Catalytic ozonation of p-chlorobenzoic acid by activated carbon and nickel supported activated carbon prepared from petroleum coke

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ABSTRACT

The aim of this research was to investigate catalytic activity of petroleum coke, activated carbon (AC) prepared from this material, Ni supported catalyst on activated carbon (Ni/AC) in the ozonation of aqueous phase p-chlorobenzoic acid (p-CBA). Activated carbon and Ni/AC catalyst were characterized by XRD and SEM. The presence of petroleum coke did not improve the degradation of p-CBA compared to ozonation alone, but it was advantageous for p-CBA mineralization (total organic carbon, TOC, reduction), indicating the generation of highly oxidant species ($^{\bullet}$OH) in the medium. The presence of either activated carbon or Ni/AC considerably improves TOC removal during p-CBA ozonation. Ni/AC catalyst shows the better catalytic activity and stability based on five repeated tests during p-CBA ozonation. During the ozonation (50 mg/h ozone flow rate) of a 10 mg/L p-CBA (pH 4.31), it can be more mineralized in the presence of Ni/AC catalyst (5.0 g/L), TOC removal rate is over 60% in 60 min, 43% using activated carbon as catalyst, only 30% with ozonation alone.

1. Introduction

Advanced oxidation processes (AOPs), making use of different reacting systems, are all characterized by the same chemical feature (production of OH radicals, $^{\bullet}$OH). $^{\bullet}$OH is extraordinarily reactive species, it attacks most part of organic molecules with rate constants usually in the order of 10^6 to 10^9 M^{-1} s^{-1}[1]. AOPs are frequently selected as a treatment option to oxidize refractory and toxic organic compounds present in waters. Because of their high cost in treatment, traditional AOPs, such as photocatalysis and catalytic wet oxidation process, can hardly meet the requirements of the practical applications [2,3]. Heterogeneous catalytic ozonation, a novel alternative to traditional AOPs, has received wide interest as a promising technology for removing refractory organic pollutants in waters. It provides many advantages and is often used in a reactor operating at ambient temperature to mineralize refractory organic compounds to carbon dioxide, water and mineral acids, without UV radiation and high reaction temperature and pressure [4].

Recently, activated carbon adsorption combined with ozone oxidative regeneration of adsorbent (activated carbon) offers an attractive option for organic pollutant removal. Indeed, activated carbon presents a large surface area where organic pollutants could be adsorbed [5], while ozone readily destroys adsorbed aromatic molecules, helping to regenerate activated carbon adsorption capacity [6]. In this combined treatment, there is evidence that the presence of activated carbon during the reaction between organic pollutants and ozone, improves removal efficiency, probably due to catalytic effects provided by the carbon surface [7]. Activated carbon has been shown to promote ozone transformation in aqueous phase. It starts chain reactions that continue in aqueous phase, accelerating ozone transformation into secondary radicals ($^{\bullet}$OH) [8–12]. However, there is practically no information available in the published literature on the supported Ni catalyst on activated carbon to enhance the oxidation of organic pollutants by ozone.

p-Chlorobenzoic acid (p-CBA) is an important intermediate for pesticides, pharmaceutics and dye. Due to its bio-recalcitrant property, p-CBA accumulates in the environment as intermediate during biodegradation of chlorinated aromatics like polychlorinated biphenyls [13–16]. In the present work, p-CBA was chosen as a model compound to analyze catalytic activity of petroleum coke, activated carbon prepared from this material and supported Ni catalyst on it.

2. Experimental

2.1. Preparation of activated carbon

The petroleum coke was supplied by Guangzhou Petrochemical Factory (Guangzhou, China), and its particle size ranged from 0.2 to 0.45 mm. KOH solution was used as activating agent for petroleum

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Table 1
Components of petroleum coke

Component	Content (%)
Carbon	85.7
Water	1.2
Volatile	11.2
S	0.8
V	0.02
Fe	0.08
Ni	0.05
Mg	0.05
Ash	0.9

Fig. 1. The X-ray powder diffraction patterns of activated carbon and Ni/AC.

coke activation. Activated carbon was prepared, with KOH/coke mass ratio (1.0). Petroleum coke (25 g) was mixed with 100 mL of a KOH solution (250 g/L), they were mixed about 24 h in a vibrator. This mixture was heated to 450 °C in N_2 flow (400 mL/min) and held at 450 °C for 120 min, then again heated to 800 °C and carbonized at 800 °C for 120 min under a N_2 flow (400 mL/min). In all heat treatments, the oven heating rate was 2 °C/min. Finally, the samples were washed with deionized water to constant conductance. Elemental analysis of petroleum coke used was done with a Fisons Instruments 1108 CHNS analyzer. The mineral matter components were analyzed by X-ray fluorescence equipment. The content of different elements in petroleum coke is listed in Table 1.

### 2.2. Preparation of the supported Ni catalyst on petroleum coke and activated carbon

Before use, petroleum coke and activated carbon prepared from this material were thoroughly washed with deionized water and dried in an oven at 105 °C for 24 h. The supported Ni catalyst on petroleum coke and activated carbon prepared from this material was prepared by the dipping method with an aqueous solution of Ni $(NO_3)_2$ in a shaking incubator at 160 rpm and 30 °C for 2 h. The wet sample was dried at room temperature. And then it was heated to 450 °C at a rate of 3 °C/min in N_2 flow (400 mL/min) and calcined at 450 °C for 2 h to obtain the required catalyst.

2.3. Catalyst characterization

The crystalline phase of Ni_xO_y was determined using an X-ray diffractometer (Rigaku, D/max-RB, Japan) employing Cu Kα radiation. The accelerating voltage and applied current were 40 kV and 120 mA, respectively. The surface morphology of the samples was visualized using a Thermal FE Environment Scanning Electron Microscope (Quanta 400) with an accelerating voltage of 20 kV.
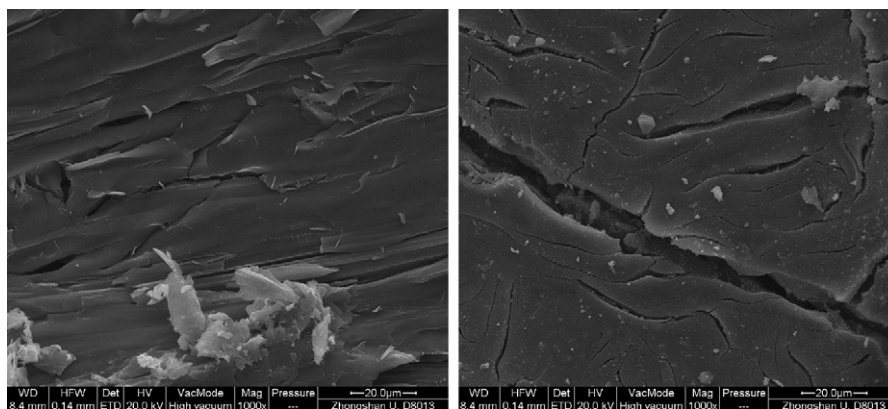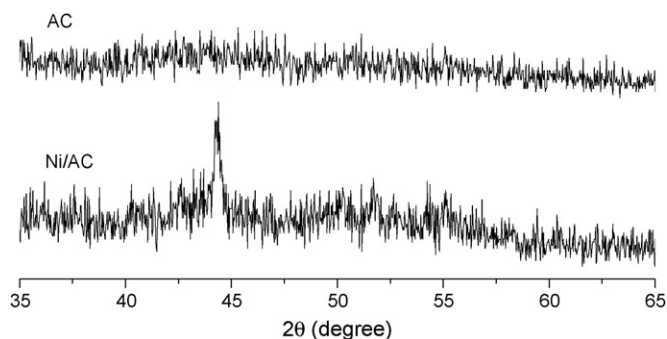
2.4. Catalytic ozonation procedure

The experimental system consisted of a 1.4-L tubular borosilicate glass oxidation reactor ($h = 500$ mm, $\Phi_{in} = 60$ mm) equipped with gas inlet and outlet, reactive alimentation and sampling accessories for catalytic ozonation experiments. p-CBA (1 L) around 10 mg/L solution (pH 4.31) was added into the reactor. Simultaneously, 5 g of catalyst was added (fluidized status). Ozone was produced from pure oxygen by using a DHX-SS-001 ozone generator (made in China). Ozonized oxygen (ozone input rate: 50.0 mg/h) was continuously bubbled into the solution through a porous glass plate and flowed upward in the annular section. The excess ozone in the outlet gas was absorbed by 5% $Na_2S_2O_3$ solution. Samples were taken at regular intervals to analyze p-CBA and total organic carbon (TOC) concentrations. $Na_2S_2O_3$ solution was used to stop the continuous ozonation reaction in the sample. In order to determine the contribution of adsorptive process, p-CBA solution was treated with oxygen keeping it in agitation for 60 min. The reduction of p-CBA and TOC observed in these experiments can be considered solely due to the adsorption of p-CBA on petroleum coke. Once the contribution of adsorption to overall removal of the organic matter is known, it can be deduced catalytic contribution to this removal as the difference between the total reduction in TOC and the reduction due to the adsorption process.

2.5. Analytical methods

Test solution was prepared with 10.0 mg/L p-CBA. Its concentration was analyzed by means of a high-performance liquid chromatography (Shimadzu, LC10A HPLC) with a UV detector (SPD-10AV) at 234 nm. A Discovery C18 column (150 mm × 4.6 mm) was used, the mobile phase was a mixture of methanol and water

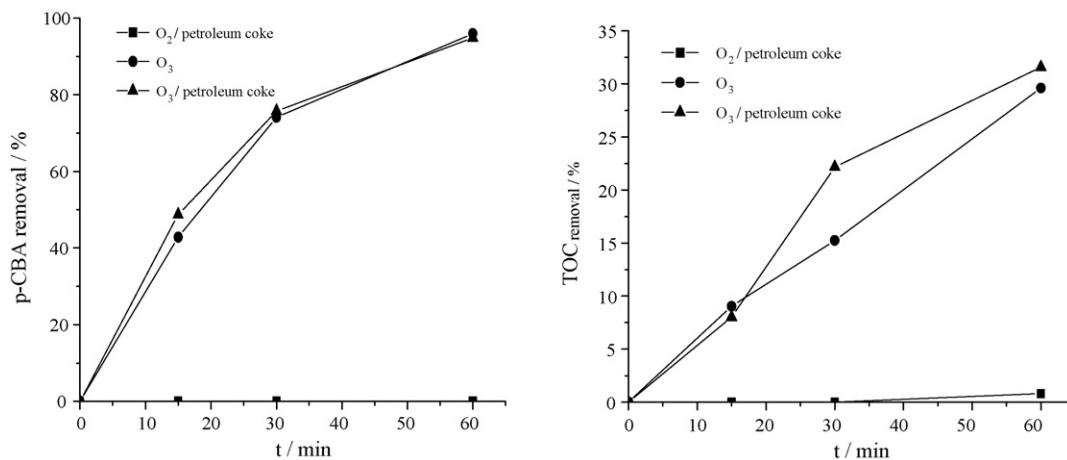Fig. 2. The SEM micrographs obtained from activated carbon and Ni/AC.

Fig. 3. Effect of added petroleum coke on degradation of *p*-CBA and TOC removal.

at 55:45 (v/v). (eluting solvent rate = 1.0 mL/min, column temperature = 40 °C). TOC was determined by a Shimadzu TOC 5000 analyzer after filtration through 0.45-μm prefilter.

3. Results and discussion

3.1. Characterization of activated carbon prepared from petroleum coke and supported Ni catalyst on it

Activated carbon (AC) prepared from petroleum coke and supported Ni catalyst on it (Ni/AC) are studied by XRD. Fig. 1 displays the X-ray powder diffraction patterns of activated carbon and Ni/AC. In activated carbon sample, no main diffraction peak is shown. In Ni/AC sample, the main diffraction peak corresponds to Ni_xO_y (Ni^{2+} and Ni^{3+}) at $2\theta = 42.3°$. Due to these properties, one can suppose a high catalytic activity for Ni/AC catalyst in the ozonation process of *p*-CBA.

The SEM micrographs obtained from activated carbon and Ni/AC are shown in Fig. 2. Compared with the surface of activated carbon, many Ni_xO_y particles are shown on the surface of Ni/AC catalyst, which can suppose a high catalytic activity in the ozonation process of *p*-CBA.

3.2. Effect of added petroleum coke on degradation of p-CBA and TOC removal

Fig. 3 shows that there is no adsorption of *p*-CBA on petroleum coke, because of the surface characterization of petroleum coke ($S_{N2} < 30\,m^2/g$, $V_{micropores} \approx 0\,cm^3/g$) [17]. The presence of petroleum coke during ozonation process did not increase the degradation of *p*-CBA, but slightly reduced the degradation of *p*-CBA after 30 min reaction time compared with ozonation alone. But it increased the mineralization rate (TOC reduction) of *p*-CBA. Its TOC removal rate is over 22% in 30 min, only 15% with ozonation alone in the same time. Previous studies [17–19] revealed that metal contents present in petroleum coke and activated carbon can act as catalytic sites in the ozonation process. These results indicated that the intermediate compounds (such as formic acid and oxalic acid) produced during the ozonation process of *p*-CBA were not easily mineralized. According to former research [20], some organic acids were produced in the ozonation process of aromatics, such as formic acid and oxalic acid. Ozonation alone can only achieve a very limited mineralization of formic and oxalic acids because ozonation rate constants of formic acid and oxalic acid are reported to be low in the acidic pH, but the reaction rate

constants of formic acid and oxalic acid with •OH were reported to be 1.3×10^8 and 1.4×10^6 $(mol/L)^{-1}\,s^{-1}$, respectively [1]. It is demonstrated in Fig. 3 that there is practically no adsorption of *p*-CBA on petroleum coke. Therefore, the reduction in TOC concentration (Fig. 3) observed during *p*-CBA ozonation in the presence of petroleum coke is largely due to the generation of highly oxidant species (•OH) in the system, capable of transforming the organic matter into CO_2.

3.3. The evolution of p-CBA and TOC concentration during ozonation in the presence of activated carbon prepared from original and demineralized petroleum coke

Fig. 4 depicts the increase of *p*-CBA and TOC removal with oxidation time during ozonation in the presence of activated carbon prepared from petroleum coke and activated carbon prepared from demineralized petroleum coke (demineralized activated carbon, which was prepared by petroleum coke washed by 3.9% HCl aqueous solution). The results show that there is no obvious difference for degrading *p*-CBA between activated carbon and the demineralized activated carbon.

TOC is a very important parameter to evaluate the purification efficiency of a system. It can be seen from Fig. 4 that the presence of activated carbon is advantageous for TOC reduction, compared with the presence of the demineralized activated carbon. For example, in 30 min oxidation time, TOC removal rate in the presence of the demineralized activated carbon is about 27%, that in the presence of activated carbon is about 37%. Therefore, the greater reduction in TOC concentration (Fig. 4) observed during *p*-CBA ozonation in the presence of activated carbon is largely due to the generation of highly oxidant species (•OH) in the system, capable of transforming the organic matter into CO_2. Furthermore, it can be deduced from the results presented in Fig. 4 that the demineralization of petroleum coke removes its capacity to promote the generation of highly oxidant species (•OH) and, therefore, to transform the TOC into CO_2. It could be deduced that the mineral matter (such as V, Fe and Ni) of the petroleum coke presents a higher activity in ozone transformation into highly oxidant species (•OH) [17–19], which is advantageous for mineralization of *p*-CBA. These results confirm that the mineral matter present in the petroleum coke positively contributes to its activity to enhance *p*-CBA ozonation process, making petroleum coke a very interesting material for the preparation of carbonaceous catalysts in the ozonation of aromatic compounds.

Table 2
Characterization of petroleum coke and of activated carbons prepared from this material

Sample	S_{N2} (m²/g)	V_{mic} (cm³/g)	V_{meso} (cm³/g)	V_{macro} (cm³/g)
Petroleum coke	<30	0.02	No	0.011
Activated carbon	1619	0.55	0.063	0.132

3.4. Comparison of p-CBA ozonation in the presence of petroleum coke with activated carbon

In order to develop the porosity of petroleum coke and thereby facilitate access of the ozone to its surface metallic active sites, petroleum coke was chemically activated using KOH and following the procedure indicated in Section 2. Table 2 shows the results of the textural characterization of activated carbon prepared from petroleum coke. These results indicate that the activation process considerably developed the porosity, increasing the volume of micropores (V_{mic}), mesopores (V_{meso}) and macropores (V_{macro}). Thus, the surface area of petroleum coke markedly increased after the activation.

Fig. 5 depicts the results of p-CBA ozonation in the presence of petroleum coke and activated carbon. p-CBA oxidation and mineralization rate were observed to increase when the ozonation was performed in their presence. Fig. 3 shows that no p-CBA was adsorbed on the petroleum coke after 60 min. Therefore, the increased removal rate of this pollutant in the presence of petroleum coke is solely due to an increase in the ozone decomposition rate into highly oxidant species (•OH) in the system [17]. After reaction 30 min, TOC removal rate (35%) in the presence of activated carbon is greater than that (22%) in the presence of petroleum coke. These results also show that the chemical activation process increases the activity of petroleum coke in p-CBA ozonation process. The activation of petroleum coke produces an increase of p-CBA mineralization, mainly due to development of the porosity of the coke, allowing greater accessibility of the ozone to its surface active sites and mineral matter (Table 1) and an increase in the surface basicity of the original coke [17] which favors ozone reduction on its surface and thereby enhances its transformation into highly oxidant species (•OH) [8,17,18].

Fig. 5 also depicts the evolution of the TOC as a function of p-CBA ozonation time in the presence of petroleum coke and activated carbon samples, showing an increase in the TOC removal

with a longer treatment time. The reduction in the TOC concentration during p-CBA ozonation in the presence of petroleum coke and activated carbon is due to mineralization of organic matter to CO_2 because of the generation of •OH enhanced by the presence of petroleum coke and activated carbon in the system.

3.5. Effect of Ni loading order on catalytic activity

For comparison, the performance of catalyst A (supported Ni catalyst on activated carbon prepared from petroleum coke), catalyst B (activated carbon prepared from petroleum coke) and catalyst C (first supported Ni on petroleum coke, then it is activated by KOH solution) in degrading p-CBA by ozonation is presented in Fig. 6. As it is apparent, the Ni loading order has an important influence on its catalytic activity for degradation of p-CBA and TOC removal during p-CBA ozonation. The result reveals that the highest p-CBA conversion and TOC removal rate is shown in the presence of catalyst A, the least efficient is shown in the presence of catalyst C. p-CBA can be quickly mineralized in the presence of catalyst A, the TOC removal rate is over 60% in 60 min, only 43% with catalyst B. These results preliminarily suggest that Ni is a better active component for the catalytic ozonation of p-CBA. The development of the porosity of the petroleum coke chemical activation process adsorbs more active component Ni and increases its surface active sites which enhance ozone transformation into highly oxidant species (•OH). But TOC removal rate is only 30% with catalyst C in 60 min. These results suggest that a fewer active component Ni can be loaded on petroleum coke than activated carbon because its surface area is very small. In addition, the supported Ni on petroleum coke may influence its chemical activation process.

3.6. Stability of supported Ni catalyst on activated carbon prepared from petroleum coke

In order to investigate stability of supported Ni catalyst on activated carbon prepared from petroleum coke (Ni/AC). The test was repeated with a new batch of 10 mg/L p-CBA solution under the same conditions (5-g catalyst, 60 min oxidation time and 50 mg/h ozone flow rate). The same test process was repeated for five times and the test results are shown in Fig. 7. It showed that p-CBA and TOC removal efficiency kept to a nearly constant rate, which suggested that the cat-
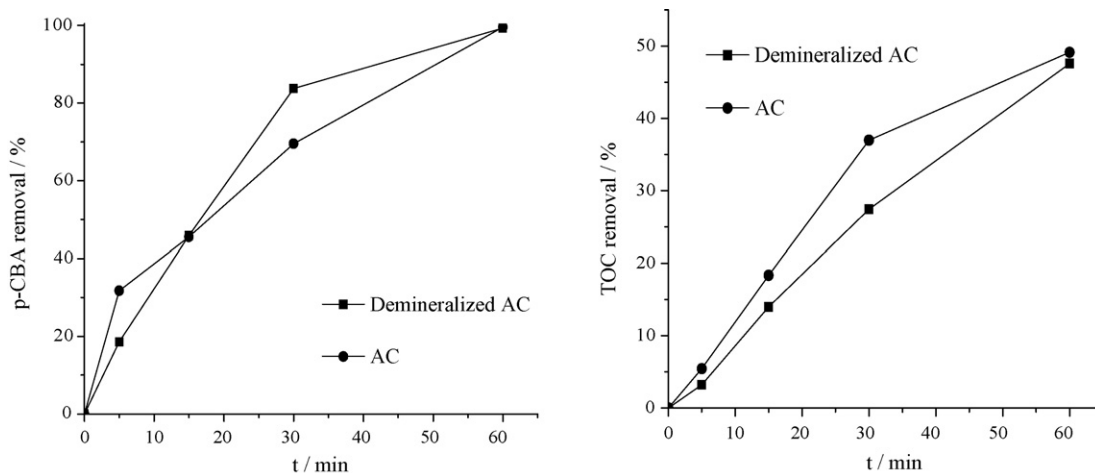
Fig. 4. Effect of added activated carbon and demineralized activated carbon on degradation of p-CBA and TOC removal.
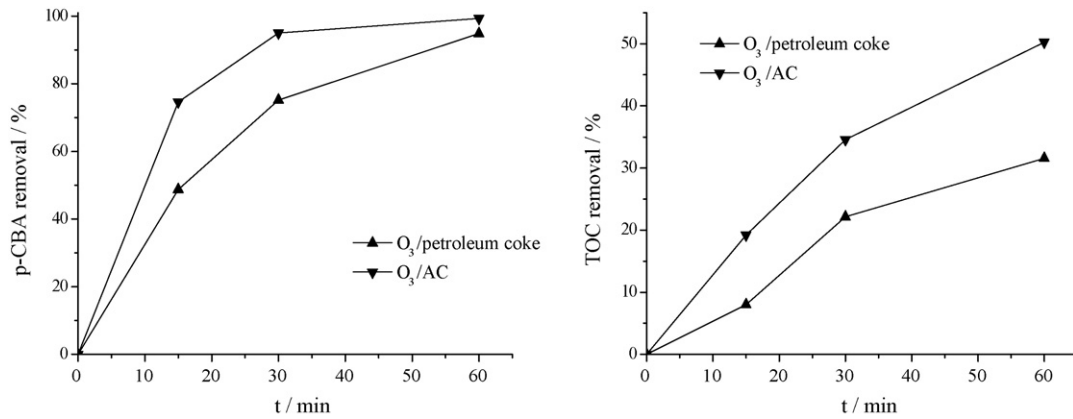
Fig. 5. *p*-CBA ozonation in the presence of petroleum coke and activated carbon.
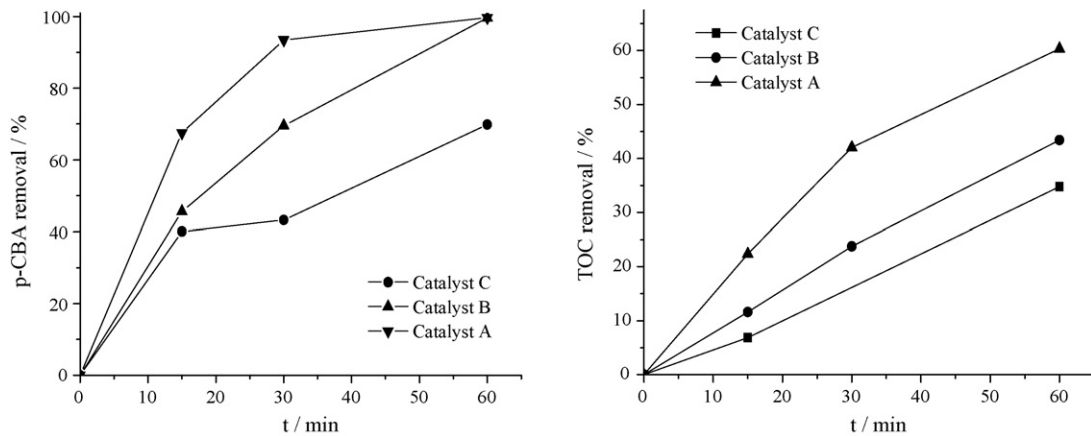

Fig. 6. Effect of Ni loading order on catalytic activity (catalyst A: supported Ni catalyst on activated carbon prepared from petroleum coke; catalyst B: activated carbon prepared from petroleum coke and catalyst C: first supported Ni on petroleum coke, then it is activated by KOH solution).

alytic capacity of Ni/AC was not decreasing with repeated times under such treatment conditions. This demonstrated that Ni/AC catalyst was effective and stable in the ozonation of *p*-CBA.
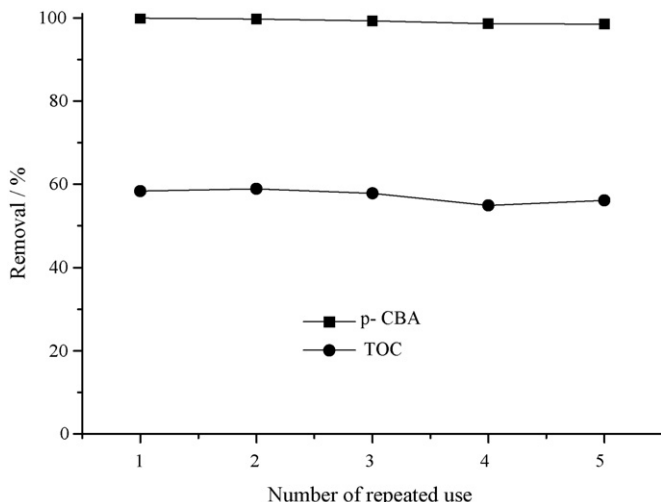

Fig. 7. The stability test of Ni/AC catalyst in the ozonation process of *p*-CBA.

4. Conclusion

Activated carbon prepared from petroleum coke and supported Ni catalyst on it were characterized by XRD and SEM.

The presence of petroleum coke did not improve the degradation of *p*-CBA compared to ozonation alone, but it was beneficial for mineralization (TOC reduction) of *p*-CBA. TOC removal rate during *p*-CBA ozonation is over 22% in 30 min with petroleum coke, only 15% with ozonation alone. There is practically no adsorption of *p*-CBA on the original coke. Therefore, the increase of TOC removal observed indicates the generation of highly oxidant species ($\bullet$OH) during *p*-CBA ozonation, capable of transforming the organic matter into CO_2.

The presence of activated carbon prepared from the original petroleum coke is advantageous for TOC reduction, compared with the presence of activated carbon prepared from the demineralized petroleum coke. These results confirm that the mineral matter present in petroleum coke positively contributes to its activity to enhance *p*-CBA ozonation process.

For *p*-CBA ozonation process, the presence of activated carbon improved TOC removal rate (35%) after reaction 30 min, compared with the presence of petroleum coke (22%). These results show that the chemical activation process increases the activity and porosity of petroleum coke.

The Ni loading order has an important influence on its catalytic activity for degradation of *p*-CBA and TOC removal during *p*-CBA

ozonation. Ni/AC catalyst considerably improves TOC removal during p-CBA ozonation with 50 mg/h ozone flow rate, a 10 mg/L p-CBA (pH 4.31) can be more mineralized in the presence of it (5.0 g/L), TOC removal rate is over 60% in 60 min, 43% using activated carbon as catalyst, only 30% with ozonation alone.

Acknowledgements

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