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Catalytic Ozonation as a Promising Technology for Application in Water Treatment: Advantages and Constraints

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Abstract

Freshwater pollution compromises drinking water in a worldwide context. Water pollution is one of the major environmental challenges facing humanity. Therefore, the application of methods to control the pollution in water is a growing research field. Among the methods, ozone has been widely applied due to its high oxidation potential. However, one disadvantage is the presence of refractory organic compounds that are partially oxidized leaving mineralization incomplete. Several approaches have been considered to improve the oxidizing power, reducing the reaction time, and increasing the mineralization degree of ozone. So far, the combination of a solid catalyst with ozone (catalytic ozonation) has shown to enhance the degradation of refractory organic compounds in water. This chapter presents the combination of different metallic oxides (Al_2O_3 , TiO_2 , SiO_2 , and NiO) with ozone to determine the effect of ozone decomposition and the subsequent elimination of one chlorinated compound (2,4-D). The chemical structure of the initial compound (2,4-D, benzoic and phthalic acid), as well as the initial catalyst dosage (0.1 and 0.5 g L^{-1}) with the mentioned compounds, was also studied. Moreover, the degradation of two aromatic compounds (naphthalene and naproxen) with different proportions of ethanol (representing the organic matter of wastewater) was analyzed to establish their effect on the catalytic ozonation process.

Keywords: ozone, catalyst, hydroxyl radical, water, cosolvent

1. Introduction

The increasing worldwide pollution by complex mixtures of chemical compound is a crucial environmental problem facing humanity [1]. Currently, conventional treatments are insufficient to achieve full recovery of industrial effluents; therefore, the so-called advanced oxidation processes (AOP) have generated more interest in recent years as can be seen by the increasing number of published articles from 1970 to date, **Figure 1a**.

The main feature of the AOP is the generation of oxidizing species such as hydroxyl radical ($\bullet\text{OH}$) that decompose and even mineralize pollutants [2]. The AOP can be classified into homogeneous and heterogeneous processes [3], but basically, the heterogeneous route is preferred, since it allows the recovery and reuse of the catalyst during several treatment cycles. Among the AOP, ozone (O_3) has been widely used due to its high oxidation potential (2.07 V) that can further increase with the presence of a catalyst as a result of $\bullet\text{OH}$ species (2.8 V). This method is commonly known as catalytic ozonation. **Figure 1b** shows the growing interest that this promising method has taken.

Research on catalytic ozonation has demonstrated that several parameters participate in the processes [4–6]. One of the most important is the pH of the reaction medium, because it has an effect on the catalyst surface charge (for instance, zero charge point), which influences the reactants adsorption and the overall efficiency of the process [4, 5]. Likewise, changes in the pH also affect the ozone decomposition, in such a way that a basic pH favors its decomposition into $\bullet\text{OH}$, making the catalyst presence needless. Obviously, the concentrations of catalyst, ozone, and pollutant also have a significant effect on the degradation/mineralization process [4, 6]. Generally speaking, at increasing of catalyst concentration basically enhances the pollutant degradation and a similar tendency occurs when increasing the ozone concentration [4, 6]. On the contrary, at high concentrations of the pollutant, an inverse trend is observed, hindering the transformation of the pollutant [4, 6].

In addition to the above, there is a wide variety of materials studied in catalytic ozonation for instance metal oxides, supported metals, activated carbon, and zeolites [7–9]. Each of these

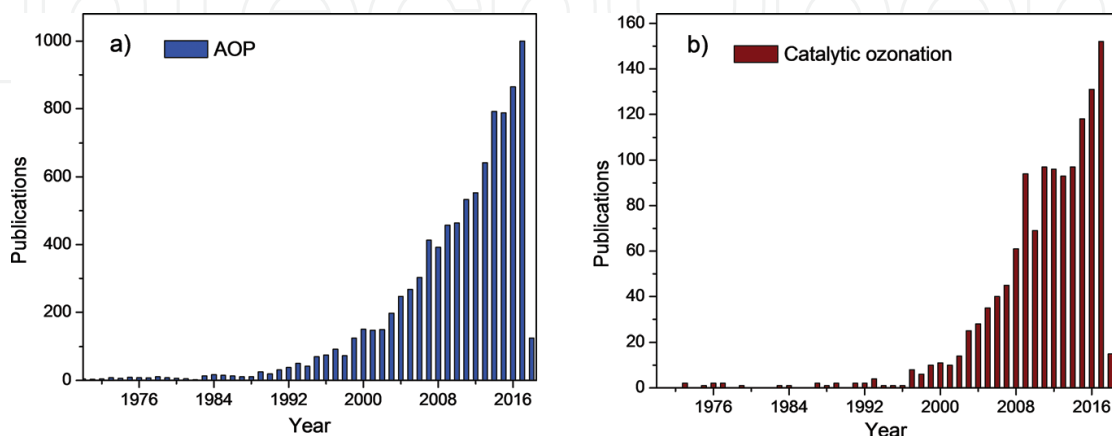


Figure 1. Publications per year indexed in SCOPUS database using the keyword: (a) “advanced oxidation processes” and (b) “catalytic ozonation”.

materials has different properties and characteristics such as, specific area, particle size, and zero charge point, among others. As a result, there is still controversy regarding the reaction mechanism that takes place in catalytic ozonation process so far three possibilities have been established [10]: (1) ozone is adsorbed on the surface of the catalyst to react with the active sites and form $\bullet\text{OH}$, (2) the organic molecule is adsorbed on the surface of the catalyst and subsequently attacked by ozone or $\bullet\text{OH}$, and (3) both, the ozone and compound are adsorbed on the surface of the catalyst to react.

Although catalytic ozonation overcomes the disadvantages of conventional ozonation, it has its own limitations due to the leachates probable generation in the system and inactivation of the catalyst after several cycles of use. The intention of this chapter is to introduce the key aspects of heterogeneous catalytic ozonation, aiming to explain the role of the catalyst on the degradation of different organic compounds (2,4-D, phthalic acid, benzoic acid, naproxen, naphthalene). Additionally, the interferences of organic matter (represented with different proportions of ethanol) to eliminate compounds by catalytic ozonation was studied to demonstrate the advantages and constrains of the process for future applications.

2. Experimental conditions

2.1. Materials

2,4-Dichlorophenoxyacetic acid, naphthalene, phthalic, and benzoic acids were obtained from Sigma-Aldrich and used as received, while naproxen was acquired from J.T. Baker. Some properties of these compounds are presented in **Table 1**.

2.2. Experimental procedure

The reaction was carried out at semi-batch conditions in a 500-mL Pyrex reactor by the continuous bubbling of ozone/oxygen mixture through a ceramic porous diffuser located at the bottom of the reactor. Ozone was produced using a corona discharge type generator HTU500G (AZCO Industries Limited–Canada) The ozone concentration in the gas phase was measured using a BMT 964 BT (BMT Messtechnik, Berlin) employing a flow of 0.5 L min^{-1} , and working temperature of 21°C . Two initial concentrations of ozone were used: (1) 30 mg L^{-1} for 2,4-D, PA, and BA, and (2) 5 mg L^{-1} for NAP and NP. The interference study was performed with NAP and NP in the presence of ethanol (10:90, 30:70 and 50:50 v/v of ethanol/water). Ethanol was used as a cosolvent to increase the solubility of both compounds and to simulate the high load of organic matter in the catalytic system. The flow diagram of the ozonation procedure is illustrated in **Figure 2**.

2.3. Analytical methods

The model compounds selected in this work were analyzed by high-performance liquid chromatography (HPLC) using a Perkin Elmer Flexar with photodiode array detector (PDA) at the following conditions, **Table 2**.

Compound	Chemical structure	M (g mol ⁻¹)	pKa
2,4-dichlorophenoxyaceti acid (2,4-D)		221.04	2.73
Phthalic acid (PA)		166.14	2.89 5.50
Benzoic acid (BA)		122.12	4.2
Naphthalene (NP)		128.17	---
Naproxen (NAP)		230.26	4.2

Table 1. Properties of the selected aromatic compounds.

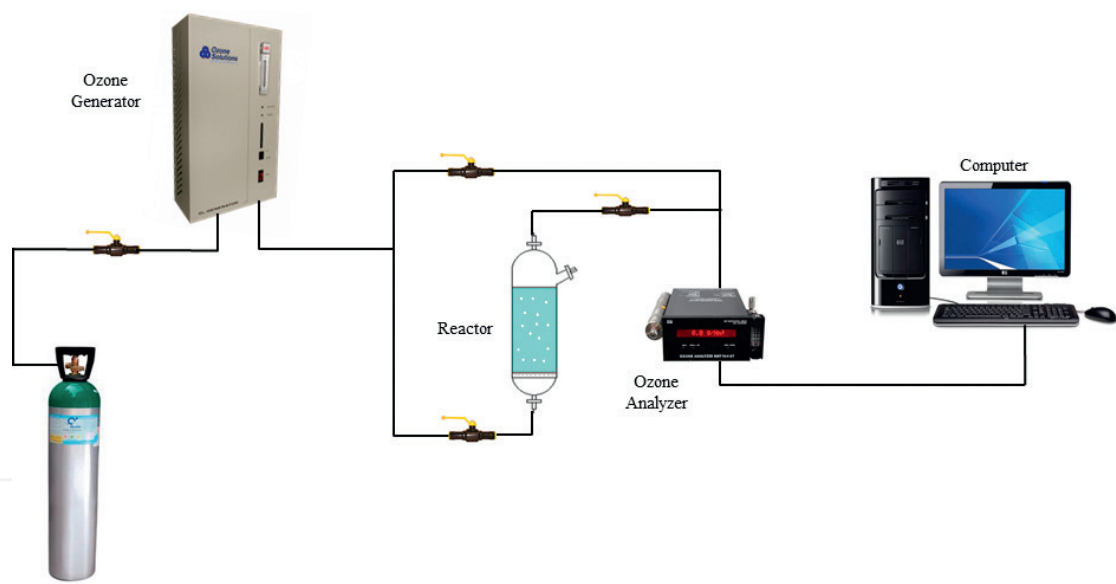


Figure 2. Schematic diagram of the experimental setup.

The chemical oxygen demand (COD) was evaluated using COD tubes for a low range of Hanna instruments HI 94754A-25 with 2 mL of sample. The digested samples were analyzed in a UV–VIS Perkin Elmer Lambda 2S at 600 nm.

The study of naproxen byproducts was analyzed by electrospray ionization Tandem Mass Spectrometry (ESI-MS–MS) by direct injection of the sample using the electrospray ionization interface (MICROTOF-Q II 10392) in the negative ion scan mode. The capillary voltage was 2700 V and temperature was set at 180°C. The pressure and spray gas flow rate were at 0.4 Bar and 4 L min⁻¹, respectively. The spectra were acquired over the m/z range from 50 to 3000.

Compound	Analytical column	Analytical conditions
2,4-D	Prevail Organic Acid, 5 μ m (150 x 4.6mm)	40% acetonitrile: 60% 25 mM KH ₂ PO ₄ (pH 2.6, H ₃ PO ₄), 1mL min ⁻¹ , 225nm
PA		60% acetonitrile: 40% 25 mM KH ₂ PO ₄ (pH 2.6, H ₃ PO ₄), 1mL min ⁻¹ , 210nm
Oxalic acid		100% 25 mM KH ₂ PO ₄ (pH 2.3, H ₃ PO ₄), 1mL min ⁻¹ , 210nm
BA	Platinum C18, 5 μ m (250 x 4.6mm)	70% acetonitrile: 30% water, 1mL min ⁻¹ , 210nm
NP		70% acetonitrile: 30% water, 0.3mL min ⁻¹ , 210nm
NAP		50% acetonitrile: 50% water (pH 2.5, H ₃ PO ₄), 0.3mL min ⁻¹ , 240nm

Table 2. Analytical conditions of the selected compounds.

2.4. Characterization techniques

The zeta potential of the catalyst (pH_{Z_{PC}}) was determined by Malvern Zetasizer at 25°C using the titration method with HCl and NaOH both at 0.01 N. Surface area and pore size measurements were carried out an Micromeritics Autochem II 2920 equipment, through N₂ adsorption using Brunauer-Emmet-Teller (BET) model. Photoelectron general-level spectra of the catalysts were obtained with an X-ray photoelectron spectrometer (ThermoFisher Scientific K-Alpha) with a monochromatized AlK α X-ray source (1487 eV). The base pressure of the system was 10⁻⁹ mbar. Prior to X-ray photoelectron spectroscopy (XPS) analysis, all samples were dried at 100°C for 24 h, posteriorly, they were dispersed and embedded in a 5 × 5 mm indium foil and fixed with Cu double-sided tape to the sample holder. Narrow scans were collected at 60 eV analyzer pass energy and a 400- μ m spot size.

3. Results and discussion

3.1. Effect of the type of metal oxide on ozone decomposition

The ozone decomposition over the surface of the catalyst occurs by the interaction between H₂O and a metal oxide which tends to strongly adsorb H₂O molecules. The adsorbed H₂O dissociates to OH⁻ and H⁺, forming surface hydroxyl group with the surface metal and oxygen sites, respectively [11]. Therefore, ozone can react with the surface hydroxyl group generating •OH on the surface of the metal oxide. There are several techniques to determine the presence of higher oxidant species like •OH. Among the techniques is electron paramagnetic resonance (EPR), adding an inhibitor to reaction system (t-butanol) or measuring dissolved ozone directly in the medium. In this work, the indirect method of dissolved ozone measurements was carried out with the aim to determine the ozone decomposition and possible formation of •OH in presence of catalysts (Al₂O₃, TiO₂, SiO₂, NiO) in water.

Figure 3 shows the profiles of dissolved ozone concentrations as a function of time by conventional and catalytic ozonation in unbuffered water. Ozone concentration profile without catalyst presents an initial value of 4.3 mg L^{-1} which coincide with Henry's Law in steady state at 20°C [12].

After adding some catalyst in the system, the initial value of ozone diminished in comparison with ozone alone. This fact is due to the ozone decomposition in water.

In presence of NiO catalyst, the initial value of ozone concentration diminished around 27% under the same experimental conditions that conventional ozonation. With TiO_2 catalyst, the difference between the dissolved ozone concentrations was insignificant in comparison with ozone alone. The ozone decomposition increased according to the following order: TiO_2 (4%) < Al_2O_3 (14%) < SiO_2 (19%) < NiO (27%). It is interesting to note that the profile of ozone concentration decreases at 95% in 30 min in the absence of a catalyst. While in the catalytic processes, such decrease was around 21 min. The latter development was the result of the minor ozone concentration in the catalytic systems.

These results are the consequence of the adsorption of ozone over the catalyst surface and the physicochemical characteristics of each metallic oxide. The main physical variables reported are surface area, density, pore volume, mechanical strength, and commercial availability [7]. Among the chemical properties, the most important is the chemical stability and the presence of active surface sites mostly Lewis acid sites. **Table 3** summarized some physicochemical properties of metallic oxides.

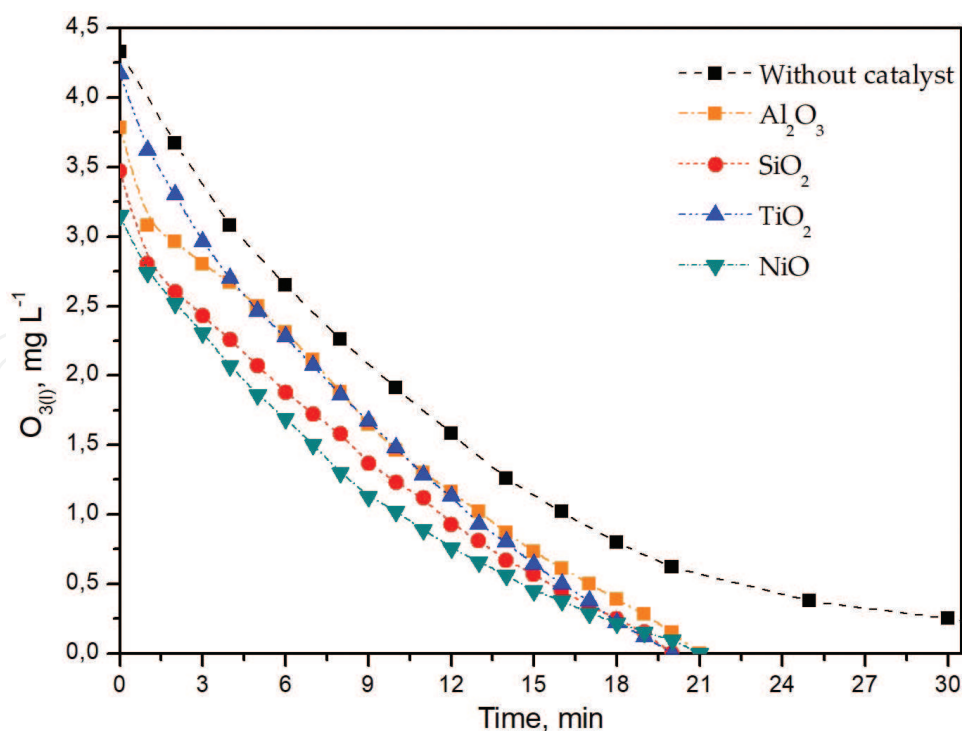


Figure 3. Dissolved ozone concentrations dynamics in function of time by conventional and catalytic ozonation in unbuffered water.

Catalyst	Surface area $\text{m}^2 \text{g}^{-1}$	Pore volume $\text{cm}^3 \text{g}^{-1}$	pH_{ZPC}
Al_2O_3	25	0.0126	8.5
SiO_2	179	0.0901	2.8
TiO_2	44	0.022	6.5
NiO	---	---	11.6

Table 3. Physicochemical properties of the metallic oxides.

As can be seen in **Table 3**, even though there are notable differences in the specific surface of the respective oxides, the most outstanding property is the highest value of the pH_{ZPC} (11.6) presented by nickel oxide. This catalyst may adsorb very favorably ozone and then it would promote a chain reaction involving $\bullet\text{OH}$ generation. In consequence, the mineralization degree of an organic compound would increase by the presence of NiO.

To confirm this hypothesis, 2,4-D was considered as a model organic compound to study its degradation. 2,4-D is an herbicide widely used to control broadleaf weeds in cereal and grain crops, recreation areas, golf courses, and gardening. The biodegradation is a common method used for the elimination of 2,4-D in aqueous solution, however, its degradation efficiency is not effective due to its higher concentrations (>1 ppm) and large periods of treatment (months) [13]. For this reason, several publications about 2,4-D degradation have been reported using AOPs [14–18].

The removal of 2,4-D was carried out in presence of Al_2O_3 , TiO_2 , SiO_2 , and NiO with ozone, as shown in **Figure 4**. NiO exhibits the highest activity (around 65%) in comparison with the other metal oxides after 60 min of reaction. This can be explained in terms of NiO capacity to decompose ozone and the formation of $\bullet\text{OH}$. Other catalysts have shown slight differences in the mineralization degree with conventional ozonation that effect can be attributable to the lower production of oxidant species by each oxide.

In addition to the ozone decomposition capacity by metallic oxides, the pH solution is an important parameter that modifies the charge surface of the hydroxyl group at oxide/water interface. Under our experimental conditions, three of the catalysts (TiO_2 , Al_2O_3 , and NiO) were protonated (MeOH^+), since pH is below the pH_{ZPC} , in consequence, the adsorption of anions is favored as reported by [19]. Generally, the pH of ozonated solutions changes to acid as the treatment time increases by the formation of short-chain organic acids. Nonetheless, pH solution changes from 3.1 to 6.2 in the 2,4-D ozonation with NiO as a catalyst. The above result is due to the decomposition of the main compound as well as the formed byproducts. Despite being only 8%, the difference between the ozone decomposition with SiO_2 and NiO, the mineralization degree achieved was several units apart (23 and 60% for SiO_2 and NiO, respectively). The latter indicates that an indirect mechanism could not be enough to mineralize 60% of 2,4-D. Thus, it is possible that more than one mechanism interferes in the heterogeneous catalytic ozonation. Therefore,

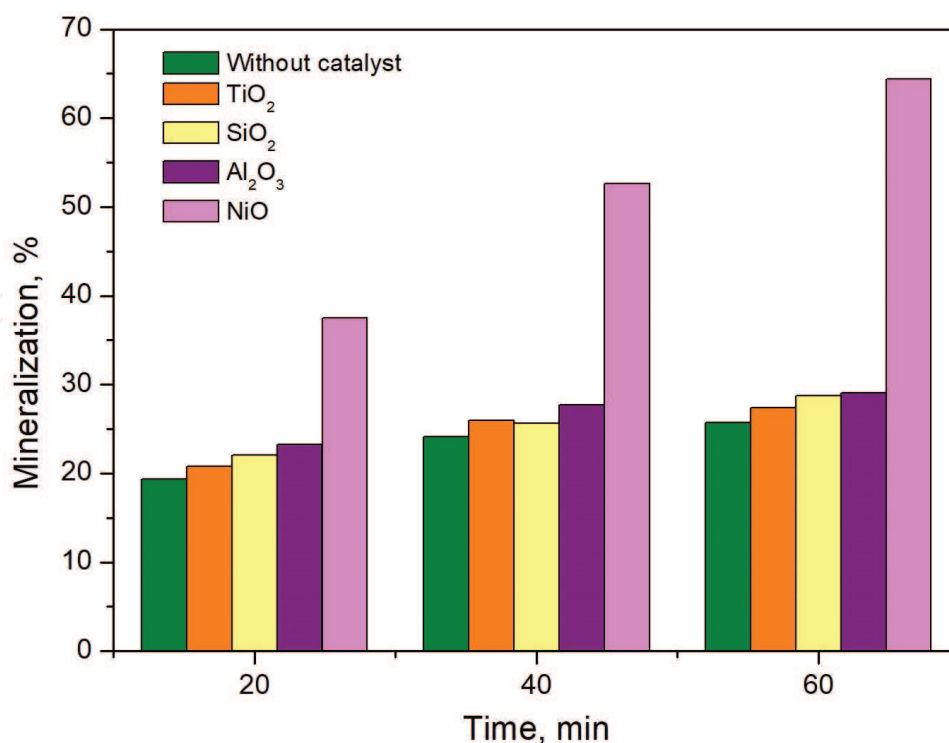


Figure 4. Mineralization percentage obtained in the 2,4-D ozonation in function of reaction time with several metallic oxides.

the adsorption and decomposition of the complex species (organic compound-metal oxide) on the surface catalyst were considered as another mechanism and XPS was used to confirm it.

The general XPS spectrum of fresh NiO displays common signals of adventitious carbon (284.5 eV), oxygen (530 eV), and nickel (850–870 eV) as observed in **Figure 5**. When the NiO is present in the 2,4-D ozonation, an additional signal between 196 and 206 eV attributed to Cl2p region (signal not detected in any other metallic oxide). This peak indicates that there is an interaction between the by-products with active surface sites of NiO. An increase in the ozonation time eliminates adsorbed organic matter (C1s and Cl2p regions) onto NiO surface and consequently diminishes the intensity of the signals.

Moreover, the analysis of the Cl2p region confirms that the dechlorination is one of the steps involved in the mechanism of the reaction [20]. Hence, the use of general XPS spectrum allowed us to detect the presence of chemical species related to byproducts. As a result, the presence of NiO in the 2,4-D removal significantly increased the mineralization degree during 60 min of ozonation as a result of the combination of three mechanisms: (1) conventional ozonation, (2) ozone decomposition (27%) and •OH generation, as well as (3) formation of organic complex species onto NiO.

3.2. Effect of the initial compounds in the combination of ozone with NiO

For many decades, the conventional ozonation method has been widely used for disinfection and degradation of organic pollutants. However, this technique presents a high selectivity. In consequence, the efficiency of ozonation process is dependent on the chemical structure of the organic compounds to be degraded.

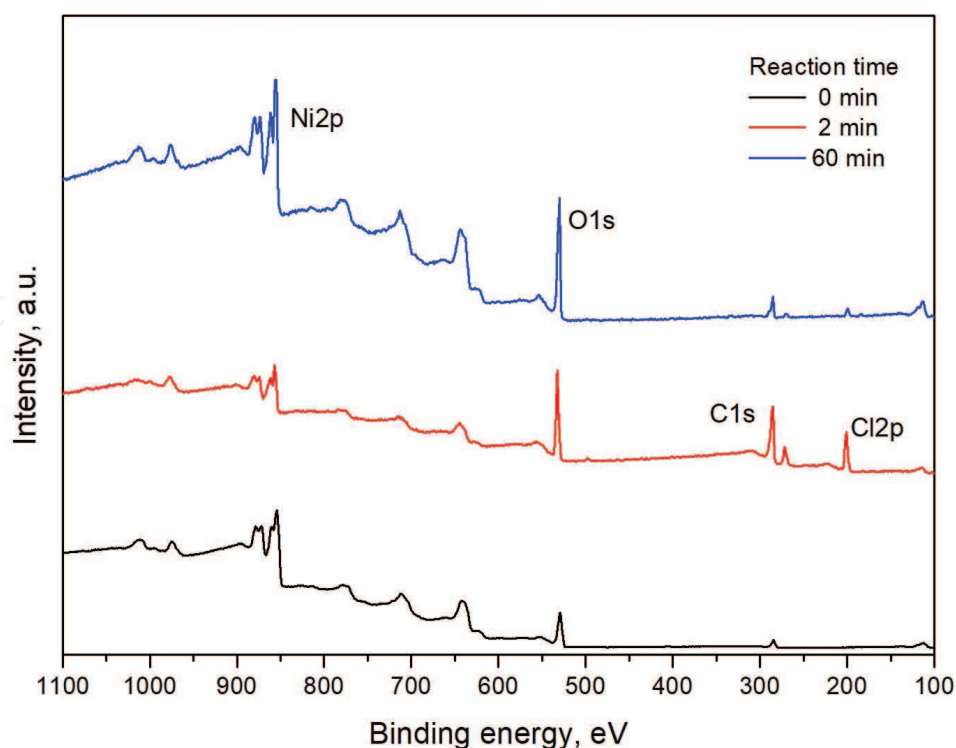


Figure 5. General XPS spectra of NiO after the 2,4-D ozonation.

2,4-D, BA, and PA were selected as target compounds to study the chemical structure effect on conventional and catalytic ozonation in water. The difference in the chemical structure between BA and PA is the number of the carboxylic groups present in each molecule. BA is widely used as a reagent in the pharmaceutical industry, while PA is employed in the textile sector [23, 24]. Both compounds are toxic, and exhibit low degradation [21, 22]. The evaluation of these compounds was carried out with NiO because the catalyst significantly increased the mineralization degree during 2,4-D catalytic ozonation at pH 3.1 (see Section 3.1).

Figure 6a and **b** show the mineralization profile of the three organic acids under non-catalyzed and catalyzed ozonation, respectively. By the first route (**Figure 6a**), it is clearly noticed that the mineralization rates of BA and PA were higher than that obtained for 2,4-D, reaching 35 and 42% of mineralization degree during 60 min, respectively. This result indicates that BA, PA, and some generated byproducts are easily eliminated with ozone. It is important to highlight that the BA and PA have similar degradation pathways; therefore, the difference between both mineralization percentages was minor to 10%.

In the case of 2,4-D, the formation of chlorinated compounds (2,4-dichlorophenol) is favored due to the high value of the herbicide degradation rate constant ($k = 16.7 \times 10^3 \text{ L mol}^{-1} \text{ min}^{-1}$) [20]. It is known that the presence of chlorinated compounds reduces the mineralization percentage of conventional ozonation treatments. Moreover, none of the studied compounds obtained total mineralization by conventional ozonation. The mineralization degree increases in the following order $2,4\text{-D} < \text{BA} < \text{PA}$. Hence, the non-catalyzed reaction was strongly influenced by chemical structures of organic compounds in the system as well as by the reaction time. Generally, the oxygenated compounds such as saturated carboxylic acids (short chain)

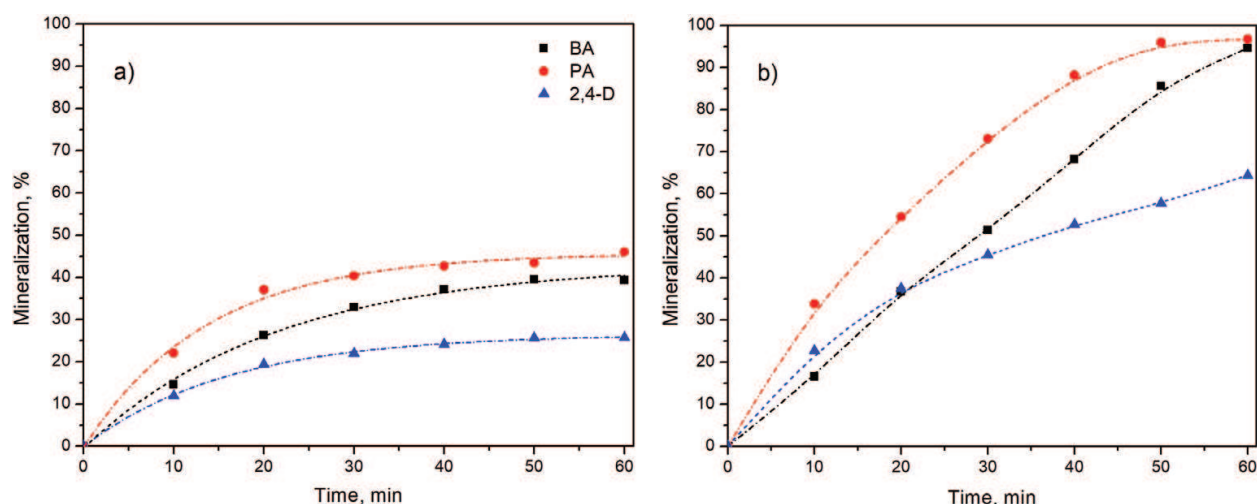


Figure 6. Evolution of mineralization degree in the elimination of 2,4-D, PA and BA by conventional (a) and catalytic (b) ozonation as a function of reaction time.

are the end products of aromatic compounds treatment by conventional ozonation [25]. The accumulation of these acids during ozonation alone reduces the efficiency of the mineralization process.

On the other hand, an improved mineralization (around 95%) was attained at 60 min for BA and PA by the catalytic ozonation process, **Figure 6b**. Furthermore, mineralization percentage of 2,4-D increase from 23 to 62% in presence of NiO as catalyst. A first interpretation of these superior results compared with the ozonation alone, would be in terms of an enhanced mineralization rate of aromatic acids due to ozone interaction with NiO surface. As a result, the formation of free radicals that initiate radical type reactions on the surface of the catalysts as well as in the liquid phase was expected [26]. Hence, the addition of NiO significantly increased the mineralization rate of the studied aromatic acids during 60 min of the treatment. In sum, the catalytic ozonation achieved the elimination of the main compound along with the byproducts generated in the reaction. This fact makes of catalytic ozonation a promising alternative to eliminate recalcitrant compounds obtaining higher mineralization percentages due to the low selectivity of the process.

3.3. Influence of catalyst dosage on organic compounds elimination

The impact of catalyst dosage on catalytic ozonation of different pollutants has been reported in many research works [27–29]. Basically, at increasing catalyst concentration, a higher efficiency of the organic pollutants degradation is observed. However, an inhibiting effect may exert further increase of catalyst dosage by adsorption of organic compounds on the surface-active sites of the catalyst.

The study of BA, PA, and 2,4-D degradation profiles showed an insignificant effect by varying the catalyst concentration (results not shown). This fact is due to that direct reaction with molecular ozone was a feasible method to decompose model compounds achieving up to 95% removal of three compounds in 20 min [20, 30]. Oxalic acid (OA) is the main recalcitrant

product formed from the model compounds elimination and it was chosen to study the catalyst dose influence. **Figure 7** shows the OA concentration as a function of ozonation time at two NiO concentrations (0.1 and 0.5 g L⁻¹).

When NiO was introduced into the system, the concentration profile of oxalic acid changed considerably in all the model compounds in comparison with conventional ozonation which show an accumulation profile of OA. In the case of BA elimination, the OA concentration was around 9 mg L⁻¹ which is almost 6 times lesser than conventional ozonation during 60 min at 0.1 g L⁻¹ of catalyst dose, **Figure 7a**. The increase of NiO loading (0.5 g L⁻¹) produced a minor amount of OA (4 mg L⁻¹) in the process. The PA degradation generated higher OA concentration than BA decomposition at the same catalyst concentration, due to the stoichiometric ratio between model organic compound and OA. In general, the behavior of this final product is similar in the three organic acids (2,4-D, PA, and BA) because the increase in the catalyst dosage diminished the OA concentration, **Figure 7b** and **c**. The outcome of the latter can be explained on account of more active sites result of the increase of dosage on NiO.

Without a doubt, heterogeneous catalysts in suspension are excellent promoters of ozone decomposition to favor the mineralization of toxic compounds in water. However, it must

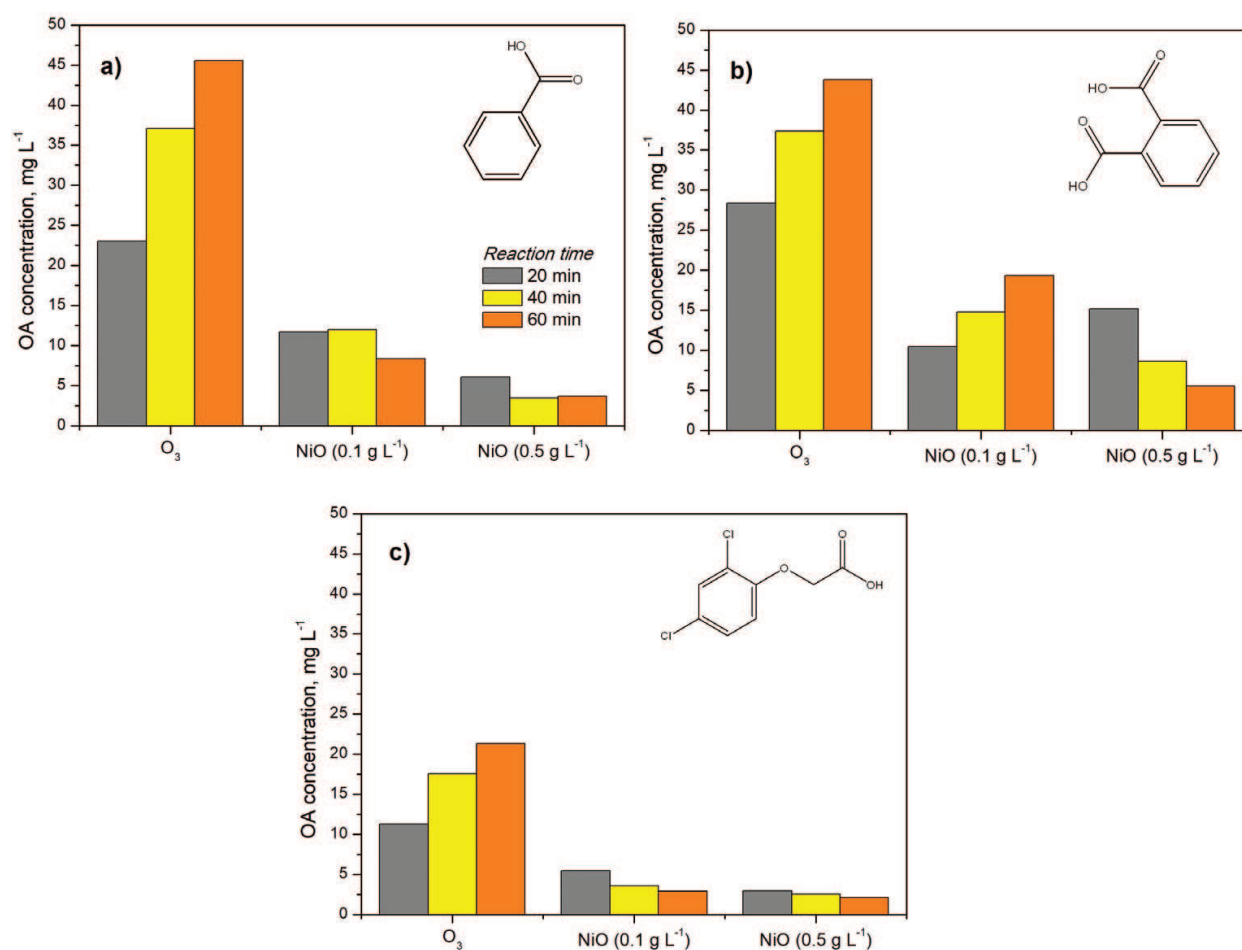


Figure 7. OA concentrations in the elimination of (a) BA, (b) PA and (c) 2,4-D in water.

be taken into account that the use of powder catalysts would involve additional processes as filtration, drying, and so on for their separation and recovery, which should be avoided.

3.4. Effect of cosolvent in naphthalene and naproxen degradation with NiO

Catalytic ozonation is an efficient technology that overcomes the drawbacks of conventional ozonation. Nevertheless, this technology's main disadvantages are the surface adsorption of byproducts generated, the catalyst recuperation, and the presence of interferences in wastewater such as salts and organic matter [7, 31, 32]. In view of the successful results found in the catalytic ozonation with NiO (i.e., high mineralization degree of several organic compounds) previously described, we decided to study the effect of organic matter over NP (polycyclic aromatic hydrocarbon, a toxic compound with teratogenic and mutagenic activity [33]) and NAP (nonsteroidal anti-inflammatory drug) degradation with the same catalyst.

The dynamics of NP degradation by catalytic and conventional ozonation under different amounts of ethanol are shown in **Figure 8**. The treatment of NP attained 100% of removal in solutions with 10% v/v of ethanol after 20 min and 98% of elimination at 30% v/v during 60 min. By further increasing the ethanol concentration to 50% v/v, the removal only reached 55% after 60 min indicating, that greater organic loads affect NP removal. The latter fact points out the feasibility of low-concentration toxic pollutants degradation under high organic loads by catalytic ozonation or some other treatments such as biological systems in order to reach higher removal rates [34–36]. The degradation profiles obtained by conventional and catalytic ozonation show no significant difference despite being the $\bullet\text{OH}$ reaction rate constants in the

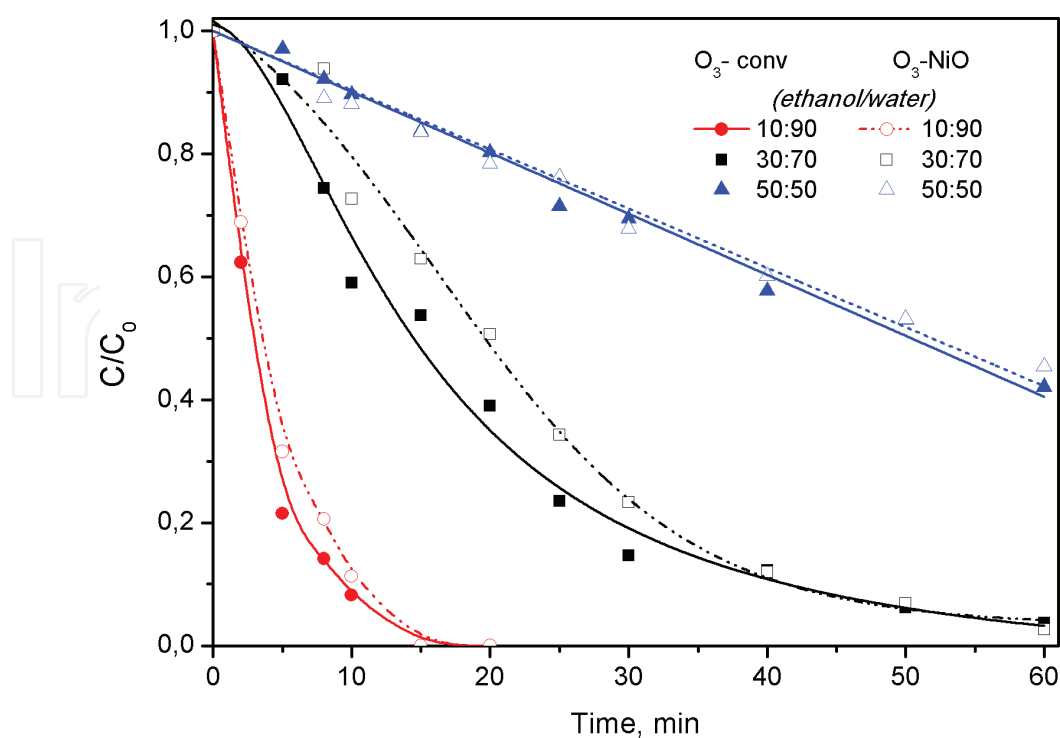


Figure 8. NP degradation under different ethanol/water ratios by conventional and catalytic ozonation.

order of $10^9 \text{ M}^{-1} \text{ s}^{-1}$ for ethanol and NP [37, 38]. This similarity is probable by the high concentration of ethanol that consumes most of the $\bullet\text{OH}$ produced by the catalyst as the main radical species reported with NiO [30, 39].

Similarly, with 2,4-D, BA, and PA degradation (Section 3.3), the NP decomposition also results in the formation of OA as the final product, **Figure 9a**. However, it is not only produced from NP as shown in **Figure 9b**. Both figures exhibit that higher ethanol concentration enhances OA production and that the presence of NiO reduces its concentration in 60 min of treatment. It is worth mentioning that the treatments with 30% v/v of ethanol had in the first 5 min a rise in OA concentration followed by a degradation of the molecule in presence of a catalyst. Such pattern of formation-degradation of NP byproducts was the product of the NiO catalytic action (**Figure 9**).

The catalyst surface was analyzed after the catalytic ozonation of NP (results no showed). The signals obtained from XPS for NiO with 30:70 ethanol/water in absence of NP at O1s and C1s regions showed signals of $-\text{COH}$, $-\text{C}=\text{O}$, $-\text{OC}=\text{O}$, and $-\text{C}-\text{C}$ species related to the interaction of ethanol and byproducts with the catalyst. The presence of these species indicated that the adsorption of organic matter or byproducts contribute to reducing the active sites available in the catalyst and resulted in a lower catalytic ozonation efficiency.

One way to determine the catalyst efficiency in catalytic ozonation process is through COD or total organic carbon (TOC). Unfortunately, due to the low solubility of NP in water and the high load of organic matter resulted from ethanol presence, these global parameters could not be obtained. For this reason, NAP (a nonsteroidal anti-inflammatory drug and a recalcitrant pollutant in water bodies [40, 41]) was selected to be studied without the interference of organic matter in catalytic ozonation with NiO. These types of pharmaceutical pollutants in wastewater are a growing concern because of their molecules that are designed to trigger biologic functions and affect different species even at low concentrations (ng L^{-1} or $\mu\text{g L}^{-1}$).

Figure 10 presents NAP degradation by catalytic ozonation with NiO during 20 min for solutions with and without ethanol. The degradation time was short in mixtures with lower ethanol concentrations and even smaller in absence of solvent (the signal disappears in 5 min). The latter indicates that NAP molecule requires inferior reaction times than NP. However,

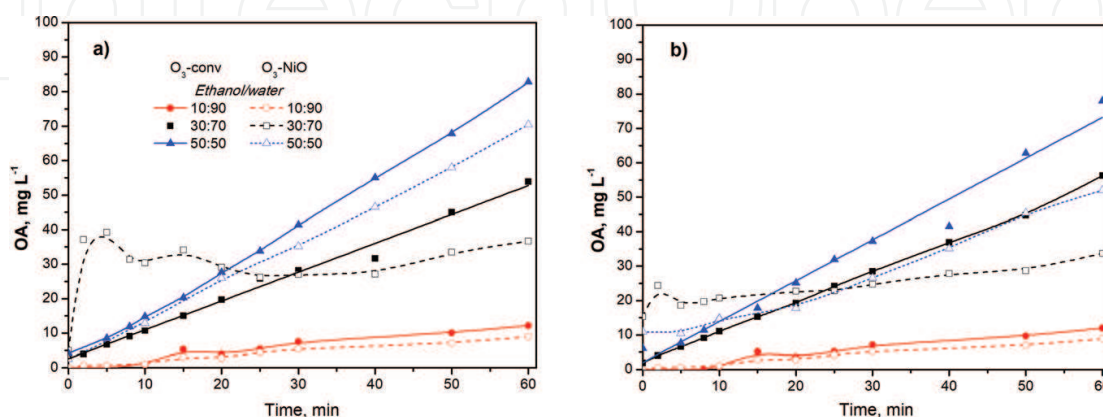


Figure 9. OA concentration in conventional and catalytic ozonation (a) with NP and (b) without NP.

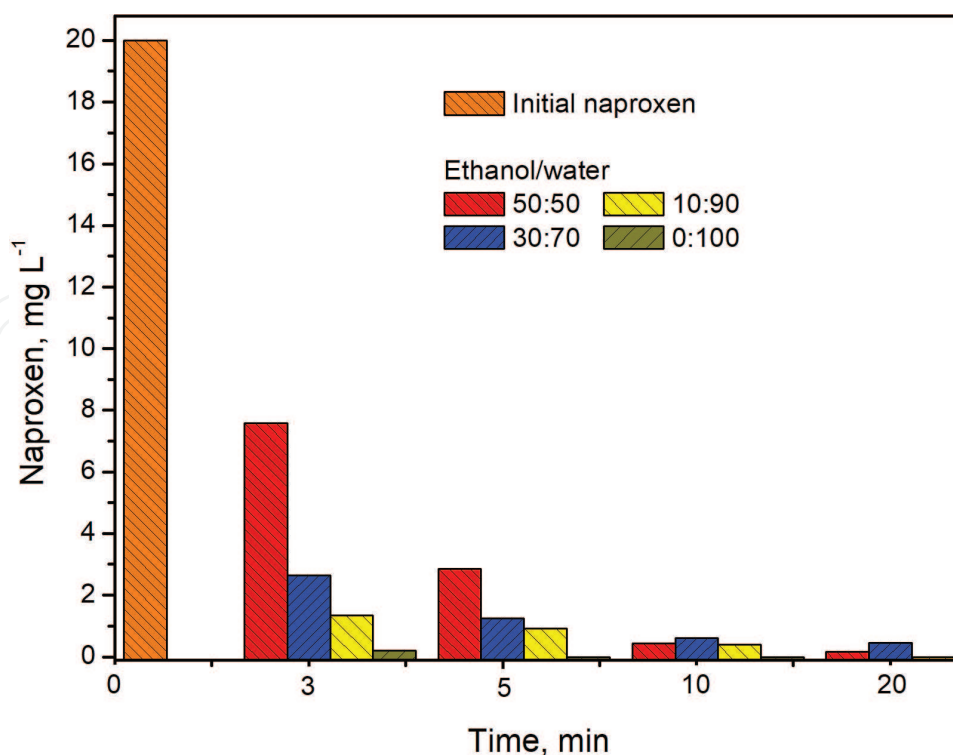


Figure 10. NAP concentration in catalytic ozonation with different ethanol/water proportions.

ESI-MS-MS demonstrated that the presence of ethanol in the NAP degradation produces aromatic structures as byproducts contrary to the samples that do not contain ethanol which did not present those ions (data not shown). Similar structures were observed or proposed by other investigators [42, 43]. The COD of solutions ozonated without cosolvent are shown in **Table 4** proving the catalyst activity (2.3 mg L^{-1}) in comparison to conventional ozonation (11.2 mg L^{-1}). The reduction of the COD and absence of byproducts in ESI-MS-MS from the samples without ethanol demonstrated the effect of the catalyst in the mineralization of NAP. Moreover, it provides information about the effect of organic matter in the catalytic ozonation process and exhibit that ethanol diminished the mineralization of the pharmaceutical product. Comparable results have been obtained during NAP elimination with ethanol (used as a scavenger) in thermally activated persulfate (technology that produces oxidant species: $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$) [44]. Therefore, the results presented in Section 3 demonstrated that NiO is an excellent catalyst for the elimination of a variety of toxic organic compounds in water.

In addition to the effect of the chemical structure of the pollutant, the catalyst dosage and the presence of interference (organic matter) play an important role in the degradation process. This work did not take into account the pH effect, which has strong influence on the charge of both, catalyst and organic compound, favoring certain surface reactions. Indeed, it is well known that conventional ozonation is more effective at basic conditions owing to the combination of direct and indirect mechanisms. In the case of catalytic ozonation, both mechanisms can occur since some catalysts as NiO promotes the ozone decomposition at acidic conditions. Therefore, a proper selection of the reaction on pH must be carefully analyzed to avoid catalyst deactivation (lixiviation).

Treatment	COD mg L ⁻¹
Without O ₃	15.2
O ₃ conv	11.2
O ₃ -NiO	2.3

Table 4. COD of NAP degradation without ethanol and under different ozonation process (60 min).

Nowadays various researches have focused their investigations on the synthesis of catalysts with the intention to fulfill the three requirements of selectivity, activity, and stability in the ozonation process [45–47]. The stability is affected by the reuse of catalyst, mainly when there are changes in any of their physicochemical properties. In this situation, it is necessary to use activation techniques which could increase the operating costs. Hence, studies of catalytic ozonation will continue to increase searching for the catalyst that gathers all the necessary characteristics to maximize its activity making of it a feasible alternative for the elimination of toxic compounds in wastewater or the industrial sector.

4. Conclusions

According to our results, we can conclude the following:

1. The dissolved ozone concentrations dynamics demonstrated that NiO achieved the higher ozone decomposition (27%) due to adsorption of a considerable amount of hydroxyl groups.
2. NiO was a good catalyst to mineralize a high concentration of herbicide (80 mg L⁻¹) in comparison with TiO₂, SiO₂, and Al₂O₃ during 1 h of reaction with ozone. This fact was explained in terms of the combination of three mechanisms: (1) conventional ozonation, (2) ozone decomposition and possible formation of •OH, and (3) the complex compounds formation. The last mechanism was demonstrated by the presence of a signal attributed to chlorinated compounds on the surface of NiO at 2 min by XPS spectra. The intensity of signal diminished with the ozonation time (60 min). Thereby, the 2,4-D elimination using the combination ozone-NiO was also performed by means of surface reaction (complex compounds).
3. The nearly complete mineralization (around 95%) of PA and BA was achieved with NiO during 60 min. The difference in the mineralization degree between both compounds was insignificant (<3%) due to the same degradation pathway, since the initial chemical structure is alike and catalytic ozonation also presented lower selectivity in the reaction. Meanwhile, the mineralization degree of 2,4-D was around 60% in the same treatment time for both organic acids. In contrast, conventional ozonation showed higher selectivity obtaining the following trend of mineralization rates PA > BA > 2,4-D.
4. Oxalic acid as recalcitrant product originated from organic acids decomposition was removed proportionally to the initial catalyst dosage as a result of increasing •OH generation by the ozone decomposition.

5. NP degradation is faster at low ethanol concentration (100% in 20 min for 10% v/v) and diminishes as the relation cosolvent:water increases (55% during 60 min at 50% v/v) indicating that the presence of organic matter affects the catalytic ozonation process. This could be due to the adsorption of organic matter or some byproducts over the surface catalyst, as demonstrated XPS signals, reducing the active sites available in the catalyst and lowering the catalytic ozonation efficiency.
6. Contrary to NP results, NAP degradation is faster even at higher ethanol concentrations (90% in 20 min at 50% v/v). This indicated that despite the elevated organic matter content, it is still possible to achieve the complete elimination of NAP. The COD analysis from the ozonated sample without ethanol proved the effect of NiO (2.3 mg L^{-1}) in comparison with conventional ozonation (11.2 mg L^{-1}) during 60 min of treatment.

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Conflict of interest

The authors declare that they have no conflict of interest.

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