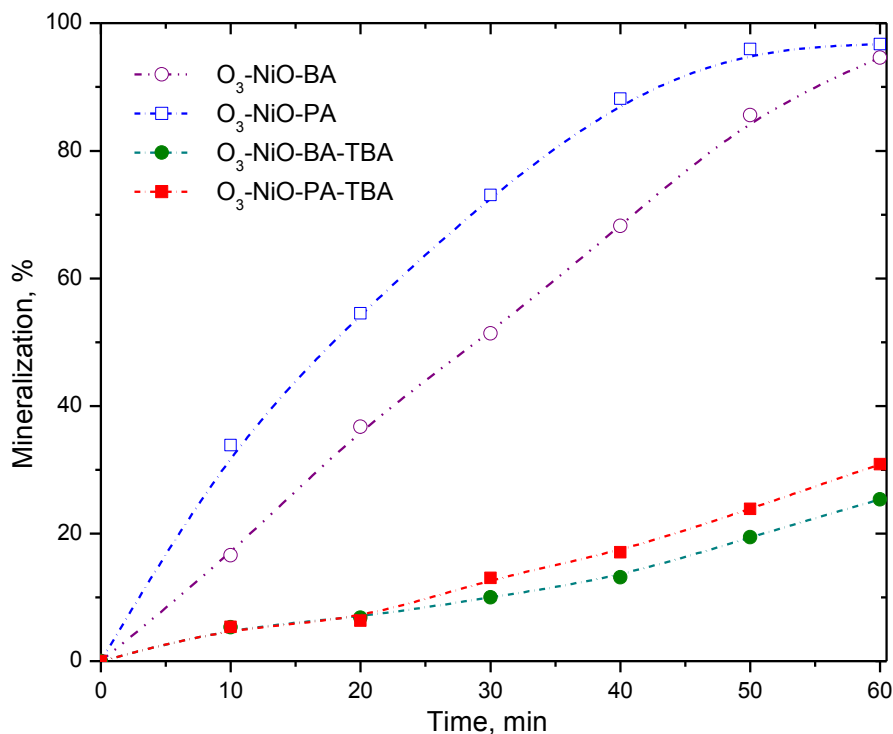


Figure 3 Mineralization degree of BA and PA without or with TBA addition.

According to the literature [34], ozone interacts with the hydroxyl groups generated from water adsorption on Lewis acid sites, then, the production of oxidant species is initiated, favoring the pollutant degradation. Thus, it is worthy to investigate what about the functional groups on the surface of NiO, which could be responsible of increasing the degradation rate. ATR-FTIR experiments were carried out in absence and presence of BA at $t = 0, 20$ and 60 min of reaction time. As shown in Fig. 4A, the first peak at 1350 cm^{-1} corresponds to the rocking vibration of the CH_2 groups while the second peak at $1570\text{--}1625\text{ cm}^{-1}$ is a characteristic peak to the bending vibration of the free or adsorbed water. Checking the spectrum of BA after 20 min of reaction time is clearly observed an increase of the intensity of H_2O peak. However, after 60 min reaction time, the H_2O peak decreased due to surface chemisorbed water can act as active sites participating with ozone to form oxidant species as $\bullet\text{OH}$. Furthermore, the apparition of a new peak around 1025 cm^{-1} (60 min) is attributed to the vibrational tension of --C=C-- , which can be due to intermediates compounds adsorbed on the NiO surface.

In the case of PA, the results showed a similar behavior than those observed in BA (Fig. 4B). The only difference between BA and PA spectra was observed at 20 min, the second peak at 1625 cm^{-1} of PA presented a lower intensity than that of BA (1570 cm^{-1}). This previous result can be interpreted as to TOC rate of PA was bigger than BA, in consequence there is an increment in consume of surface hydroxyl groups of NiO used during the PA elimination.

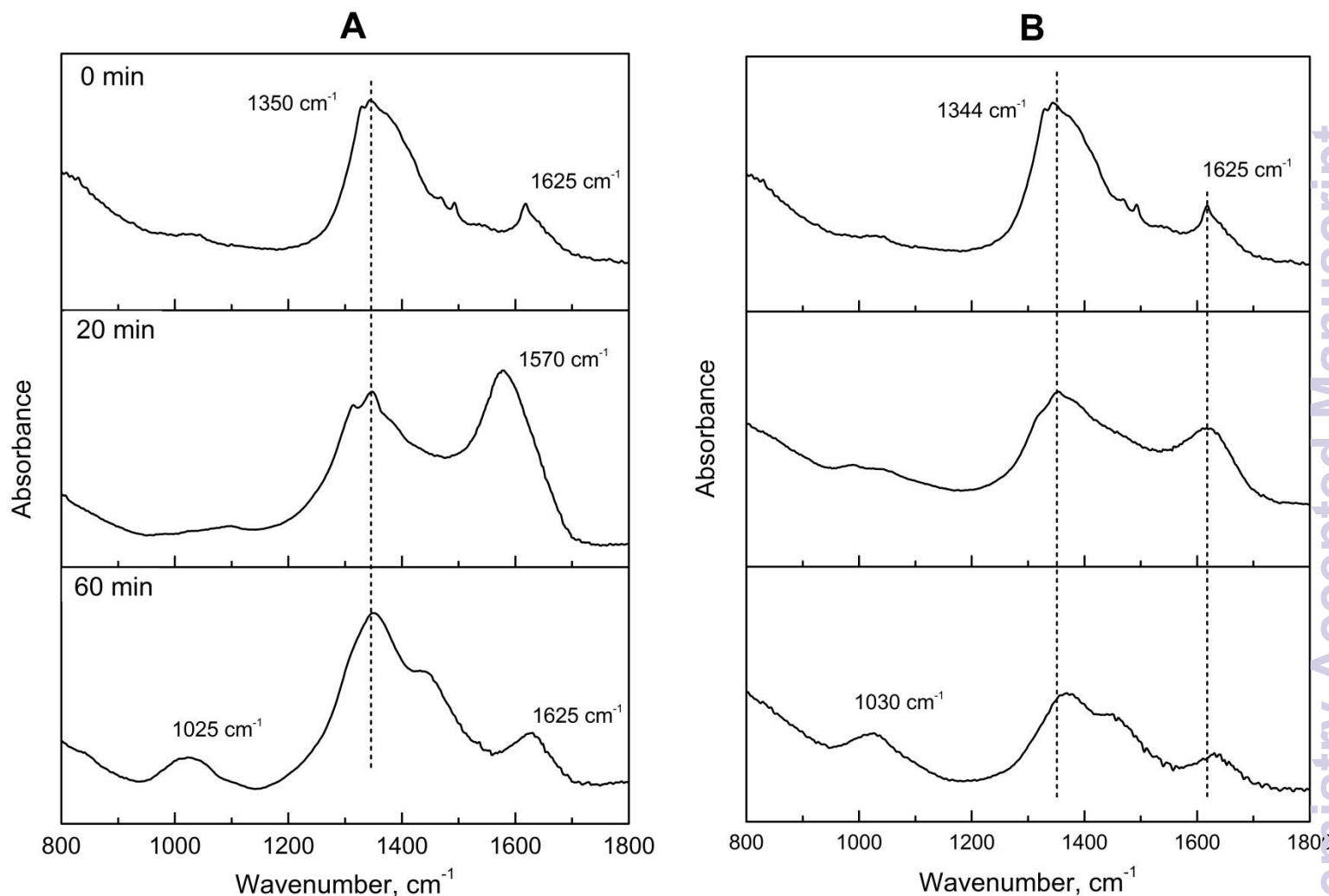


Figure 4 ATR-FTIR spectra of NiO obtained during the catalytic ozonation of A) BA and B) PA at 0, 20 and 60 min of reaction time.

With the propose of providing more information related with the nature of the ligands associated on the catalyst surface, XPS was used as a powerful tool to identify and follow-up the evolution of main species involved in the BA and PA elimination processes. Although, Ni species are considered as the only active sites, the diverse XPS spectra of Ni2p did not show difference in all analyzed samples. For this reason, C1s and O1s XPS core lever spectra were analyzed for fresh and ozonated NiO, as well as for the successive BA elimination processes. Raw data were fitted with a combination of Gaussian–Lorentzian mix function and Shirley background subtraction (Fig. 5). It is noteworthy by direct observation of C1s curves, Figures 5a to 5e, the chemical evolution and/or emergence of carbon species produced during the different reaction stages.

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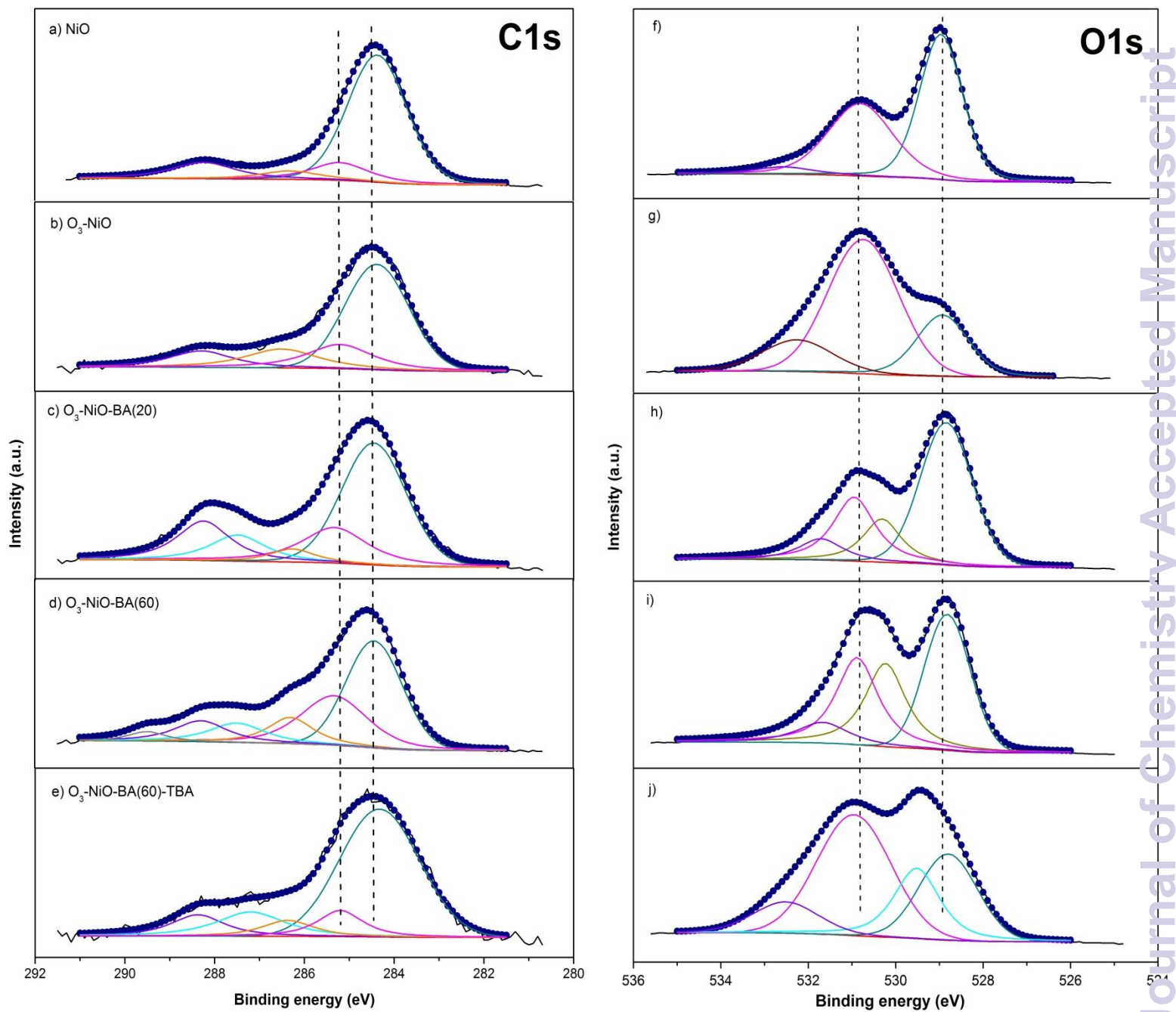


Figure 5 XPS high resolution spectra of the C1s (a-e) and O1s (f-j) regions for NiO catalyst: (a,f) fresh, (b,g) ozonated, (c,h) at 20 min, (d,i) at 60 min and (e,j) at 60 min in presence of TBA, after ozonation of benzoic acid

From the C1s XPS core level spectra fitting, it was established that, and for all cases, the main peak at 284.5 eV corresponds to adventitious carbon which nearly presents a constant concentration in all samples. The C1s region for NiO and O₃-NiO samples have been fitted employing three basic contributions, situated at 285.3, 286.5 and 288.3 eV which correspond to -C-C-, C=O and -COOH, respectively. NiO-fresh presents the lowest content in C-OH species whereas O₃-NiO exhibited decay tendency for C-C and C=O. Regarding the samples which underwent BA removal processes, and besides the -C-C-, C=O and -COOH, the existence of additional chemical species are clearly noticeable at high binding energies and, as mentioned previously, it can be discern from Fig. 5c to 5e. The latter was foreseeable due to the adsorption of some intermediaries onto the catalyst surface during BA decomposition by ozone.

The analysis for O1s region permitted agreeing the above mentioned facts. In Figs. 5f to 5j, it can be elucidated the passage from a two-component system, fresh nickel oxide, to a four-component system by ozonated and used BA elimination catalysts. Fresh nickel oxide O1s XPS spectrum was decomposed in two peaks located at 528.8 ±0.1 eV assigned to lattice oxygen in Ni-O and 530.8 ±0.1 eV related Ni-OH bonds, specifically Ni(OH)₂ (Fig. 5f). On applying the same model to the ozonated sample, a third contribution is needed to recover the experimental spectrum (Fig. 5g). An additional contribution can be assigned to (O₂)₂-peroxi species, 532.3 ±0.1 eV, but this specie is less stable, so the signal likely corresponds to H₂O. For samples of O₃-NiO-BA(20) and O₃-NiO-BA(60), the presence of adsorbed organic groups on NiO was established by the need of two additional peaks assigned to C-O, 530 ±0.1 eV and at 531.7 ±0.1 eV for C=O. The relative amount of those signals increases as a function of the ozonation time including the peak of Ni(OH)₂, see Figs. 5h and i. On the other hand, the samples O₃-NiO and O₃-NiO-BA(60)-TBA showed a decrease in intensity for Ni-O bond contribution was noticed while for the rest samples not significant change was perceived (Figs. 5g and 5j).

Furthermore, both samples presented a bigger intensity of peak attributed to Ni(OH)₂ which acts as Lewis acid sites having a contribution in the generation of active oxidizing species. As previously, it was identified by FTIR, the OH group also favoring the generation of these species, for instance hydroxyl radicals which improved the efficiency in BA decomposition and the subsequent increase of the mineralization degree of the intermediates. In view of these results, it can be established that NiO (when interacted with ozone) favored the production of Ni(OH)₂, Fig. 5g. Nonetheless, in presence of organic matter, the Ni(OH)₂ reacted with the compounds generating organic acid for the case of BA. When TBA was introduced in the BA elimination, it was blocking the active centers (Ni-O) on the catalyst surface, therefore the spectra of XPS was similar than O₃-NiO, for the peak of Ni-O and Ni(OH)₂.

Fig. 6 summarizes the type of surface-bound functional groups on NiO under different reaction conditions identified by XPS. In the case of the region C1s, Fig. 6A shows the intensity of -C-C-, -C-OH-, -C=O and -COOH, for each analyzed catalyst (NiO, O₃-NiO, O₃-NiO-BA(20), O₃-NiO-BA(60) and O₃-NiO-BA(20)-TBA) excluding the adventitious carbon, which remained constant in all the studied catalysts. As can be observed, all functional groups were detected, in greater or lesser intensity in all catalysts, except for -C=O- group, which was not negligibly detected in NiO or O₃-NiO. Note that the higher amount of -C-C- species was found after 60 min of catalytic ozonation of BA (i.e. O₃-NiO-BA(60)), however, at around 12% intensity for -C-OH-, -C=O and -COOH groups was identified for the same catalyst.

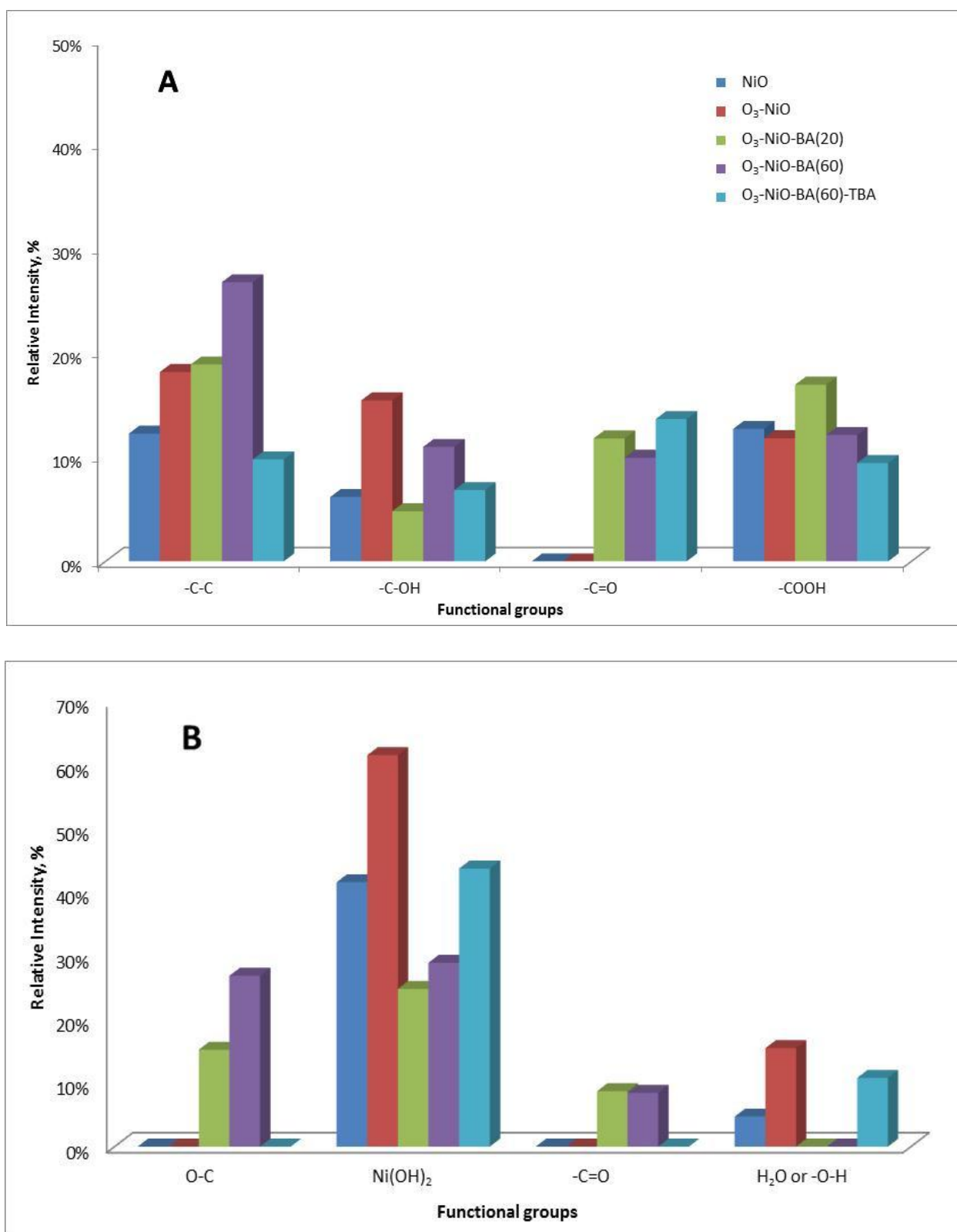


Figure 6 Relative intensity of functional groups estimated from: (A) C1s and (B) O1s for NiO, under different reaction conditions.

Importantly, in the case of catalyst without BA (NiO and O₃-NiO), the functional groups -C-C, -COH and COOH were also identified, which was attributed to the interaction of adventitious carbon with ozone. As expected, TBA addition decreased the intensity of the majority of functional groups, except for -C=O, which was attributed to a decrease in the amount of •OH radicals responsible of the BA oxidation. As a preliminary conclusion, these results are indicative that NiO surface was involved in the BA degradation due to the presence of organic matter (byproducts) shown in Fig. 6A.

Furthermore, a careful analysis of the O1s region, Fig. 6B, showed the presence of -O-C, Ni(OH)₂, -C=O and H₂O (O-H) signals for all the studied catalysts, with a predominance of hydroxylated Ni species. As can be seen, the ozonation of NiO produced the highest Ni(OH)₂ (65%) and O-H (12%) intensity signals, which can be considered as the creation of surface active sites. On the contrary, in the presence of BA (O₃-NiO-BA(60)), the Ni(OH)₂ and O-H intensity signals were decreased at around 50% and 100%, respectively after 60 min ozonation in comparison with O₃-NiO. In addition, the presence of -O-C, and -C=O signals confirmed the presence of organic byproducts adsorbed on the NiO surface generated by BA decomposition. It is worthwhile to mention that the active sites consumption was different under all reaction conditions, for instance, in Fig. 6b is clearly shown that the intensity of Ni(OH)₂ and O-H signals were only reduced 15% and 5%, respectively in O₃-NiO-BA(60)-TBA, in comparison with O₃-NiO and the -O-C and -C=O signals were not detected.

Finally, Fig. 7 illustrates the proposed mechanism for the catalytic ozonation of BA in presence and without TBA. NiO promotes the ozone decomposition and byproducts absorption generated of BA decomposition, when TBA is present in the reaction, it blocks part of active sites then the BA elimination grade was reduced (as previously was demonstrated Fig. 3).

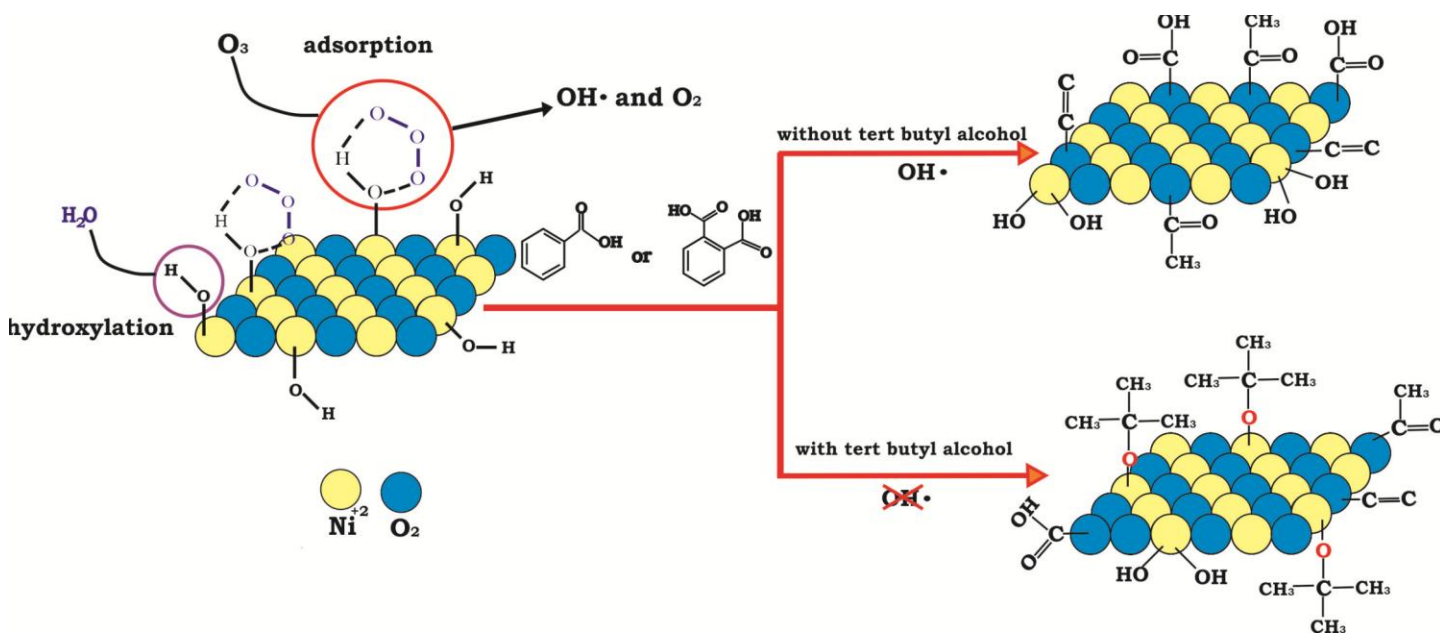


Figure 7 Proposed reaction mechanism for BA elimination in presence of NiO with or without TBA.

XPS spectra and analysis of functional groups for C1s and O1s regions of the PA elimination presented a similar behavior and for this reason were not shown here.

By this reason only the analysis of atomic percentages or two acids are showed in Fig. 8. It is clearly observed that the atomic percentages did not change significantly after 20 min of ozonation for two acids (BA and PA). Nevertheless, at 60 min phthalic and benzoic acids increased the atomic percentage of carbon that indicated the adsorption of the organic matter on catalyst surface during the ozonation process. Hence, the number of carboxylate group presented in the organic compound (benzoic and phthalic acids) did not influence the reaction mechanism in the catalytic ozonation.

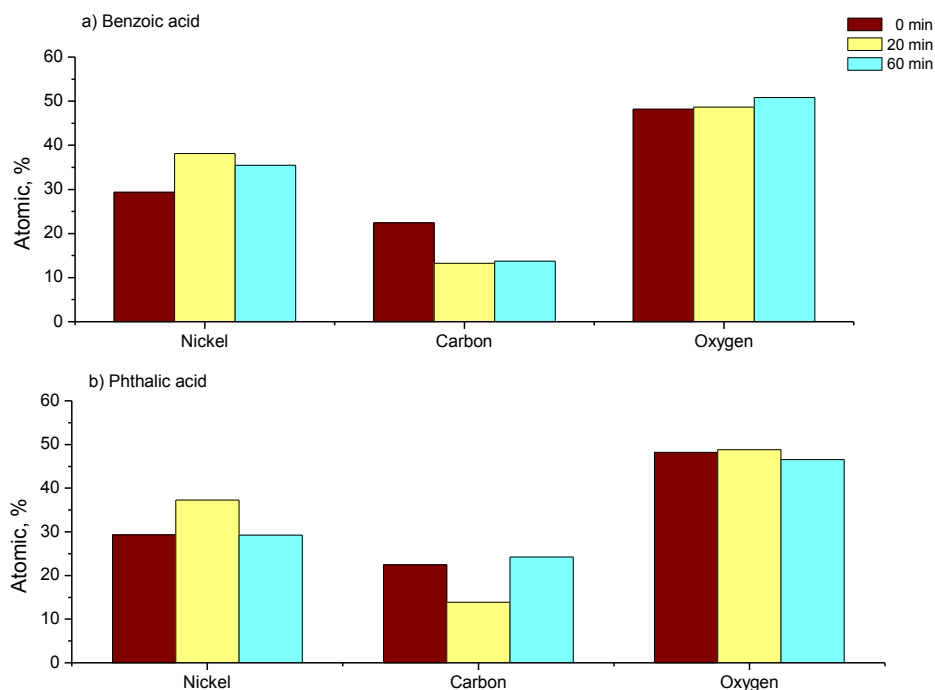


Figure 8 Surface elemental composition obtained from XPS spectra from NiO catalyst at different reaction times: (a) benzoic acid and (b) phthalic acid.

4. Conclusions

The degradation of benzoic acid and phthalic acid by ozone in aqueous solution in presence of nickel oxide as catalyst was around 100% at 20 min of reaction time. It was found that unsupported NiO is a feasible candidate to mineralize an average of 93% of 80 mg L⁻¹ of organic acids in short reaction times (1 h). The faster decomposition of both organic acids was achieved with an optimal NiO of 0.5 g L⁻¹. The mineralization degree of the organic acids was significantly increased with the presence of NiO in comparison with the conventional ozonation, which was attributed to the combination of two consecutive reactions: (a) direct reaction with molecular ozone and (b) indirect decomposition by •OH radicals. The main identified byproduct (OXA) was only eliminated in the presence of NiO. Furthermore, the presence of diverse group in the region O1s detected by XPS, confirmed that ozone was adsorbed on the catalyst surface forming hydroxyl radicals which served to eliminate the oxalic acid byproduct.

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