

Enhanced ozonation of dichloroacetic acid in aqueous solution using nanometer ZnO powders

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Abstract

Nanometer zinc oxide (ZnO) powders were used as a catalyst to enhance the ozonation for the degradation of dichloroacetic acid (DCAA) in aqueous solution. The batch experiments were carried out to investigate the effects of key factors such as catalyst dosage, ozone dosage, solution pH and *tert*-butyl alcohol (*t*-BuOH) on the degradation efficiency of DCAA. Density functional theory (DFT) was adopted to explore the mechanism of generating hydroxyl radical ($\cdot\text{OH}$) on the ZnO surface. The results showed that adsorption and ozonation processes were not effective for DCAA removal, and the addition of ZnO catalyst improved the degradation efficiency of DCAA during ozonation, which caused an increase of 22.8% for DCAA decomposition compared to the case of ozonation alone after 25 min. Under the same experimental conditions, the DCAA decomposition was enhanced by increasing catalyst dosage from 100 to 500 mg/L and ozone dosage from 0.83 to 3.2 mg/L. The catalytic ozonation process is more pronounced than the ozonation process alone at pH 3.93, 6.88, and 10. With increasing the concentration of *t*-BuOH from 10 to 200 mg/L, the degradation of DCAA was significantly inhibited in the process of catalytic ozonation, indicating that ZnO catalytic ozonation followed $\cdot\text{OH}$ reaction mechanism. Based on the experimental results and DFT analysis, it is deduced that the generation of $\cdot\text{OH}$ on the ZnO surface is ascribed to the adsorption of molecule ozone followed by the interaction of adsorbed ozone with active sites of the catalyst surface. It is also concluded that ZnO may be an effective catalyst for DCAA removal, which could promote the formation of $\cdot\text{OH}$ derived from the catalytic decomposition of ozone.

Key words: dichloroacetic acid; catalytic ozonation; density functional theory; hydroxyl radical

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Introduction

Disinfection byproducts (DBPs) formed by the interaction of chemical disinfectants with natural organic matter have become a worldwide environmental problem due to potential threat to human health. Among all of DBPs, trihalomethanes (THMs) and haloacetic acids (HAAs) are the most common DBPs found in drinking water. It has been known that THMs and HAAs are considered as potentially toxic, carcinogenic, and/or mutagenic to humans if ingested over extended years, or have possible adverse reproductive effects during pregnancy (Guo and Chen, 2009; Kallen and Robert, 2000). Drinking water safety has already become one of the most important tasks of water pollution treatment in the 21st century. Considering the potential health risks to human being, these DBPs in drinking water must be removed or decomposed before entering the distribution system. However, the traditional drinking water treatment processes can not remove these DBPs efficiently (Wobma et al., 2000). Thus, it is neces-

sary to develop efficient processes for these DBPs removal.

As a kind of chemical oxidation method, ozonation has proved to be an attractive and increasingly important way for the degradation of organic pollutants in aqueous solution. Unfortunately, it can not degrade some organic acids of small molecular effectively, such as acetic acid, oxalic acid and glyoxalic acid, and may produce more toxic and resistant byproducts (He et al., 2008; Ping et al., 2002). Therefore, there is a need to develop new alternative methods based on the oxidation of DBPs removal from drinking water. Consequently, various advanced oxidation processes (AOPs) for the purpose of generating hydroxyl radical ($\cdot\text{OH}$) have been investigated as potential method for the degradation or decreasing formation of DBPs, such as UV/O₃ (Chin and Berube, 2005), UV/H₂O₂ (Wang et al., 2006), O₃/H₂O₂ and O₃/H₂O₂/UV (Wang et al., 2009b), Fenton and UV/Fenton-like processes (Lim et al., 2007), photocatalytic oxidation (Liu et al., 2008), ultrasonic irradiation (Zhao et al., 2009a).

Catalytic ozonation, a promising AOP of introducing homogeneous or heterogeneous catalyst to ozonation, can increase ozonation efficiency and ozone utilization degree.

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Especially, heterogeneous catalytic ozonation processes have received increasing attention recently due to the potentially higher effectiveness in the degradation and mineralization of refractory organic pollutants and easier recovery processing (Zhao et al., 2008). At the same time, the reaction mechanisms of heterogeneous catalytic ozonation have also been investigated (Ernst et al., 2004; Valdes et al., 2008; Zhao et al., 2009b, 2009c). In these cases, two mechanisms are proposed as follows (Trapido et al., 2005). In the first mechanism, the organic compound adsorbed on the catalyst is oxidized by ozone or $\cdot\text{OH}$ to generate oxidation byproducts. The final byproducts desorb in solution, and then are oxidized by ozone or $\cdot\text{OH}$. In the second mechanism, the catalyst reacts with both ozone and adsorbed organics. After ozone oxidizes the reduced catalyst, organic compound adsorbed on oxidized catalyst will be oxidized by an electron-transfer reaction to the organic radical species, which are easily desorbed from catalyst and subsequently oxidized by $\cdot\text{OH}$ or O_3 either in bulk solution or, more likely, into the thickness of electric double layer. However, catalytic ozonation is still under investigation. There are many catalysis phenomena that cannot be fully explained. In particular, the adsorption of molecule ozone on the metal oxide surface is the most controversial (Trapido et al., 2005). Therefore, further investigation is needed to explore the interaction between ozone and metal oxide catalyst surface in the process of heterogeneous catalytic ozonation.

In the present article, nanometer ZnO was employed as a heterogeneous catalyst for catalytic ozonation degradation of dichloroacetic acid (DCAA) in aqueous solution, which is non-toxic, insoluble, and cheaper transition metal oxide widely used in various processes (Eslami et al., 2008; Jung and Choi, 2006; Wang et al., 2009a). DCAA was selected as the model pollutant in the degradation experiments, because of its greatest health risk to human being compared to monochloroacetic acid (MCAA) and trichloroacetic acid (TCAA) (Guo and Chen, 2009). The objective of this study is to estimate the influencing factors on the degradation efficiency of DCAA in aqueous solution by ZnO catalytic ozonation, including catalyst dosage, ozone dosage, initial solution pH and *tert*-butyl alcohol, and to investigate the mechanism of the decomposition of molecule ozone and related reactions on the surface of ZnO catalyst using density functional theory (DFT) calculations.

1 Materials and methods

1.1 Materials

Methyl *tert*-butyl ether (MTBE) and methanol of HPLC grade were obtained from Dikma (USA). Dichloroacetic acid (DCAA) (99%) and 1,2-dibromopropane (> 99%) were purchased from Acros Organics (USA). The concentration of DCAA stock solutions was 100 mg/L. All other chemical reagents were analytical grade and were used without further purification. ZnO was supplied from Aldrich (USA). According to the Scherrer equation (Wang et al., 2008), its size was about 90 nm, and its surface area

(11 m²/g) was determined by a BET surface area analyzer (ASAP 2020M, Micromeritics, USA). All the glass vessels used in the experiments were soaked in the solution of $\text{H}_2\text{SO}_4\text{-K}_2\text{Cr}_2\text{O}_7$ over night, and then washed several times with tap water and distilled water.

1.2 Experimental procedures

Experiments were performed in a laboratory batch reactor, which consisted of a glass flat-bottomed flask with the inside diameter of 45 cm and the volume of 1.2 L. All experiments were performed at $(20 \pm 1)^\circ\text{C}$ using a thermal-collecting magnetic stirring apparatus (DF-1, Jintan Ronghua Instrument Manufacture Co., Ltd., China). Ozone was generated from dried oxygen (99.999%, Harbin Gas Co., Ltd., China) using a laboratory ozone generator (DHX-SS-1G, Harbin Jiu Jiu Electrochemistry Engineering Ltd., China) and subsequently fed into Milli-Q water (Millipore SAS, Molsheim, France) through a porous silicon diffuser located at the bottom of the reactor until aqueous ozone reached a steady concentration. Then, the DCAA stock solution and the catalyst were quickly added into the ozone bearing water. The reactor was immediately sealed and the catalytic ozonation experiments were initiated with magnetic stirring. The initial aqueous ozone concentration can be controlled in terms of changing the electric current of the ozone generator and the time of introducing ozone. The residual ozone in the off-gas was adsorbed by 2% KI solution. In order to keep the solution pH constant during the reactions, phosphate buffer of 1.0 mmol/L was adopted in the experiments. The initial concentration of DCAA was 0.1 mg/L. Samples (50 mL) were withdrawn at different intervals to determine the residual concentration of DCAA. The oxidation reaction was quenched by the addition of a small amount of 0.1 mol/L sodium thiosulfate. Before gas chromatography (GC) analysis, suspensions were filtered with 0.45 μm microfilters to collect the filtrate.

1.3 Analytical methods

The aqueous ozone concentration was measured by the indigo method (Hoigne and Bader, 1981). Analysis of DCAA in the sample was carried out by a GC with an electron capture detector (6890D, Agilent, USA) and a capillary column (Hewlett Packard HP-5, 30.3 m \times 320 μm \times 0.25 μm) according to U.S. EPA Method 552.3 (Domino et al., 2003).

1.4 Calculation details

All the calculations were performed using density functional theory (DFT) calculation with the generalized gradient approximation (GGA) with the Perdew, Burke and Ernzerhof (PBE) exchange correlation (Kresse and Furthmuller, 1996; Kresse and Hafner, 1993). Molecular orbitals were expanded into a double-numerical basis with polarization functions. All electron basis sets were used for O atoms, and effective core potentials were used for Zn atoms, that is, the outer electrons ($3d^{10}4s^1$) for Zn atoms were treated as valence electrons and the remaining electrons were replaced by effective core potentials.

A fermi smearing of 0.005 Hartree (Ha) and a cutoff energy of 5.0 were used to improve the computational performance. Throughout calculations the spinpolarized approach was used. The Brillouin zone integrations were performed using a $4 \times 4 \times 1$ Monkhorst-Pack grid. The convergence criterion of optimal geometry based on the energy, force and displacement convergence, were 1×10^{-5} Ha, 2×10^{-3} Ha/Å and 5×10^{-3} Å, respectively. In this study, our investigation focuses on five layers ZnO electronic structure according to the previous successful simulation to multilayer slabs (Nakagawa et al., 2006). Among the different surfaces of ZnO crystal, cleavage of ZnO along the (100) plane yields a nonpolar and rather stable surface. Hence, ZnO (100) crystal surface ($S_{\text{ZnO}(100)}$) was built to discuss the catalytic activities for ZnO-catalyzed ozonation. The $S_{\text{ZnO}(100)}$ slabs were separated from their periodic images normal to the surface by a vacuum gap (15 Å), which was sufficiently large to eliminate slab-slab interactions. Periodic slabs based on the (2×2) surface unit cell were used in our calculations as a good compromise between the desire to reduce defect-defect interaction and computational limitations.

2 Results and discussion

2.1 Comparison of different processes in the degradation of DCAA

The degradation efficiencies of DCAA were investigated in the different processes, including ozonation alone, ozonation/ZnO and adsorption of ZnO, under the same experimental conditions.

As can be seen in Fig. 1, the degradation efficiencies of DCAA in aqueous solution all raise with the increase of reaction time in the processes of ozonation alone and ozonation/ZnO. The highest degradation efficiency of DCAA is obtained for combined ZnO and ozone system. The introduction of ZnO to ozonation can cause 55.2% DCAA conversion, an increment of 22.8% compared to the case of ozonation alone, indicating that the presence of

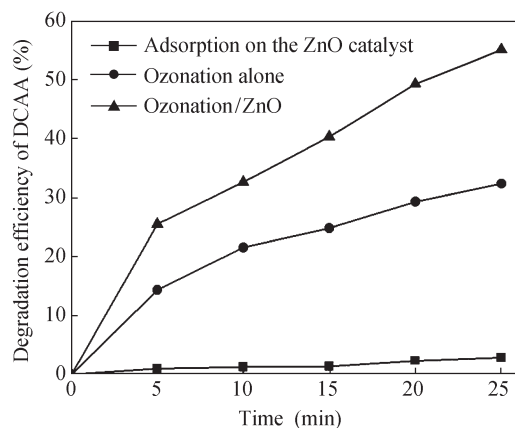


Fig. 1 Comparison of the degradation efficiency of DCAA in the different processes. Conditions: temperature $(20 \pm 1)^\circ\text{C}$; initial pH 6.88; initial concentration of DCAA 100 $\mu\text{g/L}$; initial ozone concentration 1.96 mg/L; catalyst dosage 100 mg/L.

ZnO can significantly enhance the degradation efficiency of DCAA. In order to assess the effect of adsorption on the degradation efficiency of DCAA, an adsorption experiment in the absence of ozone but with ZnO was performed under the same experimental conditions. It can be seen that only 2.9% of DCAA is removed by adsorption on the surface of ZnO within 25 min, indicating that the adsorption of DCAA is too little to make a significant contribution to the degradation efficiency of DCAA. Therefore, the influence of adsorption on DCAA elimination can be neglected in comparison to catalytic ozonation.

It is well known that ozone may either react directly with organic compounds, or indirectly generate $\cdot\text{OH}$ to dominate subsequent oxidation reactions. In the first case, ozone, one of the most powerful oxidants, favorably attacks the functional groups with high electron density due to the resonance structures of molecular ozone. Thus, DCAA is hardly oxidized by ozone alone, due to the electron-withdrawing properties of COO^- and chlorine atom. In the second case, the decomposition of ozone produces $\cdot\text{OH}$ via a chain reaction, and the oxidizing potential of $\cdot\text{OH}$ is much higher than that of molecular ozone, which is unselective and more reactive towards organic compounds. The reaction rate of $\cdot\text{OH}$ with organic molecules is in the range of 10^6 to 10^9 L/(mol·sec) (Andreozzi et al., 1999). The reaction rate constant of DCAA with $\cdot\text{OH}$ is 3.9×10^9 L/(mol·sec), while the reaction rate constant of DCAA with ozone alone is only 0.09 L/(mol·sec) (Qin et al., 2009). Therefore, it is deduced that the degradation of DCAA is attributed to $\cdot\text{OH}$ oxidation in the processes of ozonation alone and catalytic ozonation.

2.2 Effect of the amount of catalyst and ozone

In the heterogeneous catalytic ozonation process, the catalyst is introduced to ozonation and initiates the decomposition of ozone, resulting in the generation of $\cdot\text{OH}$. Thus, the catalyst dosage plays an important role in the catalytic ozonation process, which will influence the amount of $\cdot\text{OH}$ formation. In addition, in order to make effective use of the catalyst in the practical application, it seems reasonable to explore the effect of catalyst dosage on the degradation efficiency. The influence of catalyst dosage on the degradation of DCAA has been investigated in catalytic ozonation process via changing the applied catalyst mass in the range of 100–500 mg/L under the same experimental conditions. It can be seen that catalyst dosage exerts a positive influence on DCAA conversion in catalytic ozonation process. Many researchers have also reported that an increase in the catalyst concentration is benefit for the degradation of organic pollutants (Jung and Choi, 2006; Muruganandham and Wu, 2008). As shown in Fig. 2a, the degradation efficiency of DCAA increases positively by 14.4% when the amount of ZnO increases from 100 to 500 mg/L in catalyzed ozonation process. It is suggested that the amount increase of catalyst enhances the heterogeneous catalytic surface, and then provides more active sites for ozone and DCAA, leading to an acceleration of $\cdot\text{OH}$ initiation which improves the degradation efficiency of DCAA. Therefore, the increase

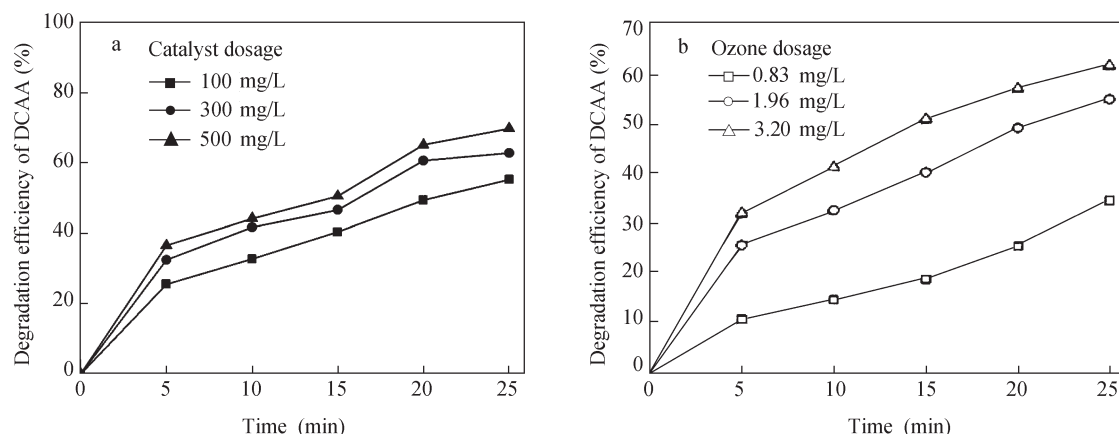


Fig. 2 Degradation efficiency of DCAA with different catalyst mass (a) and different ozone dosages (b). Conditions: temperature (20 ± 1)°C; initial pH: 6.88; initial concentration of DCAA 100 $\mu\text{g/L}$.

of ZnO amount from 100 to 500 mg/L yields an increase in the degradation efficiencies of DCAA in the heterogeneous catalytic ozonation.

The purpose of catalytic ozonation is to accelerate the decomposition of ozone for generating more oxidation potential species, such as $\cdot\text{OH}$. Therefore, ozone dosage is also an important factor which influences the amount and rate of $\cdot\text{OH}$ production. The ozonation experiments have been carried out in the presence of ZnO with the aim to determinate the effect of ozone dosage ranging from 0.83 to 3.2 mg/L on the degradation efficiency of DCAA. According to Fig. 2b, when 0.83 mg/L ozone is applied in the catalytic ozonation process, 34.8% of DCAA removal can be observed in 25 min. However, when the ozone dosage increases from 0.83 to 3.2 mg/L, the degradation efficiency of DCAA in catalytic ozonation is raised up to 62%, showing that the increase of ozone dosage also has a positive effect on the decomposition of DCAA. It may be related to more ozone adsorbed on the surface of ZnO catalyst. The radical chain reaction is accelerated on the catalyst surface, leading to the generation of more $\cdot\text{OH}$.

2.3 Effect of pH

The pH value of solution is an important parameter in the processes of ozonation alone and catalytic ozonation, which can affect the surface properties of catalyst, the dissociation of pollutants, and the generation of free radicals. Therefore, it is significant to find out the influence of pH on the degradation efficiency of DCAA in the ZnO catalytic ozonation. The effects of pH on the degradation of DCAA are shown in Fig. 3. It is clear that both ozonation alone and catalytic ozonation processes are pH sensitive for DCAA removal. As indicated, the DCAA oxidation by ozonation alone is very slow under pH 3.93, and only 12.7% of DCAA removal is observed after 25 min ozonation. The degradation efficiency of DCAA increases with the raising pH value, due to the contribution of increasing $\cdot\text{OH}$ to the oxidation. DCAA conversions of 32.4% and 71.5% are obtained at initial pH 6.88 and pH 10 after 25 min ozonation, respectively.

Comparing ZnO catalytic ozonation with ozonation

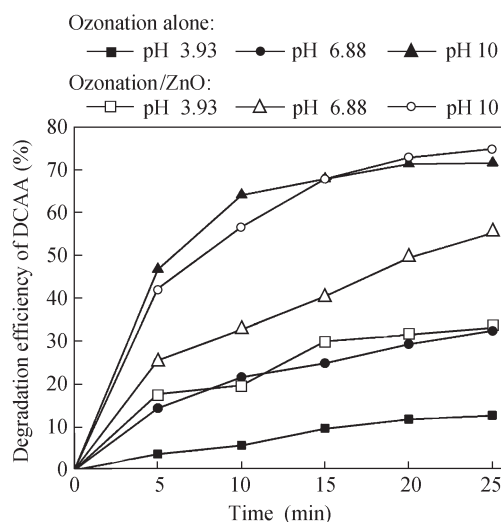
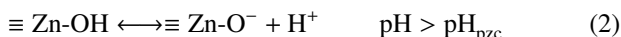


Fig. 3 Degradation efficiency of DCAA under different pH values. Conditions: temperature (20 ± 1)°C; initial concentration of DCAA 100 $\mu\text{g/L}$; initial ozone concentration 1.96 mg/L; catalyst dosage: 100 mg/L.

alone, the presence of ZnO catalyst in the ozonation system enhances the degradation of DCAA for all the pH values studied, meaning that ZnO as the catalyst is active towards the oxidation removal of DCAA under acidic and basic conditions. It also can be found that higher pH value favors the degradation of DCAA during the catalytic ozonation, which is similar to that during the ozonation alone. 33% and 55.2% of DCAA removals are obtained in catalytic ozonation at pH 3.93 and pH 6.88, respectively, and 74.8% of DCAA conversion is observed after only 25 min of catalytic ozonation at initial pH 10 with ZnO catalyst. These results show that the presence of ZnO catalyst accelerates the decomposition of aqueous ozone into $\cdot\text{OH}$ more easily while the solution becomes neutral or basic rather than acid circumstances. Hence, more DCAA can be oxidized in a solution with higher pH value, due to higher concentration of $\cdot\text{OH}$ than acid solution.

In addition, the pH value of the solution will influence the charge properties of catalyst surface depending on the ability of the surface hydroxyl groups to dissociate or to be

protonated.



Since the point of zero charge (PZC) of nano-sized ZnO powder is about pH 9.2 (Jung and Choi, 2006), below this pH_{pzc} , the surface of ZnO catalyst is positively charged. With the increase of pH in aqueous solution, the number of the positively charged site on the ZnO surface is reduced gradually and uncharged ZnO surface will be predominant. Then, when solution pH is higher than the pH_{pzc} of ZnO, the surface hydroxyl groups on ZnO are negatively charged, where ozone exhibits a higher reactivity than a positively charged or uncharged surface due to its electrophilic characteristics (Jung and Choi, 2006). Additionally, initial pH values in all experiments are higher than the $\text{p}K_{\text{a}}$ of DCAA ($\text{p}K_{\text{a}} = 1.29$). Therefore, DCAA molecules exist mainly as anionic forms (DCAA^-) under experimental conditions. In this way, both molecule ozone and DCAA anions will be simultaneously adsorbed on the surface of catalysts, and ozone molecules would react with the active sites of the catalyst to generate $\cdot\text{OH}$. Subsequently, $\cdot\text{OH}$ produced by the interaction of ozone with catalyst, at the solid-liquid interface, will be released into the aqueous phase. Adjacent $\cdot\text{OH}$ will oxidize the adsorbed DCAA anions to give the oxidation by-products, and then the oxidation byproducts will desorbed on the catalyst surface into the solution. Thereafter, the desorbed byproducts and the part of DCAA anions will be further oxidized in the bulk of aqueous phase by ozone or $\cdot\text{OH}$. Considering that the adsorption capacity of ZnO catalyst used in the experiments is negligible (Fig. 1), it is presumed that the removal of DCAA mainly occurs in the aqueous bulk, where DCAA as ionic forms are oxidized by $\cdot\text{OH}$.

2.4 Effect of *tert*-butyl alcohol

Ozone may either directly oxidize organic pollutants in water via selective reactions, or decompose to generate unselective and more reactive $\cdot\text{OH}$ via a chain reaction mechanism for subsequent oxidation reactions (Qu et al., 2004). Various pollutants are degraded based on $\cdot\text{OH}$ mechanism during heterogeneous catalytic ozonation processes (He et al., 2008; Valdes et al., 2008; Zhao et al., 2008). However, the concentration of $\cdot\text{OH}$ generated by the decomposition of ozone could not be determined instantly. The way ZnO nanoparticles act in the radical chain reaction can not be directly figured out. *tert*-butyl alcohol (*t*-BuOH), which has a reaction rate constant of $6 \times 10^8 \text{ L}/(\text{mol}\cdot\text{sec})$ with $\cdot\text{OH}$ and only $3 \times 10^{-3} \text{ L}/(\text{mol}\cdot\text{sec})$ with ozone (Yang et al., 2009), can terminate the radical chain reactions by forming secondary inert intermediates with the produced $\cdot\text{OH}$. Hence, *t*-BuOH is usually selected as the scavenger for a radical chain reaction. The influence of *t*-BuOH on the degradation efficiency of DCAA has been evaluated in the ZnO catalytic ozonation process.

As can be seen in Fig. 4, when 10 and 20 mg/L *t*-BuOH are added, there are reductions of 27.5% and 38.1% for the degradation efficiency of DCAA as compared to the

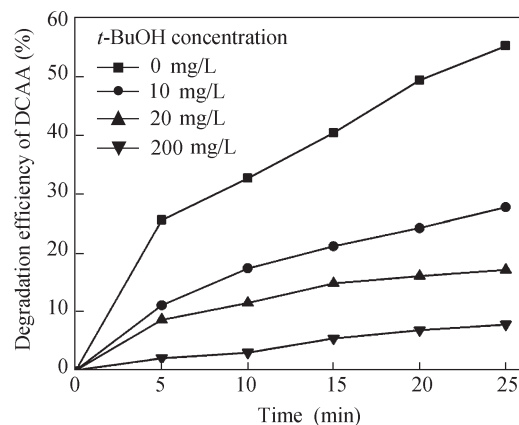


Fig. 4 Effect of *t*-BuOH on the degradation of DCAA. Conditions: temperature $(20 \pm 1)^\circ\text{C}$; initial pH 6.88; initial concentration of DCAA $100 \mu\text{g/L}$; initial ozone concentration 1.96 mg/L ; catalyst dosage 100 mg/L .

absence of *t*-BuOH, respectively. It is clear that the presence of *t*-BuOH significantly decreases the degradation efficiency of DCAA in ZnO catalytic ozonation, which are consistent with the free radical characteristics. However, *t*-BuOH concentrations mentioned above are not enough to inhibit ozone decomposition. When the concentration of *t*-BuOH increases from 20 to 200 mg/L, the degradation efficiency of DCAA is notably decreased and only 7.8% of DCAA removal can be observed in 25 min, showing that the degradation of DCAA by ozonation in the presence of ZnO follows the $\cdot\text{OH}$ reaction mechanism. Few DCAA removed from water can be ascribed to the direct oxidation by ozone and the adsorption effect of the catalyst. On the basis of experimental results, it can be found that the additions of different concentrations of *t*-BuOH have obviously negative influence on the catalytic degradation of DCAA, indicating that *t*-BuOH traps competitively and consumes rapidly $\cdot\text{OH}$ in aqueous solution, which is the main drawback of all oxidative degradation processes based on $\cdot\text{OH}$ reactions. The results also suggest that the removal of DCAA is primarily contributed to $\cdot\text{OH}$ oxidation in ZnO catalytic ozonation process. In order to investigate the generating mechanism of $\cdot\text{OH}$ on the catalyst surface, further fundamental study was carried out using DFT calculations in the following section.

2.5 Mechanism of generation of $\cdot\text{OH}$ on ZnO

According to the above experimental data, it is supposed that $\cdot\text{OH}$ in solution promotes the oxidation degradation of DCAA. Here, fundamental study was performed using DFT calculations to detect the mechanism of generation of $\cdot\text{OH}$ on $S_{\text{ZnO}(100)}$.

The catalytic ozonation is closely related to the adsorption of ozone on the surface of catalyst. As a first step toward better understanding the ozone adsorption on $S_{\text{ZnO}(100)}$, atom-bridge site adsorption and molecular-bridge site adsorption were investigated in our DFT calculations. After geometry optimization, the results showed that atom-bridge site adsorption configurations are more stable than the molecular-bridge site adsorption configurations. After the adsorption of molecule ozone

on the $S_{ZnO(100)}$, strong interaction happens between the molecule ozone and the $S_{ZnO(100)}$. According to the analysis of Mulliken charge population, 0.396 electron transfers from the surface to the molecule ozone, which leads to the generation of $O_3^{0.396-}$, corresponding to the super oxide radical species reported previously (Zhao et al., 2009b). The two bond lengths for O1–O2 and O2–O3 are 1.517 Å and 1.246 Å, respectively, and the distances for Zn1–O1 and Zn2–O1 are 2.079 Å and 2.105 Å, respectively. A one-step reaction mechanism can be seen for both the generation of the super oxide radical species on $S_{ZnO(100)}$ from the viewpoint of electronic property and geometry structure analysis. The generation of super oxide radical species is included in $\cdot OH$ generation mechanisms as effective promoter of radical chain reactions (Wohlers et al., 2009). Ozone produces super oxide radical species as intermediates during the decomposition in liquid phase. It is suggested that the $S_{ZnO(100)}$ show good catalytic activity to easily accelerate this initiation step. The overlap between O1 and O2 is smaller than that of O2–O3, and O1 possesses more Mulliken charge, which implies that O1 is more active to react with H^+ than the two other oxygen atoms (O2 and O3). While H^+ interacts to O1, the O1–O2 bond breaks with a strengthening occurred to the O2–O3 bond, leading to the generation of $\cdot OH$ and a free oxygen molecule. Then the super oxide radical species reacts with H^+ to generate a $\cdot OH$ through a one-step reaction mechanism. $\cdot OH$, which has more powerful oxidizing power than ozone and reacts with organics more rapidly, can easily generate on $S_{ZnO(100)}$, favoring the chain reaction of catalytic ozonation.

Figure 5 schematically summarizes the ozone decomposition and $\cdot OH$ production on the surface of ZnO. Theoretical studies show that a stronger interaction between ozone and the catalytic particle is observed, according to the adsorption analysis of ozone on the surface of catalyst. When ozone is adsorbed on the surface of ZnO, strong

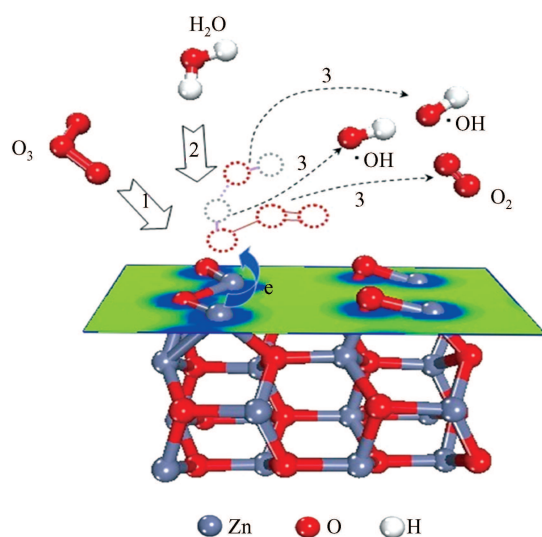


Fig. 5 Schematic diagram for ozone decomposition and the $\cdot OH$ produced on the surface of the ZnO catalyst. 1: adsorption of ozone on $S_{ZnO(100)}$; 2: interaction of water with super oxide radical species; 3: production of $\cdot OH$ and O_2 .

electronic interaction happens between the molecule ozone and the surface. The adsorbed ozone molecule reacts with the hydrogen cation, which leads to the molecule ozone decomposition and the generation of $\cdot OH$. Based on the analysis of theoretical calculation data, the strong electronic interaction between the surface and the adsorbed molecule will favor the decomposition of molecule ozone and the production of $\cdot OH$ in the present case, promoting the catalytic ozonation for the degradation of organic pollutants based on a radical reaction mechanism.

3 Conclusions

ZnO as catalyst in water significantly improved the ozonation removal of DCAA compared with ozonation alone. The degradation efficiency of DCAA increased with the increasing pH of solution, catalyst dosage and ozone dosage. The presence of *t*-BuOH had a negative effect on catalytic ozonation of DCAA. These experimental results confirmed that the degradation of DCAA by ZnO catalytic ozonation follows a radical-type mechanism. The DFT calculation results further verified the decomposition of the adsorbed ozone on catalyst surface and the enhancement of generation of $\cdot OH$ responsible for high catalytic activity of ZnO, leading to the increase of degradation efficiency of the model pollutant DCAA.

Acknowledgments

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