Catalytic activity of aluminum silicate for ozonation of chloronitrobenzenes in aqueous solution


ABSTRACT

Chemical oxidation using ozone with appropriate catalysts offers an attractive option for removing inhibitory and toxic pollutants in micro-polluted water. This work investigated the catalytic ozonation of three chloronitrobenzenes (CNBs, i.e. p-CNB, o-CNB, and m-CNB) in the presence of a novel and efficient synthesized aluminum silicate catalyst. Experiments were carried out with focus on the degradation efficiency of CNBs at different reaction pH values, water matrices and repeated uses, as well as the possible catalytic mechanism. Regardless of the water matrix, the results showed that the catalytic ozonation had considerably higher degradation efficiency of CNBs than the single ozonation process at the same ozone dose. The change of pH had an obvious effect on the removal efficiency of CNBs, which suggested that the aluminum silicate catalyst was more appropriate for application in the neutral pH condition. Ozonation processes in the presence of the aluminum silicate were significantly influenced by tert-butyl alcohol, which confirmed that the aluminum silicate catalytic ozonation followed a hydroxyl radical-type mechanism.

Key words | aluminum silicate, catalytic ozonation, CNBs, single ozonation

INTRODUCTION

Advanced oxidation processes (AOPs) have been widely investigated in water treatment, since they are promising methods for the degradation of organic compounds (Acero & Von Gunten 2001; von Gunten 2003; Deborde & von Gunten 2008). AOPs are oxidation processes that generate reactive oxidizing agents such as hydroxyl radicals, which are more reactive than molecular O₃, and are highly effective in degrading organic pollutants in wastewater because of their rapid and non-selective reaction with nearby electron-rich organic compounds (von Gunten 2007; Lee & von Gunten 2010). Recently, heterogeneous catalytic ozonation has attracted increasing attention as an effective process, which combines ozone with the solid phase metal oxide to achieve the mineralization of target organics. Moreover, many inorganic materials have been successfully employed as the catalyst used in catalytic ozonation processes and researchers have found that the catalytic ozonation process remarkably enhances the degradation efficiency of inhibitory and toxic pollutants over the single ozonation process (Beltran et al. 2010; Xu et al. 2010; Pocostales et al. 2011; Wu et al. 2011).

Chloronitrobenzenes (CNBs), some important organic intermediates, are widely used in the production of dyes, pesticides, pharmaceuticals and rubber chemicals. Unfortunately, a large volume of wastewater contains high concentrations of p-CNB, o-CNB, and m-CNB incurred in the process of chlorobenzene nitrification, which is the key step for preparation of CNBs. CNBs in the wastewater have to be removed or decomposed before wastewater discharge because of their high toxicity and stability (Guo et al. 2005, 2009). As a result, removal of CNBs in water has drawn much attention from researchers in recent years (Shen et al. 2008; Liu et al. 2011a, b; Yuan et al. 2012). Within this context, catalytic ozonation of CNBs was studied using aluminum silicate as the catalyst, which was synthesized in the laboratory. This work presents experimental results with focus on CNBs degradation by the catalytic ozonation process. The effects of radical
scavengers, initial solution pH, and water matrix in the presence of the aluminum silicate are also discussed. In addition, the mechanism of catalyzed ozonation in the presence of aluminum silicate is preliminarily investigated.

MATERIALS AND METHODS

Materials and reagents

A stock solution of CNBs (100 mg/L) was prepared by dissolving three CNBs (99.5% purity, Chem Service, USA) in Milli-Q ultrapure water (UPW) (specific resistance ≥18 MΩ cm). Methanol of high performance liquid chromatography (HPLC) grade was purchased from Sigma Aldrich (USA). The other chemicals were reagent grade and used without further purification. Perchloric acid and sodium hydroxide were added in aqueous solution to control its pH value. All glassware used in the experiments was soaked in the H2SO4-K2Cr2O7 solution overnight, and then washed with tap water and deionized water four times, respectively.

Catalyst preparation

The aluminum silicate catalyst was synthesized by an alkali precipitation method. Al(NO3)3 was used as the aluminum source and Na2SiO3 as the silicon source. Briefly, 250 mL of 0.2 mol/L Na2SiO3 solution was slowly added into 250 mL of 0.15 mol/L Al(NO3)3 solution at 298 K under magnetic stirring. The pH of the suspension was adjusted to 8–8.5, and then the suspension was put into the oven to age for 24 h at 333 K. The product obtained was filtered and washed several times with UPW until the pH of the cleaning liquid remained constant. Finally, the obtained catalyst was dried at 338 K, ground, and was then ready to use.

Experimental procedure

Catalytic activity experiments were carried out in a 1.2 L flat-bottomed flask as the reactor vessel. As shown in Figure 1, the ozone was generated from pure oxygen by an ozone generator (CF-G-3-010g, Qingdao Guolin Ltd, China). After the desired concentration of gaseous ozone was introduced into the reactor which contained 1 L deionized water, the catalyst and CNBs stock solution were immediately dosed into the reactor. The magnetic stirrer was then used to mix the aqueous solution effectively. All experiments were operated at 293 K in a thermostatic water bath. The control experiments of single ozonation (without catalyst) were carried out under the same conditions. Samples were taken at specific time intervals (0, 1, 3, 5, 10, 15 min). The residual ozone was instantly quenched by 0.1 mL aqueous Na2SO3 solution.

Analytical method

The dissolved ozone concentration was measured by the indigo method (Bader & Hoigné 1981). The concentrations of CNBs were determined by HPLC (Agilent 1200, USA) with a UV-Vis detector. A reversed-phase 4.6 mm × 150 mm C18 Waters column was used at 308 K. Elution was detected at 275 nm, and carried out by pumping methanol and water (8:2 v/v) at a flow rate of 1.0 mL/min. Total organic carbon (TOC) was analyzed with a TOC analyzer (TOC-VCPH, Shimadzu, Japan).

The surface properties of the synthesized aluminum silicate were measured by Fourier transform infrared spectroscopy (FTIR) analysis using a Spectrum One Perkin Elmer Fourier transform infrared spectrum instrument (Japan) with a spectral range of 4,000–400 cm⁻¹. The surface area, pore size, and pore volume of the catalyst were measured on a Surface Area and Porosity Analyzer.
The surface properties of the catalyst are very important for the degradation of organic pollutants in heterogeneous catalytic ozonation (Xing et al. 2008). The FTIR spectrum was measured to investigate the structure and surface functional groups of the synthesized aluminum silicate. As shown in Figure 2, the peaks at 1,060 and 1,400 cm\(^{-1}\), represent the characteristic bands of the Si–O bond and the Al–O bond, respectively. The presence of water molecules was supported by the appearance of the bending mode at 1,640 cm\(^{-1}\) and the stretching mode at 3,430 cm\(^{-1}\). This surface hydroxylation may result in the surface hydroxyl groups formation on the surface of the catalyst, and these hydroxyl groups are favorable for the formation of ·OH that can oxidize organic pollutants unselectively (Qi et al. 2009a, b). Furthermore, physical properties of the aluminum silicate were evaluated using the Brunauer–Emmett–Teller (BET) method. As shown in Table 1, the BET surface area, pore volume and pore size of the catalyst were 60.99 m\(^2\)/g, 0.099 cm\(^3\)/g, and 6.41 nm, respectively.

### Catalysts characterization

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### Catalytic activity of the aluminum silicate

Different experiments were performed to investigate the degradation efficiency of CNBs, including single ozonation, catalytic ozonation, and adsorption on the aluminum silicate. As shown in Figure 3, the lowest CNBs degradation efficiency was observed with the adsorption on the aluminum silicate after 15 min treatment, and the removal efficiencies were only 4.7, 5.2 and 6.1% for p-CNBr, o-CNBr and m-CNBr, respectively. Compared with the single and catalytic ozonation processes, the contribution of adsorption to the degradation efficiency of the CNBs can be discounted. In the presence of ozone in the aqueous solution, the removal efficiencies increased significantly. It was obvious that the aluminum silicate catalyst could enhance the oxidation of CNBs. When also treated for 15 min, removal efficiencies above 94% for all CNBs could be achieved, typically higher than that of ozonation alone. These results suggested that the aluminum silicate catalyst had sufficient
catalytic activity and incorporated into the ozonation process very well.

Because of the significance of the mineralization of organic compounds, the removal of TOC was detected in the processes. As illustrated in Figure 4, 47.5% of the initial TOC was degraded in the presence of the catalyst compared with 30.6% of TOC removed by the single ozonation process, indicating that catalytic ozonation was more effective than the single ozonation process in removing TOC from water containing CNBs. It should be noticed that the removal of TOC was always lower than the disappearance of CNBs, suggesting that the CNBs had been mineralized partly into carbon dioxide and water, and the by-products were formed via the degradation of the initial compounds in the two processes.

Scavenging effect of tert-butyl alcohol (TBA) on catalyzed ozonation

The low reaction rate constants reported in the literature for the ozonation of CNBs explain why such compounds could not be removed by ozone (Shen et al. 2008). Therefore, CNBs in aqueous solution may be oxidized by some active species produced during the catalyzed ozonation process in the presence of the aluminum silicate. In reports about metal oxides catalyzed ozonation, ·OH was the main activity species during the catalytic ozonation process (Kasprzyk-Hordern et al. 2003; Ma et al. 2005; Qi et al. 2010; Liu et al. 2011, b; Yuan et al. 2012). To investigate the active species generated during the aluminum silicate catalyzed ozonation, the aluminum silicate catalytic ozonation experiments were carried out in the presence of 1 g/L tert-butyl alcohol (TBA) as an effective scavenger. The results in Figure 5 show that the ozonation of CNBs catalyzed by the aluminum silicate was strongly inhibited in the presence of TBA. For example, after oxidation for 15 min, the highest CNBs removal rate in the presence of TBA was about 36%, whereas the lowest one without TBA was above 94%. This experimental observation indicated that ·OH was the main activity species during the catalytic ozonation process.

Effect of initial solution pH on catalyzed ozonation

As is well known, the pH value of an aqueous solution is an important factor in the generation rate of hydroxyl radicals, the utilization efficiency of ozone, the surface properties of the catalyst, and the charge of ionic or ionizable organic molecules (Bing et al. 2012). In the case of heterogeneous catalyzed ozonation, oxidation at different solution pH values follows different reaction mechanisms. It is necessary to study the effect of pH on heterogeneous catalytic ozonation to further understand the mechanism of aluminum silicate ozonation. Therefore, a series of experiments was carried out.
out under different aqueous pH conditions. Figure 6 illustrates the effect of initial solution pH on o-CNB both in catalytic ozonation and single ozonation. It can be seen that o-CNB removal increased with initial pH from 3 to 10 in the single ozonation process; in the case of the aluminum silicate catalyzed ozonation, the activity of the catalyst changed greatly in the same solution pH range. In general, the catalytic ozonation process was more effective than the single ozonation process, especially when the solution pH was 7.32, when the catalyst showed the maximum activity.

Both Fei Qi et al. (Qi et al. 2009a, b) and Tao Zhang et al. (Zhang et al. 2008) reported that surface hydroxyl groups would be mostly zero-charged near the point of zero charge pH (pHpzc) of oxides. The zero-charged surfaces of catalysts were more active than the protonated or deprotonated in promoting hydroxyl radicals generation. Therefore, given that the pHpzc of aluminum silicate was 7.25, the result confirmed that the catalyst exhibited the maximum catalytic activity when the solution pH was close to its pHpzc, which indicated that the aluminum silicate catalyst was more suitable for application in neutral pH conditions.

Degradation of CNBs in natural water

There are many matrices in natural water including natural organic matter (NOM), alkalinity and rigidity. Both in the single ozonation and catalytic ozonation, NOM and alkalinity are the main inhibiting factors as inhibitors of ·OH (Qi et al. 2009a, b). Therefore, to evaluate the catalytic ozonation of CNBs under actual treatment conditions, experiments were carried out with natural water samples from MPW (Mopanshan) and SHW (Songhua). The water quality parameters of MPW and SHW are shown in Table 2. Because of the similar pattern, only the result of o-CNB is given (Figure 7). As shown in Figure 7, the removal efficiencies of the single ozonation and catalytic ozonation of the two natural water samples were less than those in the UPW, which suggested that the catalytic activity of the aluminum silicate in the catalytic ozonation process was inhibited. At the same time, both in the single ozonation and catalytic ozonation, the removal efficiencies of o-CNB in SHW were lower than those in MPW. All the results were due to the high ·OH scavenging capacity of the water matrix, such as NOM and alkalinity, and the higher values of these water quality parameters in SHW resulted in the stronger inhibiting effect. Nevertheless, it was obvious that

Table 2 | Water quality parameters of the natural water samples

<table>
<thead>
<tr>
<th>Water sample</th>
<th>DOC (mg/L)</th>
<th>UV254 (cm⁻¹)</th>
<th>Alkalinity (mg/L)</th>
<th>Solution pH</th>
<th>Turbidity (NTU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPW</td>
<td>3.512</td>
<td>0.041</td>
<td>90.02</td>
<td>7.32</td>
<td>0.11</td>
</tr>
<tr>
<td>SHW</td>
<td>5.176</td>
<td>0.108</td>
<td>117.32</td>
<td>7.27</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Note: DOC – dissolved organic carbon.

Figure 7 | Efficiency of catalytic ozonation of o-CNB in natural water (o-CNBₐ₀ = 100 μg/L, [O₃]₀ = 0.7 mg/L, T = 293 K, the dose of catalyst was 150 mg/L). UPW – ultrapure water, MPW – Mopanshan water, SHW – Songhua water.
the catalytic ozonation still improved the degradation efficiency of p-CNB in the natural waters.

**Stability of aluminum silicate in catalytic ozonation**

In order to investigate the stability of the aluminum silicate, the catalyst from the previous study was reused in three successive ozonation experiments. As shown in Table 3, the degradation efficiency of CNBs slightly fluctuated from 93 to 98% and remained stable after being reused three times, which suggested that the aluminum silicate possessed an excellent activity and recyclability in the reaction. Further studies will focus on the ion release, the surface structure and the real life-time in natural water from a practical point of view.

### CONCLUSION

This work investigated the impact of the synthetic aluminum silicate catalyzed ozonation on three CNBs in aqueous solution. Results indicated that catalytic ozonation can improve the degradation efficiency of CNBs relative to single ozonation in different types of water matrix. Moreover, the aluminum silicate was more suitable for application in neutral pH conditions, and after being reused three times the catalyst still maintained a good catalytic activity. Therefore, it can be seen that aluminum silicate is a useful and promising catalyst for heterogeneous catalytic ozonation in water treatment.

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