Mesoporous TiO$_2$/carbon catalytic ozonation for degradation of p-chloronitrobenzene

W. Qun, Z. Jingnan, L. Hong, L. Mengling, L. Xiaohui, Y. Zhichao, H. Tao and W. Pengyu

ABSTRACT

In this study, a mesoporous TiO$_2$/Carbon catalyst (TiO$_2$/C) was prepared by a facile impregnation-carbonization approach to catalyze ozonation of p-chloronitrobenzene (p-CN). The catalyst was well characterized and the catalytic efficiency under various conditions was systematically evaluated. TiO$_2$/C has a disordered mesostructure with a high specific surface area. 92.8% of p-CN (2 μmol/L) can be degraded within 20 min in the TiO$_2$/C/O$_3$ system in the presence of 1 mg/L O$_3$, 100 mg/L catalyst, at pH = 5. Based on the evaluation of the effect of basic parameters, it could be deduced that the removal of p-CN relied on the synthetic effect of catalysis by TiO$_2$/C and the autocatalytic induction of p-CN. The removal efficiency of p-CN, the structure change and the leaching of Ti ions were also evaluated in five cycles, indicating TiO$_2$/C is stable and recyclable for catalytic ozonation in water treatment.

Key words | catalytic ozonation, mesoporous TiO$_2$/carbon, p-chloronitrobenzene

INTRODUCTION

P-chloronitrobenzene (p-CN) is a common nitro halogenated aromatic compound with high toxic and potentially carcinogenic properties, which is widely used in pesticide, medicine, dyestuffs and the manufacturing industry (Zhang et al. 2015). Similarly, aromatic hydrocarbons and their derivatives have been reported to be toxic and can be monitored by VFBIA sensitively (Abbas et al. 2018); also, they revealed toxicity by applying vicia faba bioassay and bioassays based on higher plants (Iqbal 2016; Iqbal et al. 2019). Due to the genotoxicity and the potential carcinogenicity (Travlos et al. 1996; Shen et al. 2008), p-CN has been set as one of the priority pollutants for control in China. It is difficult to remove by biological methods (Xia et al. 2011), and also refractory to the common oxidants (e.g. potassium permanganate, ClO$_2$, and ozone) due to the presence of the electron-withdrawing groups (−Cl and −NO$_2$). Thus, it is vital to find a facile and efficient way to eliminate p-CN from the aquatic environment.

Advanced oxidation processes (AOPs), characterized by the production of the aggressive hydroxyl radical (•OH) and sulfate radical (SO$_4^{2−}$), offer a direction to the problem of removing trace organic pollutants. Iqbal et al. tested the influence of the reduction of textile printing wastewater on cytotoxicity by UV/H$_2$O$_2$/TiO$_2$, and got a conclusion that

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this system is efficient (Iqbal et al. 2015). Phenol can be degraded by the pulsed high-voltage discharge process combined with H2O2, due to the fact that a photocatalytic will degraded by the pulsed high-voltage discharge process compared with other catalysts when the effect on the degradation of CNB is same, also mesoporous TiO2/C is more economical. In a word, it can provide the possibility of catalytic ozonation procedures.

Materials and Methods

Materials

Perchloric acid with purity of 70%, sodium hydroxide (96.0%), sodium dihydrogen phosphate (99.0%), sodium bicarbonate (99.5%), sodium sulfate (99.0%), sodium sulfite (97.0%) were of analytic grade and purchased from Sinopharm Chemical Reagent Co., Ltd. Tert-butyl alcohol (99.8%), p-CN B (99.5%), indigo carmine (96%), and potassium indigotrisulfonate ozone-scavenging reagent (55%) were purchased from Aladdin. Anhydrous ethanol (90%) and sodium tetraborate (99.5%) were from Kermel (Tianjin, China). Ultrapure water (resistivity ≥ 18.2 MΩ.cm) from Millipore ultrapure water system was used for solution preparation. The saturated ozone solution was produced by a TOGC2B ozone generator (Degremont, Germany) using pure oxygen as the gas source. To ensure the stabilization of ozone concentration in each experiment, saturated ozone solution concentration was analyzed by UV-vis spectrophotometer (DR5000, Hach, USA) at 260 nm before each experiment.

Preparation of catalyst

The catalyst was prepared by a slightly modified impregnation and carbonization approach (Li et al. 2015). Briefly, 0.9 g potassium oxalate dihydrate was added into 15 ml ultrapure water for 1 h stirring. At room temperature, saturated ozone solution was produced by degassing from Millipore ultrapure water system was used for solution preparation. The saturated ozone solution was produced by a TOGC2B ozone generator (Degremont, Germany) using pure oxygen as the gas source. To ensure the stabilization of ozone concentration in each experiment, saturated ozone solution concentration was analyzed by UV-vis spectrophotometer (DR5000, Hach, USA) at 260 nm before each experiment.

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SU8030, Hitachi company, Japan); N$_2$ adsorption-desorption test at 77 K (ASAP 2020, Micromeritics company, USA) was used to determine the specific surface area, pore diameter and pore volume of the catalyst.

**Analytical methods**

$\text{p-CNB}$ was analyzed on a Waters high-performance liquid chromatograph (HPLC) equipped with a symmetry C18 column (4.6 mm $\times$ 150 mm) at $\lambda = 280$ nm. The mobile phase used for HPLC analysis was methanol/water (0.5‰ acetic acid) at a proportion of 40/60 (v/v) and the flow rate of mobile phase was set as 1.0 mL/min. The ozone concentration in the reactor was analyzed by Indigo method (Bader & Hoigné 2013). Total organic carbon was monitored by a TOC analyzer (multi N/C 3,100 TOC, Jena company, Germany).

**RESULTS AND DISCUSSION**

**Characterization of the mesoporous TiO$_2$/C catalyst**

Figure 1(a) XRD pattern and (b) SEM image of mesoporous TiO$_2$/C.

As shown in Figure 1(a), TiO$_2$/C is well crystallized with two phases of anatase (i.e. anatase and rutile). According to the Scherrer formula (Wang et al. 2015):

$$d = \frac{K\lambda}{B_{1/2} \cos \theta}$$

where $K$ represents the Scherrer constant, $K = 0.89; d$ represents the grain size; $B_{1/2}$ represents FWHM of the diffraction peak; $\lambda = 0.154056$ nm. Then the grain size of TiO$_2$/C was calculated to be 9.44 nm.

The representative SEM image of TiO$_2$/C is illustrated in Figure 1(b). TiO$_2$/C shows an irregular bulk structure with many granular pellets on the surface and disordered pore channels through them. They can provide reactivity sites and increase the specific surface area of the catalyst significantly.

Besides, the nitrogen adsorption-desorption method was used to measure the specific surface area, aperture and pore volume of mesoporous TiO$_2$/C. The surface hydroxyl density was determined by the Boehm titration method.

The specific surface area of TiO$_2$/C calculated by the BET method was 467.352 m$^2$/g. The average pore size and pore volume calculated by the BJH method was 2.68 nm and 0.242 cm$^3$/g. The high specific surface area provided enough active sites for the catalytic reactions. The pore diameter was within the mesoporous range, which increased the specific area of the catalyst, and the higher single pore volume capacity also provided enough sites for catalytic oxidation. The surface hydroxyl group density was determined by the Boehm titration method to be 0.294 mmol/g. To a certain extent, the surface hydroxyl density determines the performance of the catalyst (Zhao et al. 2008).

**Effect of ozone dosage and catalyst on the degradation of p-CNB**

The effect of ozone concentration alone and with catalyst in the presence/absence of TiO$_2$/C on p-CNB degradation in

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**Figure 1** Characterization of the mesoporous TiO$_2$/C catalyst (a) XRD patterns of mesoporous TiO$_2$/C. (b) SEM Images of mesoporous TiO$_2$/C sample with different magnifications.
aqueous solution was evaluated. What’s more, the adsorption and degradation effect of p-CNBr by catalyst was studied in a catalyst alone system. The experimental results are shown in Figure 2.

As can be seen from Figure 2, the removal rate of p-CNBr at different ozone concentrations (0.5, 1.0, 2.0 mg/L) reached 62.29%, 75.60% and 87.59%, respectively. The result could be explained by the steady-state concentration reached 62.29%, 75.60% and 87.59%, respectively. The adsorption of the catalyst for p-CNBr is about 7.5% in 20 min. The results showed that the mesoporous TiO2/C could be used as catalyst to activate ozone. When the dosage of ozone is 1.0 mg/L, the catalyst has the best effect on the degradation of p-CNBr, which is increased by 22.8%. Therefore, the dosage of ozone in our following study is 1.0 mg/L.

Reaction time is an important parameter in practical application. When only 1 mg/L ozone was added into p-CNBr solution, the degradation efficiency of p-CNBr was about 75% in 20 min. When 1 mg/L ozone and 100 mg/L catalyst were simultaneously added into p-CNBr solution, the p-CNBr degradation efficiency reached 90% within 15 min. The results indicate TiO2/C can promote degradation of p-CNBr and shorten the reaction time. To better investigate the influence of various factors in the O3/TiO2/C system, the reaction time in our following study was 20 min.

**Effect of p-CNBr dosage on p-CNBr degradation**

As shown in Figure 3, the degradation efficiency of p-CNBr was improved with the increase in the dosage of p-CNBr. The O3 decomposition rate also increased with increasing p-CNBr concentration. When the dosage of p-CNBr is 4 μM, the rate constant of ozone decomposition is about 28.5 times higher than that without p-CNBr. As ozone has a poor reactivity towards p-CNBr (the rate constant is only 1.6 M⁻¹ s⁻¹), the accelerated degradation of p-CNBr could be ascribed to the generation of hydroxyl radicals from ozone chain decomposition, which could be enhanced by a higher dosage of p-CNBr (Wang & Bai 2017).

It is worth noting that when the p-CNBr dosage is 4 μM, the ozone decomposition is rapid, and it is decomposed by about 95% after 5 min. The degradation rate of p-CNBr almost stops increasing after 10 min because of the depletion of ozone. However, p-CNBr still has a partial degradation from 5 min to 10 min, probably due to the remaining ozone and the active intermediate produced in the previous stage.

**Effect of pH on p-CNBr degradation**

As is known, ozone decomposes in water due to its instability, mainly including the following reactions (Staehelin & Hoigne 1982; Buehler et al. 1984):

\[
\begin{align*}
O_3 + OH^- & \rightarrow HO_2^- + O_2 \quad k = 70 \text{ M}^{-1} \text{ s}^{-1} \\
O_3 + HO_2^- & \rightarrow HO_2^- + O_3^\cdot \quad k = 2.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1} \\
HO_2^- & \rightarrow HO_2^- + H^+ \quad k_+ = 7.9 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \\
& \quad k_- = 5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \\
O_3 + O_2 & \rightarrow O_3^- + O_2 \quad k = 1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \\
O_3^- + H^+ & \rightarrow HO_3^- \quad k_+ = 5.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \\
& \quad k_- = 3.3 \times 10^2 \text{ M}^{-1} \text{ s}^{-1} \\
HO_3^- & \rightarrow O_2 + OH^- \quad k = 1.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \\
O_3 + OH & \rightarrow O_2 + HO_2^- \quad k = 2.8 \times 10^{4} - 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}
\end{align*}
\]

The first reaction is the rate limiting step of the ozone chain decomposition reaction, and it can be concluded that the solution pH has a great impact on chain decomposition of ozone (Buffe et al. 2006).

Figure 4 shows the impacts of pH on the decomposition of ozone and the degradation of p-CNBr. When pH value
Figure 3 | Effect of p-CNB dosage on the degradation of p-CNB and decomposition of ozone. Conditions: pH = 5, T = 20 °C, [boric acid buffer] = 2 mM, [O₃]₀ = 1 mg·L⁻¹.

Figure 4 | Effect of pH on the degradation of p-CNB and decomposition of ozone. Conditions: T = 20, [boric acid buffer] = 2 mM, [O₃]₀ = 1 mg·L⁻¹, [mesoporous TiO₂/C] = 100 mg·L⁻¹, [p-CNB]₀ = 2 μM.
raised, the decomposition of ozone is accelerated, which is in accordance with the previous conclusion. In particular, when pH = 9, ozone was almost completely decomposed within 2 min, the apparent rate of which should be 8.3 times higher than that at pH = 7. The degradation rate of p-CN is in good agreement with the decomposition rate of ozone. Along with the increase of solution pH, the decomposition rate of p-CN also increased. Although the degradation rate of p-CN was high at pH = 9, the final degradation efficiency was less than the degradation percentage of p-CN at pH 5 and 7. This is perhaps due to the ozonolysis at the early stage, and the produced intermediates of phenols and quinone during the oxidation of p-CN can also consume ozone or ·OH under alkaline conditions, which slows the subsequent degradation of p-CN.

Effect of inorganic anions on p-CN degradation

There are many ions existing in natural waters, such as Na\(^+\), K\(^+\) and Ca\(^{2+}\), which have been reported to have little effect on catalytic ozonation reaction, while anions have great influence on catalytic ozonation reaction (Hoigné et al. 1983). In our study, the effects of Cl\(^-\), NO\(_3\)\(^-\), SO\(_2\)\(^-\), HCO\(_3\)\(^-\) and HPO\(_4\)\(^2-\) on mesoporous TiO\(_2\)/O\(_3\)/p-CN were investigated.

As is shown in Figure 5, HCO\(_3\)\(^-\), Cl\(^-\) and HPO\(_4\)\(^2-\) have an obvious inhibitory effect on the degradation of p-CN. HCO\(_3\)\(^-\) is a typical free radical scavenger, since it can scavenge ·OH and prevent the generation of HO\(_2\)/O\(_2\), thereby inhibiting ozone chain decomposition and then decreasing the degradation efficiency of p-CN. Because the concentration of HCO\(_3\)\(^-\) in mixed solution is about 200 µM at pH = 5, the inhibition is lower than that of Cl\(^-\) and HPO\(_4\)\(^2-\). Both Cl\(^-\) and HPO\(_4\)\(^2-\) have a high reaction rate with ·OH and then could compete with p-CN for the generated ·OH (Staehelin & Hoigne 1985; Lei et al. 2009). In addition, Lewis acid sites and surface hydroxyl groups are considered to be the sites of ozone activation. HPO\(_4\)\(^2-\) and Cl\(^-\), which are closely related to Lewis acid, have the potential to isolate the active sites of catalysts and inhibit ozone decomposition, thus reducing the catalytic activity (Schmitt & Pietrzyk 1985; Kasprzyk-Hordern et al. 2003; Nawrocki & Kasprzyk-Hordern 2010). NO\(_3\)\(^-\) and SO\(_2\)\(^-\) have a slight promoting effect on the degradation of p-CN. Similar results were also found in the previous studies (Yuan et al. 2013; Roshani et al. 2014; Ghauch et al. 2015). It is presumed that the following reaction may occurred in the mesoporous TiO\(_2\)/O\(_3\)/p-CN system (Venkatalakshapathy & Ramamurthy 1996):

\[
\begin{align*}
\text{OH} + \text{SO}_2^2- & \rightarrow \text{SO}_4^2- + \text{OH}^- \quad E^0 = 2.6V \\
\text{OH} + \text{NO}_3^- & \rightarrow \text{NO}_3^- + \text{OH}^- \quad E^0 = 2.5V
\end{align*}
\]

Although the oxidation activity of the generated active groups SO\(_2\)\(^-\) and NO\(_3\)\(^-\) is not as good as that of ·OH E\(^0\) = 2.8 V, their oxidation properties are also relatively high. In addition, they are more selective than ·OH and may hinder the reaction of ·OH with p-CN to form intermediates like phenols. All these reasons led to the slight improvement of the degradation rate of p-CN.

The effect of TBA on p-CN degradation

TBA is an effective ·OH scavenger. The reaction rate between TBA and ·OH follows a second-order constant, which is thousands of times higher than that between TBA and ozone (Ma & Graham 1999). By adding TBA into the O\(_3\)/TiO\(_2\)/C system, the generation of free radicals and the role of ·OH in p-CN degradation could be investigated.

The results showed the addition of TBA had a great influence on the whole system. After adding a certain amount of TBA, the removal efficiency of p-CN in the ozone alone system and the catalytic system was less than 5% after 20 min. On the one hand, it is shown that ozone cannot effectively oxidize p-CN and ·OH should be the dominant active species for p-CN degradation. On the other hand, in the ozone alone system, p-CN also has a considerable degradation efficiency (Shen et al. 2008). It is possible that p-CN itself or its oxidation intermediates promote chain decomposition of ozone, producing more
hydroxyl radicals. The mesoporous TiO$_2$/C, as a catalyst, also promoted the formation of ·OH and accelerated the degradation of $p$-CNB.

**The performance of catalyst on $p$-CNB degradation**

Figure 6 shows the effect of TiO$_2$/C dosage on the degradation efficiency of $p$-CNB. When the dosage of catalyst was 50, 100, and 200 mg/L, the degradation efficiency of $p$-CNB reached 87.4%, 92.80% and 96% after 20 min reaction, respectively. Compared with the O$_3$ alone system, the degradation efficiency increased by 15.61%, 22.75% and 26.98%, respectively. This result shows that the degradation efficiency of $p$-CNB can be improved by increasing TiO$_2$/C dosage. The degradation of $p$-CNB was promoted due to the fact that the increase in catalyst dosage will help to increase the contact area for ozone and $p$-CNB, providing more surface hydroxyl groups and then promoting ozonolysis to produce more hydroxyl radicals. Besides, in the first few minutes, the degradation rate of $p$-CNB was faster and reached a higher degradation percentage of $p$-CNB in a short time, which was beneficial to the application of the catalyst in practical engineering. In order to investigate the sustaining catalytic ability of TiO$_2$/C, the $p$-CNB degradation by TiO$_2$/C catalytic ozonation was conducted for five cycles. The catalytic activity of TiO$_2$/C is still in good condition after recycling. When the catalyst was reused 5 times, the degradation efficiency just decreased 0.8%, as shown in Figure S1. That is to say, TiO$_2$/C still showed great catalytic performance after 5 cycles. Figure 7 describes the comparison of XRD patterns of TiO$_2$/C before and after the catalytic reaction. The almost unchanged crystal structure also indicates TiO$_2$/C is stable. As TiO$_2$/C has such excellent performance, it has a huge prospect for practical application.

**Mechanism of degradation of $p$-CNB**

In this study, the mechanism of $p$-CNB in the TiO$_2$/C/O$_3$ system was discussed by studying the decomposition of ozone, the adsorption of $p$-CNB by catalyst and detection of the hydroxyl radical, with a feasible scheme proposed as shown in Scheme S2. After the addition of $p$-CNB, the decomposition rate of ozone is significantly accelerated, and the pseudo first-order rate constant is increased by about 3.7–9.05 times (Figure S2). Since the reaction rate of $p$-CNB and O$_3$ is low, this is not caused by the reaction of $p$-CNB with O$_3$ (Shen et al. 2008). It should be caused by the decomposition products of $p$-CNB, such as phenol, hydrazine and carboxylic acid, which can react directly with ozone (Hoigné et al. 1996). In addition, adsorption is important for the removal of organic matter in the presence of solid catalysts (Beltrán et al. 2002; Yang et al. 2007). $p$-CNB can be adsorbed on the catalyst’s surface by electrostatic force, van der Waals force and its strong hydrophobic effect. However, the results show that only 8%-10% of $p$-CNB can be removed by the adsorption of TiO$_2$/C (Figure S3). At the same time, when the catalyst dosage is in the range of 50–200 mg/L, the ozone decomposition rate is independent of the catalyst dosage, which indicates that the active sites on the surface in this dosage range do not substantially affect the decomposition of O$_3$ in the system (Figure S4). In summary, it is speculated that
the degradation of $p$-CNB mainly occurs in the solution, and the decomposition of $p$-CNB is mainly due to the oxidation of ·OH. By investigating the effect of TBA on the catalytic ozonation system, it is possible to determine the formation of ·OH in the system and the contribution of ·OH to the degradation of $p$-CNB indirectly (Zhao et al. 2008). The experimental data shows that the addition of TBA inhibits the self-decomposition of ozone in the TiO$_2$/C/O$_3$ system, which may be due to the fact that $p$-CNB adsorbed on the surface of the catalyst occupies an active site that is capable of promoting ozone decomposition and reduces the ability of the catalyst to promote ozone decomposition. When excessive TBA is added, ·OH reacts completely with TBA, which reduces the amount of O$_3$ captured by ·OH, resulting in a decrease in the rate of O$_3$ decomposition. Carboxylic acids, ketones and phenolic organic compounds are the three main types of organic compounds produced during the ozonation of $p$-CNB (Shen et al. 2008). At the beginning of the reaction, phenols accumulate in a large amount. As the reaction proceeds, the amount of phenols gradually decreases, and small molecules such as ketones and carboxylic acids increase after the benzene ring of $p$-CNB is destroyed (Arora et al. 2012).

**CONCLUSION**

Mesoporous TiO$_2$/C has a good crystal form, disordered mesostructure and high specific surface areas. It can effectively catalyze ozone to generate hydroxyl radicals and then promote $p$-CNB degradation.

The dosage of ozone, the dosage of $p$-CNB, the dosage of the catalyst, the dosage of various inorganic anions, and the solution pH have different effects on the degradation of $p$-CNB. In the TiO$_2$/C/O$_3$ system, the degradation of $p$-CNB was mediated by hydroxyl radicals generated from both the O$_3$ activation by TiO$_2$/C and the autocatalytic decomposition of ozone by the products of $p$-CNB.

TiO$_2$/C also shows a good catalytic performance after 5 cycles with an unchanged structure. The good performance of TiO$_2$/C in these experiments shows the potential application value of this catalyst in the actual drinking water treatment for $p$-CNB removal.

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