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An optimization study of nickel catalyst supported on activated carbon for the 2-nitrophenol catalytic ozonation

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ABSTRACT

Nickel-based catalysts were prepared through the impregnation of various nickel ion concentrations on activated carbons (ACs). Then, their textural and surface chemistry properties were characterized using various analytical techniques. The performance of the different catalysts was evaluated during the degradation of 2-nitrophenol by ozone in aqueous solution. In particular, a kinetic study was performed to investigate the effect of ozone/supported catalyst coupling process on nitrophenol degradation. The main results indicate that the optimum catalytic activity was observed when 4% (wt/wt) of Ni was supported on AC reaching a catalytic ozonation efficiency of 95%. The results of the total organic carbon (TOC) indicate that the presence of either AC or Ni/AC catalyst considerably improves the degradation of the phenolic compound when compared with the single ozonation process. A combine use of O_3/AC-Ni reduces TOC up to 59% in 30 min. Therefore, the 4% Ni/AC is a promising catalyst for ozonizing organic pollutants in aqueous solution.

Keywords: Ozone; Advanced oxidation process; Nickel; AC; Phenolic compound

1. Introduction

Phenolic compounds are widely used in pharmaceutical, textile and other chemical industrial processes. Hence, these high toxic and carcinogen compounds are found commonly in many industrial effluents and should be effectively removed during wastewaters treatment [1]. Numerous wastewater treatment techniques such as catalytic wet air oxidation, biological degradation, adsorption and UV-oxidation are frequently applied. However, these techniques have several drawbacks such as costs and complexity transfer at large scale. Therefore, adsorption of nitrophenol on activated carbons (ACs) is still the most promising technique [2]. Nevertheless, the maximum capacity is not sufficient to treat effluents containing higher nitrophenol concentrations [2].

The adsorption on AC coupled with ozonation seems to improve the removal efficiency of several pollutants from wastewater [3]. Ozonation allows the oxidization of organic pollutants either by a direct reaction with ozone or through the formation of hydroxyl radicals. Hoigné and Bader [4]

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noted that suspensions of AC can initiate the radical-type chain reactions that proceed in bulk solution and, therefore, the stoichiometric yield factor for the conversion of O_3 into °OH by AC. They have concluded that AC seems to represent an alternative 'clean' reagent to enhance ozone advanced oxidation process (AOP). They have also revealed that °OH is highly reactive species by attacking most part of organic molecules [4]. Further investigations have examined the heterogeneous catalytic ozonation indicating that this process is one of the most promising AOPs. It combines ozone with supported catalysts to achieve the mineralization of dissolved organic compounds at room temperature [5]. In addition, the supported catalysts can increase the ability of ozone for the removal of refractory organic pollutants.

Several investigations have studied the combination of ozone with catalysts, with or without metallic compounds [6,7]. Zeolites, alumina (Al_2O_3) [8,9] and TiO_2[10] are commonly used as catalyst support in order to improve the ozonation process. The implementation of AC as a catalyst support has also received particular attention. However, few studies have focused on the effect of preparation conditions on the catalyst characteristics and the corresponding performance during the ozonation process. In fact, the performance of AC-supported catalysts depends strongly on the textural properties of the support (surface area and porosity) as well as on its surface chemistry [11]. The latter could be submitted to thermal and/or oxidative treatments leading to a modification in the amount and nature of surface oxygen groups [12]. It could be also modified through active-phase depositions including noble metals [13].

Several noble metals have been implanted on AC and, therefore, evaluated for the ozonation of some organic compounds. Indeed, Wang et al. [14] studied the mineralization of dimethyl phthalate (DMP) in the presence of Ru/AC catalyst and indicated that the removal of the total organic carbon (TOC) remained stable up to 75% within 42 h. Li et al. [15] have examined the performance of cerium-supported AC for the DMP mineralization. The results showed that the maximum rate of TOC removal was 68%. They have confirmed that combining $Ce/AC/O_3$ is 2.5 times more efficient than AC/O_3 [15]. Shukla et al. [16] have prepared a heterogeneous cobalt catalyst through the immersion of AC on cobalt ion solution. This catalyst showed high activity in the advanced oxidation of phenol. Li et al. [17] have investigated the catalytic activity of AC prepared from petroleum coke loaded with Ni. The catalyst was evaluated during the ozonation of *p*-chlorobenzoic acid (*p*-CBA). The presence of AC or Ni/CA greatly enhanced the removal of TOC during ozonation of *p*-CBA. The mineralization occurred in the presence of the 5 g/L Ni/AC catalyst, and the removal of TOC was over 60% in 60 min. Díaz et al. [18] have examined the effect of the palladium supported on AC (Pd/AC) in the hydrogenation of phenol in aqueous phase. This catalyst showed a convenient chemical stability, and the highest phenol conversion values were obtained with the catalysts calcined at 250°C and reduced in hydrogen atmosphere at 150°C using palladium chloride as precursor.

The 2-nitrophenol is one major phenolic compound found in wastewater treatment plant due its large use in chemical industry. The degradation of 2-nitrophenol was studied using several AOP techniques. Di Paola et al. [19] have studied the heterogeneous photocatalytic degradation of nitrophenol in oxygenated aqueous suspensions containing TiO_2. The results showed the complete mineralisation of the substrates and the formation of both nitrate and ammonium ions. The authors confirmed that the degradation mechanism involves a rapid opening of the aromatic ring followed by a slower oxidation of the aliphatic compounds. The hydroxyl radicals are responsible for the primary attack of the nitrophenols with formation of dihydroxynitrobenzenes. Elshafei et al. [20] have studied the heterogeneous Fenton catalysts for the sonophotocatalytic degradation of 2-nitrophenol. Metal oxychlorides of Fe, Cu, Bi and Zn were prepared and tested in heterogeneous Fenton degradation of 20 ppm of 2-nitrophenol. The authors have confirmed that metal oxychlorides acted as robust catalysts for degradation of 2-nitrophenol. In this study, the proposed mechanism pointed out the major role of the produced hydroxyl radicals.

Carbonaceous materials are also used in several AOP processes [21,22]. Rodrigues et al. [21] have studied the *p*-nitrophenol degradation by heterogeneous Fenton's oxidation over AC-based catalysts. Authors have confirmed that the surface chemical properties of the AC play an important role in nitrophenol adsorption and, therefore, to the catalytic performance. Rodrigues et al. [21] have established a relationship between nitrophenol removal and the oxygen and nitrogen groups available on the carbon surface.

The main objective of this paper was to investigate the catalytic ozonation of 2-nitrophenol with Ni supported on AC (Ni/AC) at a 2-nitrophenol concentration comparable to the commonly found in phenolic wastewaters. This study focuses on the evaluation of the catalytic activity of different ACs (modified commercial AC and prepared from olive stones). Furthermore, the effect of preparation conditions such as metal precursor nature and the catalyst textural properties on nitrophenolozonation is analyzed.

2. Materials and methods

A commercial granular AC, type Chemviron, produced from selected-grade bituminous coal was selected as catalyst support. Furthermore, an AC using olive stone as precursor was prepared according to the method described in the following section. Both ACs were impregnated with nickel ion. The precursor employed for the deposition of nickel on AC was a solution of pure $Ni(NO_3)$, $6H_2O$. 2-Nitrophenol was supplied by Prolabo, Sion, Switzerland. The properties of the 2-nitrophenol are presented in Table 1.

2.1. OSAC preparation

The AC was prepared from olive stones as precursor. The latter was washed with deionized water to remove the impurities and then dried at room temperature for 24 h.

Table 1
Physico-chemical properties of 2-nitrophenol

Solute	2-Nitrophenol
Mass molar (g/mol)	139.11
Density (g/cm^3)	1.49
Solubility in water at 20°C (g/L)	2.10
λ_{max} (nm)	351

Table 2
Elemental analysis of olive stones (dry basis)

Element	Composition (%)
C	43.1
H	7.1
O[a]	47.4
N	0.4
Ash	1.8

[a] %O was obtained by difference.

The elemental composition of the olive stones shown in Table 2 was determined by CHNS/O NA 2100 protein CE instruments analyzer. The high carbon and low ash contents make olive stone a good precursor for production of porous ACs.

The preparation process of AC included the carbonization of the olive stone under nitrogen atmosphere followed by a physical activation using water vapour. Carbonization was performed under a continuous flow of purified nitrogen gas with a flow rate of 10 NL/h. The precursor was heated from room temperature to 600°C (5°C/min) and maintained at this final temperature during 60 min. The activation of the obtained char was then conducted at 750°C (the ramp used is 15°C/min) under 70 vol.% H_2O in N_2 during 360 min with a total gas flow rate equal to 10 NL/h. The AC referred to as olive stone activated carbon (OSAC) was obtained with a global yield of 25 wt% [22].

2.2. Preparation of AC-supported nickel catalyst

Ni was used as an active phase with a nominal loading of 5 wt%. The precursor salt employed was Ni $(NO_3)_2$ $6H_2O$. Before its application, the AC was washed with deionized water and then dried at 105°C for 24 h. The supported Ni/AC catalyst was prepared by the dipping method with an $Ni(NO_3)_2$ solution (0.001 M) in a shaking incubator at 160 rpm and 30°C for 2, 3 and 24 h, respectively. Different impregnation ratios (2%, 4% and 5%) were used. After the impregnation step, the wet samples of AC were dried at ambient temperature and then heated under nitrogen atmosphere to a temperature between 150°C and 450°C at a rate of 3°C/min and calcined during 2 h.

The Ni impregnated amount was verified after the catalyst preparation. Hence, 1 g of catalyst was immerged in 10 mL of 65% nitric acid for 24 h, at ambient temperature. The solid was filtered out from the acidic solution. The concentration of the Ni was determined using inductively coupled plasma atomic emission spectrophotometer: ICP-AES: (Activa-M Horiba Jobin Yvon, Villeneuve-d'Ascq, France).

The obtained catalysts were labelled as 'Ni/ACx,y', where x indicates the percentage of nickel used in the preparation and y indicates the calcination temperature as specified in Table 3. The impregnation ratio is the relative AC mass per gram of copper nitrate solution.

Table 3
Experimental conditions of the Ni/AC catalysts preparation

Sample	Treatment
Ni/AC2-450	Impregnated with 2% of nickel calcined at 450°C for 2 h
Ni/AC4-450	Impregnated with 4% of nickel calcined at 450°C for 2 h
Ni/AC5-450	Impregnated with 5% of nickel calcined at 450°C for 2 h
Ni/AC10-450	Impregnated with 10% of nickel calcined at 450°C for 2 h
Ni/AC4-150	Impregnated with 4% of nickel calcined at 150°C for 2 h
Ni/AC4-200	Impregnated with 4% of nickel calcined at 200°C for 2 h
Ni/AC4-250	Impregnated with 4% of nickel calcined at 250°C for 2 h
Ni/AC4-350	Impregnated with 4% of nickel calcined at 350°C for 2 h
Ni/OSAC4-350	Impregnated with 4% of nickel calcined at 350°C for 2 h

2.3. Activated carbons characterization

2.3.1. Textural properties

Characterization of the pore structure of the AC samples was made by measurement of N_2 adsorption isotherms using an automatic gas sorption analyzer (ASAP 2010, Micrometrics, Norcross, GA, USA). Specific surface area was calculated from the N_2 adsorption isotherms by applying the Brunauer–Emmett–Teller (BET) equation and yield important information about structural features. The *t*-plot method was applied to calculate the micropore surface area and micropore volume.

2.3.2. Surface chemistry

The surface chemistry of the samples was analyzed by temperature-programmed desorption coupled with mass spectroscopy (TPD-MS). 10 mg of each sample was placed in quartz tube and heat treated with a linear heating rate of 5°C/min in vacuum. The material surface chemistry was evaluated in the temperature range 25°C–900°C; the gases evolved during the heating process were continuously analyzed quantitatively by a mass spectrometer. The desorption rate of each gas as a function of temperature was determined from the TPD analysis. The total amount of each gas released was computed by time integration of the TPD curves.

2.4. Ozonation procedure

The ozonation experiments were carried out in a semi continuous gas–liquid stirred reactor of controlled temperature equipped with a stirrer for mixing and controlling the loop jacket. 2-Nitrophenol with initial concentration 35 mg/L solutions was added into the reactor which was continuously fed with an ozonated oxygen stream. The temperature in the reactor was kept constant at 20°C by a continuous thermostatic system. Ozone was produced in a pure oxygen stream using an ozone generator with a controlled power to achieve variable O_3 concentrations up to 100 mg/nL of O_2.

The determination of 2-nitrophenol concentration was carried out on UV absorption (Shimadzu 1700). A UV detector was used with the wavelength set at 351 nm.

2.5. TOC determination

The measurements of TOC were made on a TOC meter, Bioritech 700. The oxygen requirements were provided by a solution of potassium sulfate (40 g/L) called a reactant, which was continuously pumped from an external tank and fed to the bottom of the UV reactor. The reactor has a constant volume. The excess liquid was pumped into a waste tank.

2.6. Kinetic study

In order to estimate the kinetics parameters, a general pseudo-first order kinetic for nitrophenol was assumed. The evolution of the nitrophenol concentration can be described according to the following equation:

$$\ln\left(\frac{C_0}{C}\right) = k_{app}t \qquad (1)$$

where k_{app} (min^{-1}) is the pseudo-first order rate constant. It is considered as the global rate constant including several intermediate steps of adsorption, oxidation and desorption. C and C_0 are the residual and initial concentrations of nitrophenol, respectively.

3. Results and discussion

3.1. AC and Ni/AC characterization

3.1.1. Textural properties

Nitrogen adsorption–desorption isotherms presented in Fig. 1 illustrate the evolution of porosity from the raw AC to the nickel-loaded AC.

As it can be observed in Fig. 1, and according to the IUPAC classification, the raw AC presents type I isotherm indicating a microporous material with contribution of mesoporosity [23]. The isotherm of raw material presented a sharp increase of nitrogen at low pressure, a horizontal plateau while no adsorption–desorption hysteresis cycle was obtained. When Ni was impregnated on the surface of the AC, no modifications were obtained for the raw AC. It can be observed from the isotherm of Ni/AC that a relatively important porosity development was obtained. This effect may be attributed to the Ni incorporation into carbon matrix. The same effect was observed from Haro et al. [24] when AC was impregnated by Ni. At low relative pressure, the two isotherms were approximately overlapped indicating that microporosity seems to be not affected by Ni insertion. Such behaviour may be attributed to the size of Ni ions (0.26 nm) which may access mesoporosity and higher microporosity but not the narrow micropore diameters.

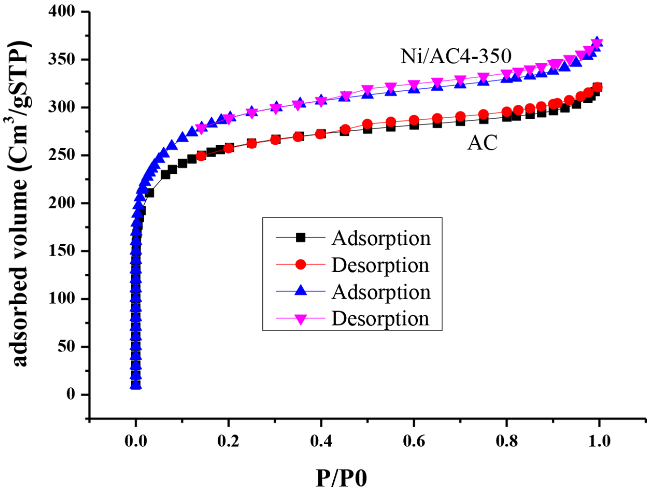

Fig. 1. Nitrogen sorption isotherm for AC and Ni/AC4-350.

Textural properties of the different samples are shown in Table 4. Commercial Chemviron granular AC has a large surface area and a developed porosity making it suitable as a catalyst support. Chemviron AC has a microporous structure in which the micropore volume is 94% of the total pore volume with a mean diameter of 4 nm. Table 4 shows that the specific surface area increased slightly from the raw AC to Ni/AC4. However, when the impregnation ratio increased from 4% to 10%, the specific surface area (S_{BET}) decreased. Such behaviour indicates that for low impregnation rate the Ni particles were globally fixed on the internal surface. In contrast, for high impregnation rate, the nickel nanoparticles were fixed on the external surface of the carbon. This statement is proved by an increment of the micropore volume resulting from the heat treatment during the calcination step. On the other hand, when the calcination temperature increased to 350°C, the specific surface area of the catalyst increased from 938 to 1,040 m^2/g. This is mainly due to the development of the porosity of the catalyst under the heat treatment. The highest surface area value was 1,007 m^2/g. This value was obtained when the Ni/AC was impregnated with 4% Ni loading and calcined at 350°C for 2 h. When the calcination temperature up to 450°C, the S_{BET} decreases from 1,007 to 967 m^2/g due to the destruction of the carbon texture for a high calcination temperature.

3.1.2. Surface chemistry characterization

Fig. 2 shows the AC and Ni/AC4-350 surface functionality analyzed by TPD-MS technique. The rate of desorbed gases during thermal treatment is plotted versus temperature. In the case of Ni/AC4-350, an increase in the amount of surface oxygen groups is evidenced by the increase of the CO and CO_2 peaks, respectively, at (600°C–900°C) and (100°C–400°C).

Table 4
Textural properties of Chemviron AC and supported catalysts

Sample	S_{BET} (m^2/g)	Vμ(cm^3/g)	VT (cm^3/g)	Dμ(Å)
AC	938	0.45	0.48	40.5
OSAC	920	0.38	0.53	40.6
Ni/AC2-450	958	0.46	0.49	40.6
Ni/AC4-450	967	0.36	0.48	40.3
Ni/AC5-450	944	0.45	0.49	41.2
Ni/AC10-450	942	0.45	0.47	39.7
Ni/AC4-150	973	0.48	0.57	40.7
Ni/AC4-200	944	0.46	0.49	41.2
Ni/AC4-250	938	0.47	0.49	40.3
Ni/AC4-350	1,007	0.49	0.50	41.8
Ni/OSAC4-350	946	0.38	0.51	40.8

The CO_2 evolves at low temperatures (200°C–400°C) as a result of the decomposition of carboxyl or anhydride groups [25], whereas the CO evolves at higher temperatures (600°C–800°C) suggesting the existence of basic or neutral functional oxygenated groups stable at high temperatures such as ethers, phenols and quinones [25]. The peak of CO is more developed due to the presence of phenol, carbonyl and quinone groups [26].These groups are the result of the thermal treatment.

Besides, desorption peaks related to water (not shown) and H_2 are also detected. The water profile exhibits a small peak at 200°C and a very intense one placed around 750°C. The first peak can be assigned to physiosorbed water. While the second peak can be attributed to the water evolution coming from the decomposition of two neighbouring carboxylic acids forming an anhydride carboxylic acid [25,27].

Table 5 shows the amounts of the released CO, CO_2, H_2 and H_2O during the TPD-MS. These amounts were obtained by integration of the areas under the TPD peaks. The obtained values confirmed an increase in the amount of surface oxygen groups for Ni/AC4-350 comparing with the AC sample.

3.2. Ni/AC optimization for the 2-nitrophenol degradation

In order to optimize the elaboration of the carbon support catalyst, the influence of the impregnated nickel amounts, calcination temperature and time on their performance for the ozonation of 2-nitrophenol was examined.

3.2.1. Effect of residence time

The impregnation time (imp) is an important factor for the catalyst preparation. Hence, various imps were selected (2, 3 and 24 h). Comparison between the performances of the different samples is shown in Fig. 3. The amount of nitrophenol uptake by the AC was calculated using Eq. (1).

It can be seen that the higher catalyst activity was obtained for an imp of 24 h. For this time, the amount of impregnated nickel is important, and the carbon was reaching the high adsorbent amount of nickel on its surface. But the difference between the activities of the catalyst obtained with 24 h residence time and these obtained for 2 and 3 h is not very significant. In fact; more than 80% of nitrophenol was eliminated only for 5 min when AC impregnated for 24 h was used. This result is obtained, respectively, for 10 and 15 min when we used AC impregnated for 3 and 2 h. Therefore, for all the experiments, we selected the residence time equal to 2 h.

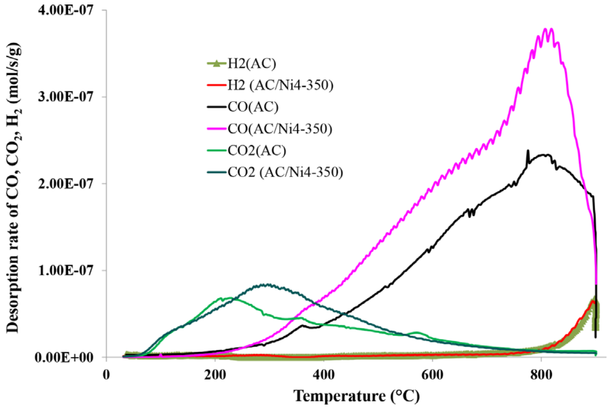

Fig. 2. H_2, CO and CO_2 desorption rates as a function of the applied temperature during a TPD-MS analysis of the ACs AC and Ni/AC4-350.

Table 5
Amount of CO, CO_2, H_2O and H_2 obtained by integration of the different peaks for AC and Ni/AC4-350 catalyst

Material	CO (mmol/g)	CO_2 (mmol/g)	H_2 (mmol/g)	H_2O (mmol/g)
AC	0.953	0.292	0.065	1.33
Ni/AC4-350	1.370	0.347	0.066	0.066

3.2.2. Effect of impregnation percentage

Different impregnation percentages were tested to evaluate the effect of this parameter on Ni/AC activity. Different Ni/AC impregnated for 2 h and calcinated at 450°C were tested for nitrophenol degradation. Comparison between samples prepared with different Ni percentage is shown in Fig. 4.

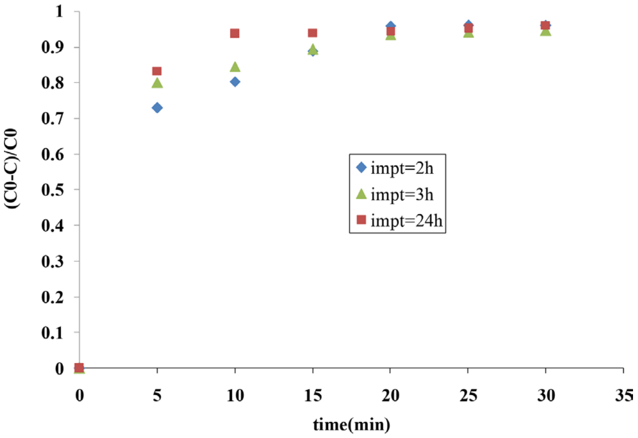

Fig. 3. Effect of impregnation time (C_N = 35 mg/L; C_{O3} = 6 mg/L; T = 20°C, N = 400 rpm; Q_{gaz} = 0.36 L/min, $m_{Ni/AC}$ = 1 g, %imp = 4%, calcination temperature = 350°C).

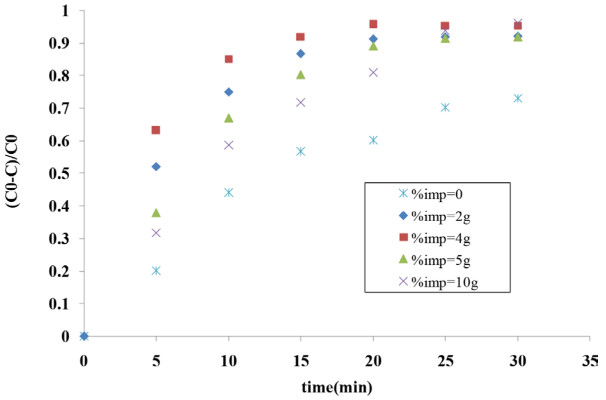

Fig. 4. Effect of % of impregnation C_N = 35 mg/L; C_{O3} = 6 mg/L; T = 20°C, N = 400 rpm; Q_{gaz} = 0.36 L/min, $m_{Ni/AC}$ = 1 g, calcination temperature = 350°C).

It is seen that nitrophenol conversion in the presence of AC (0% imp) decreased slowly and only 60% conversion was obtained after 30 min. The addition of Ni content shows that the catalytic activity of AC/Ni catalysts increases significantly. In particular, Ni/AC-4-450 exhibits the best catalytic performance, and nitrophenol conversion increases quickly to higher than 90% after 30 min. This behaviour is in agreement with the textural properties determination. In fact, the highest specific area was also obtained for Ni/AC-4-450. Hence, for high impregnation ratio, the nickel nanoparticle can be agglomerated on the surface of the catalyst due to the high amount of nickel as consequence of the surface area and the catalyst activity decrease.

The kinetic parameters were extracted using the pseudo first order as shown in Fig. 5, and the obtained values are presented in Table 6. The theoretical data were evaluated by the different statistic coefficients including the determination coefficient (R^2) and root mean squared error (RMSE) described in Fig. 5.

The correlation coefficients (R^2) are all high and close to 1, and the RMSE values are small. The model pseudo first order can be considered to be good to describe the response in the experimental investigated region.

The results show that the use of Ni Ni/AC-4-450 for heterogeneous catalytic ozonation enhances significantly the nitrophenol degradation efficiency. In fact, the rate of nitrophenol degradation increased from 0.05 min^{-1} Ni/AC to 0.166 min^{-1} for Ni/AC-4-450. The 4% impregnation ratio enhances three times the rate of nitrophenol oxidation. When the impregnation rate exceeds 4% the oxidation rate decreases. Higher conversions obtained during the catalytic processes lead to the assumption that Ni catalysts favoured hydroxyl radical formation. Ni impregnation could affect the pore structure and Ni dispersion and, therefore, the oxidative activity. This optimization study indicates clearly that the optimum impregnation percentage was 4%.

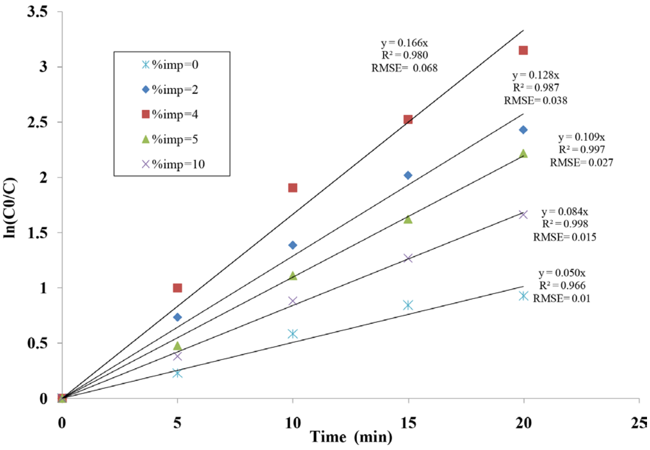

Fig. 5. Pseudo-first order parameters calculated for different impregnation percentage (regression coefficient between 0.98 and 1).

Table 6
Kinetic parameters for different nickel concentrations

Ni/AC	k_{app} (min^{-1})
Ni/AC	0.05
Ni/AC-2-450	0.128
Ni/AC-4-450	0.166
Ni/AC-5-450	0.109
Ni/AC-10-450	0.084

3.2.3. Effect of calcination temperature

In order to optimize the calcination temperature for the Ni/AC activity during nitrophenol ozonation, kinetic experiments were carried out in the same conditions with different calcination temperature from 150°C to 450°C for the optimized impregnation percentage (4%). Comparison between the different samples is shown in Fig. 6.

It is observed that the best catalyst activity was obtained for 350°C calcination temperature. Such behaviour is attributed to the high surface area of the catalyst calcined at 350°C as shown in Table 4. Such property is a key parameter for the molecule interaction with the active site of the catalyst.

Pseudo-first order parameters extracted for different impregnation percentage are shown in Table 7. It is clearly confirmed that the efficient catalyst was obtained using the temperature calcination equal to 350°C.

3.2.4. Effect of the support on the catalytic activity of AC/Ni

The effect of the support properties on the nitrophenol degradation was also investigated. Therefore, based on the optimized conditions in the previous section, the AC prepared using olive stone as precursor (OSAC) was loaded

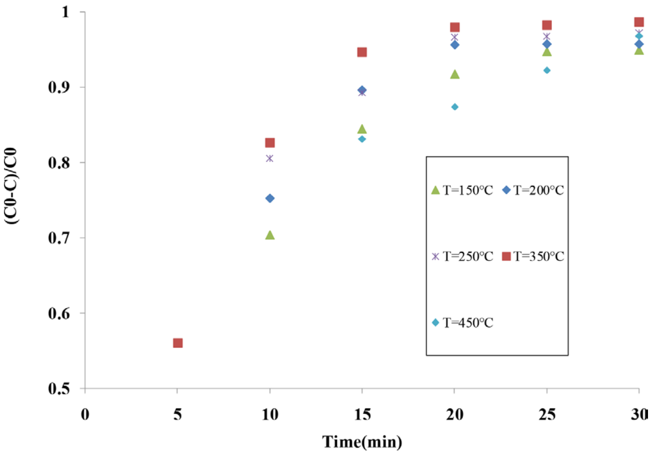

Fig. 6. Effect of calcination temperature on Nitrophenol degradation (C_N = 35 mg/L; C_{O3} = 6 mg/L; T = 20°C, N = 400 rpm; Q_{gaz} = 0.36 L/min, $m_{Ni/AC}$ = 1 g, %imp = 4).

Table 7
Kinetic parameters for different calcination temperature

Ni/AC	k_{app} (min^{-1})
Ni/AC-4-150	0.122
Ni/AC-4-200	0.152
Ni/AC-4-250	0.16
Ni/AC-4-350	0.191

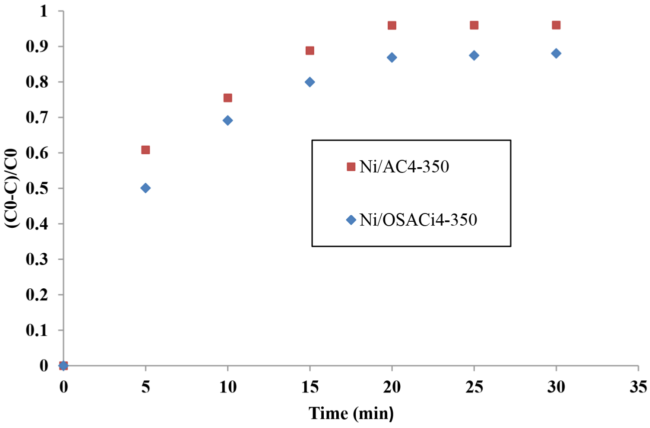

Fig. 7. Effect of support nature(C_N = 35 mg/L; C_{O3} = 6 mg/L; T = 20°C, N = 400 rpm; Q_{gaz} = 0.36 L/min, $m_{Ni/AC}$ = 1 g, pH = 6.44.

with 4% Ni and calcinated at 350°C. The textural properties of the Ni/OSAC catalyst were already presented in Table 2.

Fig. 7 shows a comparison between the degradation of nitrophenol on the presence of the Ni/OSAC-4-350 and Ni/AC-4-350. It can be observed that the conversion rate in the presence of Ni/AC-4-350 is significantly higher confirming that textural properties of the AC are crucial factor for the catalyst activity.

3.3. Catalytic activity of nitrophenolozonation

As far as AC catalytic ozonation is concerned, Jans and Hoigné confirmed that the decomposition of ozone in water in the presence of an AC or a black carbon yields hydroxyl radicals in the aqueous phase [28]. In order to further investigate the mechanism of 2-nitrophenol ozonation, as well as the effect of nickel addition to the surface of AC on its catalyst activity, kinetic experiments of nitrophenol degradation were carried out in the same conditions in the absence and presence of the commercial AC and the optimized catalyst Ni/AC-4-350.

Fig. 8 shows the nitrophenol ozonation in the absence and presence of the different prepared materials. The extracted kinetic parameters are also presented in Table 8.

It is interesting to note that after 15 min, the conversion of nitrophenol with only ozone was 50% while in the presence of Ni/AC4-350 was 72%. After 20 min, nitrophenol degradation in the presence of Ni/AC achieves 92% while simple ozonation is limited to 72%. As a result, the insertion of Ni on AC increases the generation of OH° radicals produced by the catalyst. This observation was not predictable because ozone decomposition is initiated by the presence of Ni. As previously discussed, this increase may be attributed to the increase of oxygenated surface groups of supported AC when compared with AC sample (Table 5). These observations could confirm that the available surface area is not the only key parameter in reinforcing the reaction mechanism. Faria et al. [29] have pointed out the role of surface chemistry during the catalytic ozonation of oxalic acid.

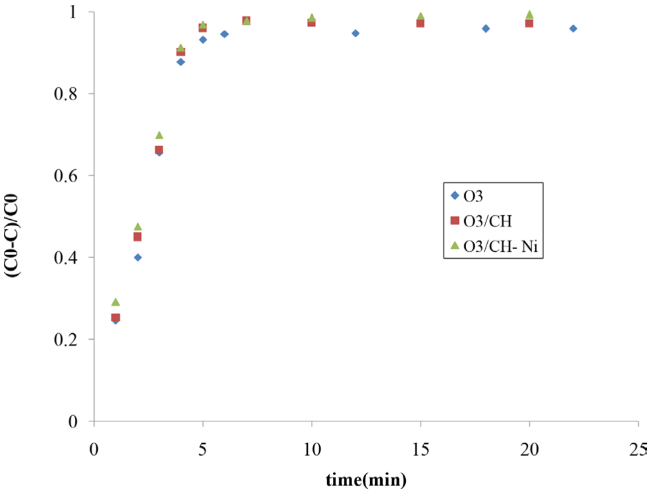

Fig. 8. Degradation efficiency of Nitrophenol using different processes (C_N = 35 mg/L; C_{O3} = 6 mg/L; T = 20°C, N = 400 rpm; Q_{gaz} = 0.36 L/min, $m_{Ni/AC}$ = 1 g, pH = 6.44).

Table 8
Kinetic parameters for different supports

Process	k_{app} (min^{-1})
O_3	0.02
O_3/AC	0.038
O_3/AC/Ni	0.05
O_3/Ni/AC4-350	0.191

3.4. Effect of the nickel addition on TOC removal

TOC is a very important parameter to evaluate the purification efficiency. During this investigation, the presence of Ni/AC has a benefit effect on TOC reduction, compared with the simple ozonation. For example, after 15 min, TOC removal rate in the presence of the catalyst Ni/AC is about 44%, while the simple ozonation is about 19%. Therefore, the greater reduction in TOC concentration observed during 2-nitrophenol ozonation in the presence of Ni/AC is largely due to the generation of highly oxidant species (°OH) in the system, capable of transforming the organic matter into CO_2. Indeed, for the aromatic compounds, the attack of these radicals is about double bonds C=C with ring opening followed by a degradation. After opening the phenol ring, subsequent degradation of by-products is done quickly, because these intermediates are also reactive with respect to OH radicals.

It could be also assumed that the mineral matter of the AC may play a role in ozone transformation into highly oxidant species (°OH), which is advantageous for mineralization of 2-nitrophenol. These results show that the mineral matter present in the AC positively contributes also to the enhancement of 2-nitrophenol ozonation process. Therefore, the Ni catalyst supported on AC is a promising material for the ozonation of aromatic compounds.

4. Conclusions

This investigation aims to synthetize an efficient catalyst for the 2-nitrophenol ozonation. Therefore, the effect of preparation method during nickel loading on microporous AC was examined. In particular, the effect of nickel percentage and calcination temperature on the catalyst performance was examined.

The main results indicate that the optimum catalytic activity was obtained for 4% (wt/wt) of Ni supported on AC and a calcination temperature of 350°C. In fact, this Ni/AC catalyst has a 2-nitrophenol ozonation efficiency of 90%. Furthermore, the TOC removal reaches 59% in the presence of Ni/AC catalyst. Therefore, the 4% Ni/AC is a promising catalyst for ozonizing organic pollutants in aqueous solution.

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