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Chapter

Catalytic Ozone Oxidation of Petrochemical Secondary Effluent: Mechanism, Application and Future Development

Yu Tan, Liya Fu, Changyong Wu, Yanan Li, Xiumei Sun and Yuexi Zhou

Abstract

Petrochemical secondary effluent contains toxic and refractory organic compounds, which are difficult to be further treated by traditional biological process. In China, most of the advanced treatment units have been built recently by catalytic ozone oxidation process to achieve the high-quality effluent. In this chapter, the mechanism and reaction process of catalytic ozone oxidation of petrochemical secondary effluent will be introduced in detail. With the operation of the catalytic ozone oxidation tank, a series of problems which are not taken into account at the beginning of the design have arisen. The chapter will talk about the problems concerning the biological flocs, colloidal macromolecule organic compounds, ozone mass transfer, and catalysts based on practical applications. In the last part of the chapter, the development trends of catalytic ozone oxidation of petrochemical secondary effluent will also be discussed.

Keywords: ozone, petrochemical wastewater, reaction mechanism, biological flocs, trends

1. Introduction

As an important part of the chemical industry, the petrochemical industry is one of the pillar industries in China and has a large proportion in the national economy. According to China Industrial Research Network, the total output value of China's petrochemical industry in 2014 has exceeded 13 trillion CNY, ranking second in the world. In 2016, the total discharge of petrochemical wastewater reached 2 billion tons, accounting for more than 10% of the national industrial wastewater discharge. The organic pollution wastewater generated during the operation of petrochemical enterprises is an important part of China's industrial wastewater. Types of pollutants, large concentration, high toxicity, as well as containing many refractory biodegradation organic substances make water quality of the petrochemical wastewater complex; its governance has become a bottleneck restricting the development of the petrochemical industry.

Complex water quality features have spawned new water treatment processes. Advanced oxidation processes (AOPs) can produce hydroxyl radicals (•OH) with strong oxidizing ability under the reaction conditions of electricity, sound, photo, catalyst, and others. Hydroxyl radical (•OH) is an important reactive oxygen species with a standard oxidation–reduction potential of +2.8 V, which is second only to fluorine in nature [1]. It can successfully decompose most pollutants including refractory organics in water and oxidize macromolecule refractory organic matter into low-toxic or nontoxic small molecular substances.

The catalytic ozone oxidation process is a kind of advanced oxidation process, which has the following characteristics: (a) it produces strong oxidizing •OH, and the oxidation process is fast, reaching 10^6 to 10^{10} L/ (mol•s); (b) it performs excellently in removing refractory organic matter with no secondary pollutants, which means the process is green and efficient; and (c) the process runs economically. Taking a petrochemical integrated sewage treatment plant in northern China as an example, ozone can directly use air as raw material by ozone generator without adding auxiliary materials, and the earliest used catalyst has been running normally for 5 years, which still has high catalytic activity now. Therefore, catalytic ozone oxidation process is widely used in the advanced treatment of petrochemical wastewater. Especially after July 1, 2015, the Ministry of Ecology and Environment began to implement the *Petrochemical industry pollutant discharge standards (GB 31571-2015)* to replace the *Integrated Wastewater Discharge Standard (GB 8978-1996),* which improves the direct drainage's COD limit of sewage treatment plant in petrochemical industrial park from 100 to 60 mg/L and adds 60 indicators of characteristic organic pollutants. Catalytic ozone oxidation process is increasingly popular in wastewater treatment due to the advantage of high efficiency, low consumption, energy saving, and environmental protection.

2. Research progress of catalytic ozone oxidation

Due to the excellent performance of catalytic ozone oxidation process in industrial wastewater treatment, substantial researches on the development of new catalysts and catalytic processes have been carried out. But so far the mechanism of catalytic ozone oxidation has not been unified in the academia, even the mechanisms proposed in many published literature are contradictory, which has largely limited the promotion of catalytic ozone oxidation process as an efficient, green technology. Several possible mechanisms on the catalytic ozone oxidation process will be introduced in the following.

According to the state of the catalyst, the catalytic ozone oxidation process can be divided into homogeneous and heterogeneous catalytic oxidation.

2.1 Homogeneous catalytic oxidation

Some transition metal cations have been shown to improve ozonation efficiency; among the most widely used are Mn(II), Fe(III), Fe(II), Co(II), Cu(II), Zn(II), and Cr(III) [2–4]. In simple terms, homogeneous catalytic oxidation is to let the transition metal ion decompose ozone or assist organics to be more easily oxidation. Two major mechanisms of homogeneous catalytic ozone oxidation can be found in the published research papers:

1. Ozone decomposes under the action of the catalyst to generate free radicals [5–7].

2. A complex coordination reaction occurs between the catalyst and the organic matter or ozone to promote the reaction between ozone and organic matter [2, 8, 9].

The free radical mechanism is similar to the Fenton reaction, and the electron transfer is achieved by oxidation and reduction of the valence metal ions. Based on the early work of Logager et al. [10], Sauleda et al. [7] explained the formation of hydroxyl radicals in the presence of Fe(II) ions:

$$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2 \tag{1}$$

$$FeO^{2+} + H_2O \rightarrow Fe^{3+} + \bullet OH + OH^- \tag{2}$$

Another mechanism is proposed by Pines and Reckhow [8] on the research catalytic ozone oxidation of oxalic acid in the presence of Co(II) ions. In general, hydroxyl radicals are more likely to be produced under alkaline conditions. However, experiments have shown that the reaction became inefficient with the increase of pH. Moreover in the presence of t-butanol (a radical scavenger), the reaction rate was also found not to change. These suggest that the free radical mechanism is not responsible for mineralization of oxalate in the Co(II)/O$_3$ system. So the hypothesis illustrated in **Figure 1** is proposed to explain the experimental phenomenon. Mineralization of oxalate is achieved by forming complexes with Co(II) ions.

Other metal ions have also been found to have similar catalytic effects. However, once metal ions are used as catalysts to promote ozone oxidation, the question on how to separate catalysts from the treated water should take into consideration. Therefore, there have been few reports on its research recently.

2.2 Heterogeneous catalytic oxidation

Among the most widely used catalysts in heterogeneous catalytic ozone oxidation are [11]:

- Metal oxides (MnO$_2$, TiO$_2$, Al$_2$O$_3$, and FeOOH).

- Metals (Cu, Ru, Pt, Co) on supports (SiO$_2$, Al$_2$O$_3$, TiO$_2$, CeO$_2$, and activated carbon).

- Activated carbon.

Adsorption is the key word in heterogeneous catalytic ozone oxidation. There are three possible ways which could be the general mechanism of heterogeneous catalytic ozone oxidation (**Figure 2**) [12]:

- Ozone is adsorbed on the surface of the catalyst.

- Organic molecule is adsorbed on the surface of the catalyst.

- Both, ozone and organic molecule, are adsorbed on the catalyst surface.

A lot of research work has been carried out for different catalysts.

2.2.1 Metal oxides

A variety of metal oxides have been shown to be effective in heterogeneous catalytic oxidation, such as MnO$_2$, Al$_2$O$_3$, TiO$_2$, and FeOOH. All published articles

$$C_2O_4^{2-}$$

$$CoC_2O_4$$
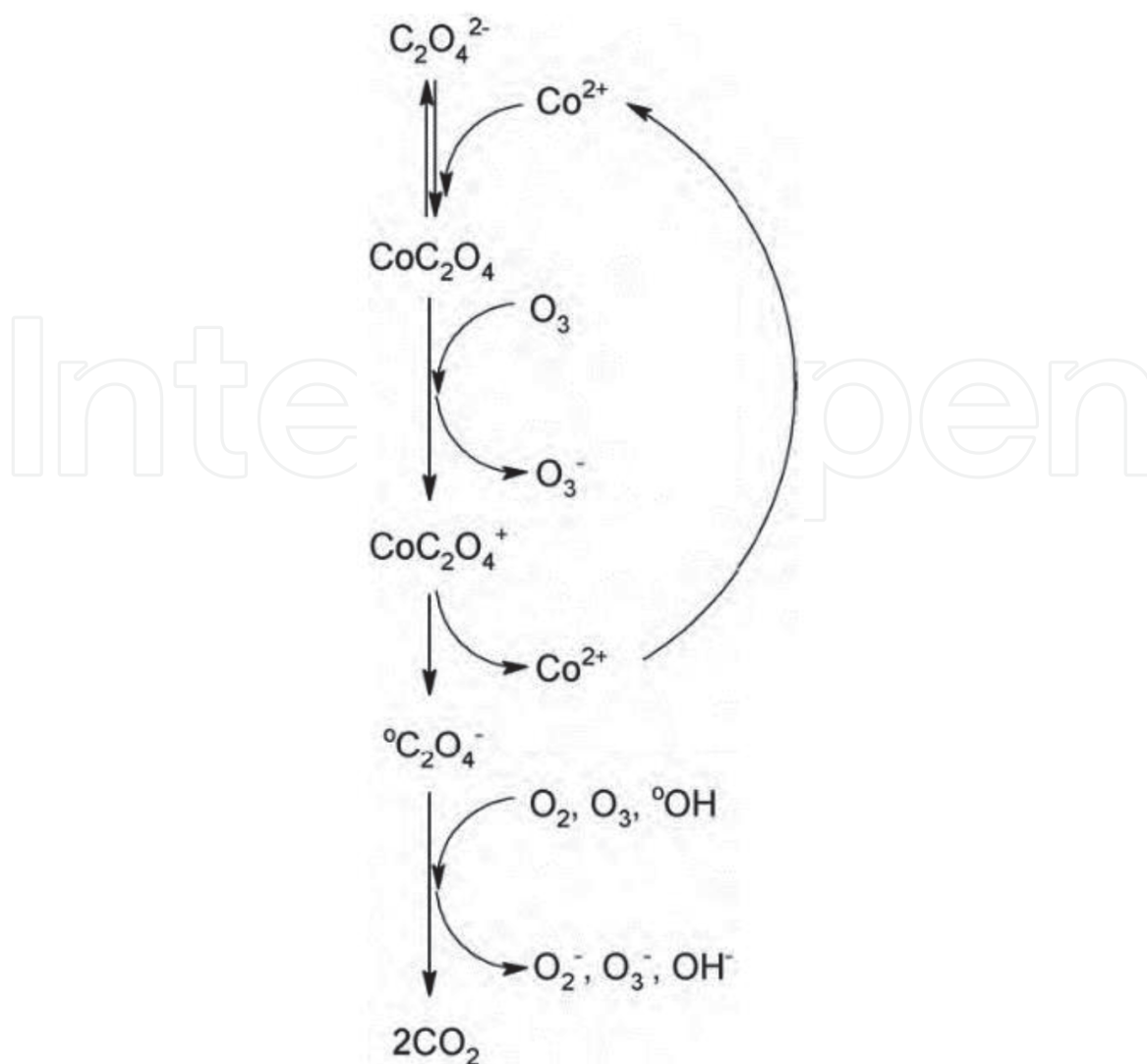
$$CoC_2O_4^+$$

$$^\circ C_2O_4^-$$

$$2CO_2$$

Figure 1.
Mechanism of oxalic acid oxidation in the presence of Co(II) ions proposed by Pines and Reckhow (modified from [8]).

have indicated that the mechanism of catalysis has a tight affinity with the surface chemistry of the oxides. More specifically, metal oxides as catalysts are surrounded by water in wastewater treatment. There is no doubt that the surface is covered by hydroxyls which have ion-exchange properties. Some of the oxides may also have Lewis acid centers which are considered as another adsorption site on their surfaces. In addition, hydrophobic sites can also be spotted on the surface on some metal oxides to explain the adsorption of organic molecules. **Table 1** lists the metal oxides commonly used as catalysts in the research and target organics for removal.

2.2.1.1 MnO_2

In the research of the catalytic mechanism of MnO_2, Andreozzi et al. [33] first found in the study that the catalytic activity of MnO_2 to degrade oxalic acid was the highest when pH = 3.2. This result, however, is contradictory with what we have known: the optimum pH for dissociating ozone to produce •OH is 5–6. This means during the process •OH is not the dominated factor for removing oxalic acid. According to Tong et al. [58], adsorption of organic molecule on the surface of MnO_2 and subsequent attack of ozone on adsorbed organic molecule are responsible for catalytic activity.
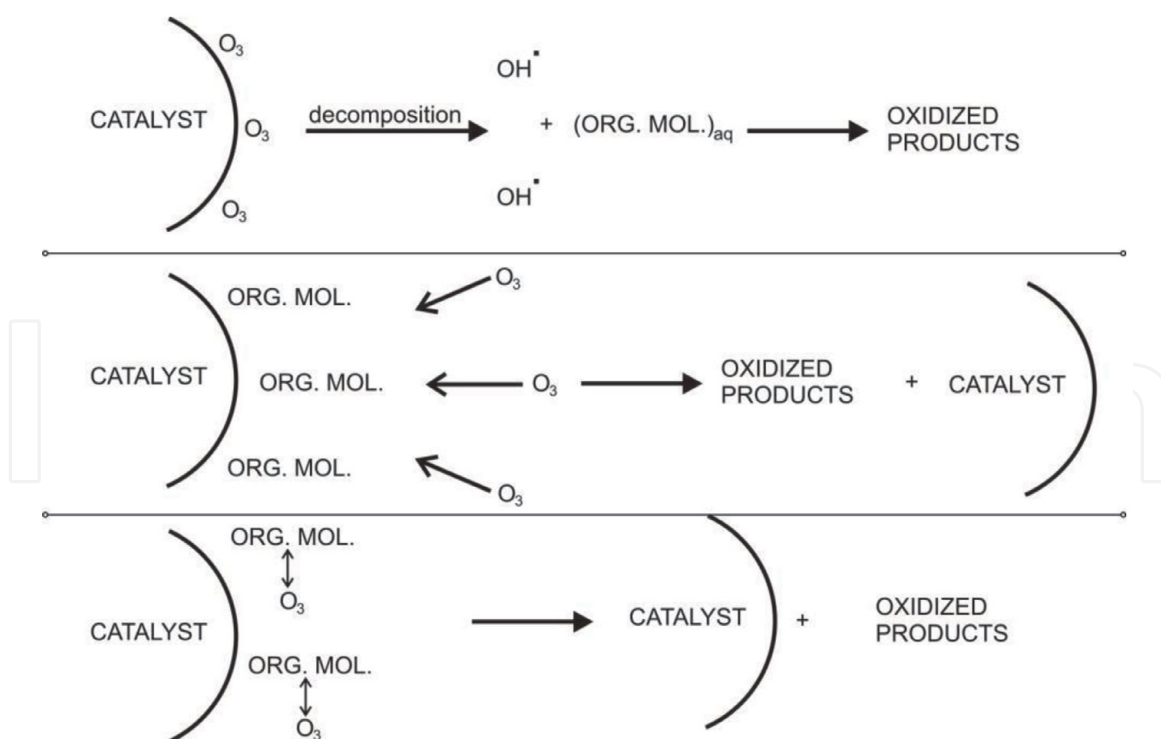
Figure 2.
Three possible cases of heterogeneous catalysis [12].

On the other hand, when atrazine was used as the characteristic pollutant, adding in t-butanol could inhibit the catalytic activity of MnO_2 [14]. If atrazine is replaced with nitrobenzene, t-butanol has light effect on catalytic activity of MnO_2 [59]. From the research, we can draw a conclusion that the catalytic mechanism of MnO_2 catalyzed ozone oxidation to degrade organic matter in water varies depending on the type of organic matter, including the mechanism of free radicals produced by decomposing ozone, the surface coordination mechanism of organic matters, and the combination of both.

2.2.1.2 Al_2O_3

Al_2O_3 is another metal oxide that is widely used as a catalyst. There is a lot of controversy about research of the catalytic mechanism of Al_2O_3. The researches of Kasprzyk-Hordern and Nawrocki had found that in the presence of Al_2O_3, there was no catalytic activity for the removal of aromatic hydrocarbons and ethers. However, in the latter experiments, it was detected that the decomposition rate of ozone is twice that of ozonation alone [60–62]. In Kasprzyk-Hordern [19] another experiment, high catalytic activity was demonstrated when the substrate is natural organic matter (NOM) in the presence of alumina. The key factor to explain this contrast is the capacity of the surface to adsorb different organic molecules, as both hydrocarbons and ethers do not adsorb on alumina from aqueous solutions while alumina revealed high adsorption capacity toward NOM. These could be the evidence of the hypothesis that the catalytic activity of Al_2O_3 depends on the surface absorption of the substrate. However, Ernst et al. [20] reported that the adsorption of organic molecules is detrimental to the catalytic activity of γ-Al_2O_3. The research showed it was the high adsorption of oxalic acid on the surface that caused the lower efficiency. Obviously, the mechanism is remained to be discussed further and deeper.

Catalyst	Target organics	References
MnO_2	Carboxylic acids (oxalic, pyruvic, sulfosalicylic, propionic, glyoxylic), N-methyl-p-aminophenol, atrazine	[3, 8, 13–17]
Al_2O_3	Carboxylic acids (oxalic, acetic, salicylic, succinic), 2-chlorophenol, chloroethanol, NOM, dimethyl phthalate	[18–23]
TiO_2	Oxalic acid, carbamazepine, naproxen, nitrobenzene, clofibric acid	[24–27]
FeOOH	p-Chlorobenzoic acid, NOM	[28–32]
TiO_2, Al_2O_3, Ni_2O_3, CuO, MoO_3, CoO, Fe_2O_3	m-Dinitrobenzene	[33]
ZnO	p-Chlorobenzoic acid	[34, 35]
$TiO_2(2.5\%)/\alpha\text{-}Al_2O_3$	NOM	[36–38]
$TiO_2(10\%)/Al_2O_3$, $Fe_2O_3(10\%)/Al_2O_3$	Oxalic acid, chloroethanol, chlorophenol	[19]
TiO_2/Al_2O_3	Fulvic acids	[38]
$TiO_2(15\%)/\gamma\text{-}Al_2O_3$	Oxalic acid	[39]
$MnO_2(10\%)/TiO_2$	Phenol	[2]
$MnO_x(10.8\%)/AC$	Nitrobenzene	[40]
$\beta\text{-}Al_2O_3$	Pyruvic acid	[41]
$\gamma\text{-}Al_2O_3$	Methylisoborneol	[42]
$\gamma\text{-}AlOOH$, $\alpha\text{-}Al_2O_3$	2,4,6-trichloroanisole	[43]
MnO_2	Phenol, NMO	[44, 45]
CeO_2	Aniline, sulfanilic acid, dyes	[46]
Co_3O_4/Al_2O_3	Pyruvic acid	[41]
CuO/Al_2O_3	Alachlor, oxalic acid, substituted phenols	[3, 47, 48]
$Co(OH)_2$	p-Chloronitrobenzene	[49]
TiO_2/AC	Methylene blue	[50]
NiO/Al_2O_3	Oxalic acid	[51]
NiO/CuO	Dichloroacetic acid	[52]
MnO_x/Al_2O_3	Phenazone, ibuprofen, phenytoin, diphenhydramine	[53]
MgO	Dye	[54]
CoO_x/ZrO_2	2,4-D	[55]
Co/CeO, Ag/CeO, Mn/CeO	Phenolic wastewater	[56, 57]

Table 1.
Common catalyst components and target organics for removal (modified from [11]).

2.2.1.3 TiO$_2$

TiO$_2$ is usually used as a photocatalyst [63–68], which also has a good catalytic effect when degrading organic matter in wastewater. The catalytic mechanism of TiO$_2$ has close affinity with the construction of TiO$_2$.

TiO$_2$, which is often used as a catalyst, is classified into rutile type and anatase type. Yang et al. [69] used rutile TiO$_2$ for catalytic ozone oxidation research and found that the efficiency of removing organic matter decreased after adding TBA to the reaction system. This implies that the free radical mechanism dominates the reaction process. On the contrary, Ye et al. [70] studied the degradation of

4-chloronitrobenzene (CNB) during catalytic and photocatalytic ozone oxidation in the presence of TiO_2. The result of the experiment is that the TOC is higher under UV condition, which does not correspond with the free radical mechanism. So far, the difference in this mechanism is still lacking in-depth explanation.

2.2.1.4 FeOOH

The mechanism of FeOOH is similar to the mechanism of homogeneous catalytic oxidation. The difference between them is that the decomposition and oxidation happen in bulk water in homogeneous catalytic oxidation, while for FeOOH, the process occurs on the surface.

1. The process satisfies the hydroxyl radical mechanism. As is illustrated in **Figure 3**, the ozone molecule first forms a surface ring with the hydroxyl group on the surface of the catalyst and then decomposes to produce Fe-OH-O¯ and O_2. Finally, Fe-OH-O¯ is directly attacked by ozone to form •OH and O_2•¯, and the water molecules complex on the surface of FeOOH to form a new hydroxyl group.

2. Organic compounds form complexes on the surface of FeOOH and are then directly oxidized by ozone molecules to degrade organic matter [72].

2.2.2 Metals on supports

Metals on supports are a type of catalysts which use supports (SiO_2, Al_2O_3, TiO_2, CeO_2, and activated carbon) to load metals (Cu, Ru, Pt, Co). They have been observed to have a high catalytic activity in catalytic ozone process.

Two main routes have been proposed to explain the catalytic mechanism [73] (**Figure 4**):

1. The metal supported on the catalyst has a constant valence state in the catalytic reaction and only functions as a coordination.

2. The metals are attacked by the ozone to generate hydroxyl radicals. Then, through the adsorption and desorption of organic matter on the surface of the catalyst, electron transfer is completed to achieve metal reduction and oxidation of organic matter.
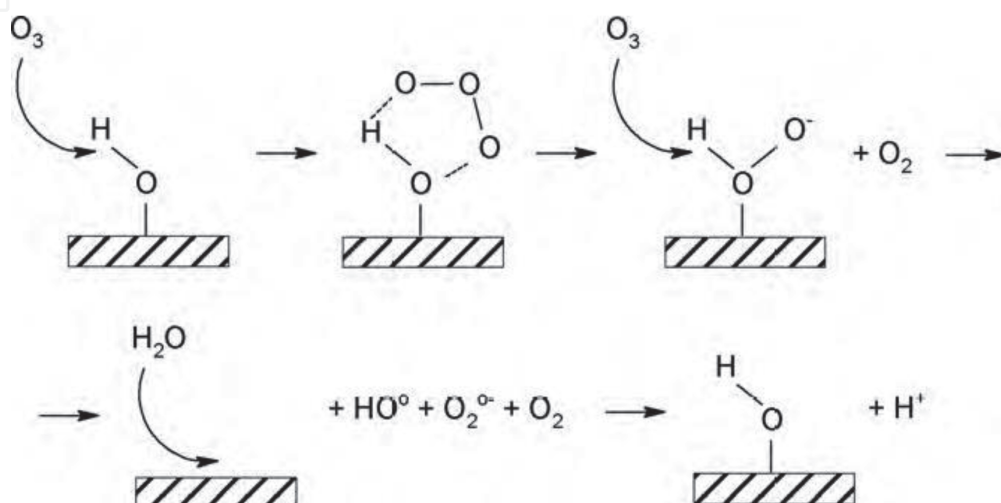

Figure 3.
Mechanism of hydroxyl radical generation in the presence of FeOOH [71].
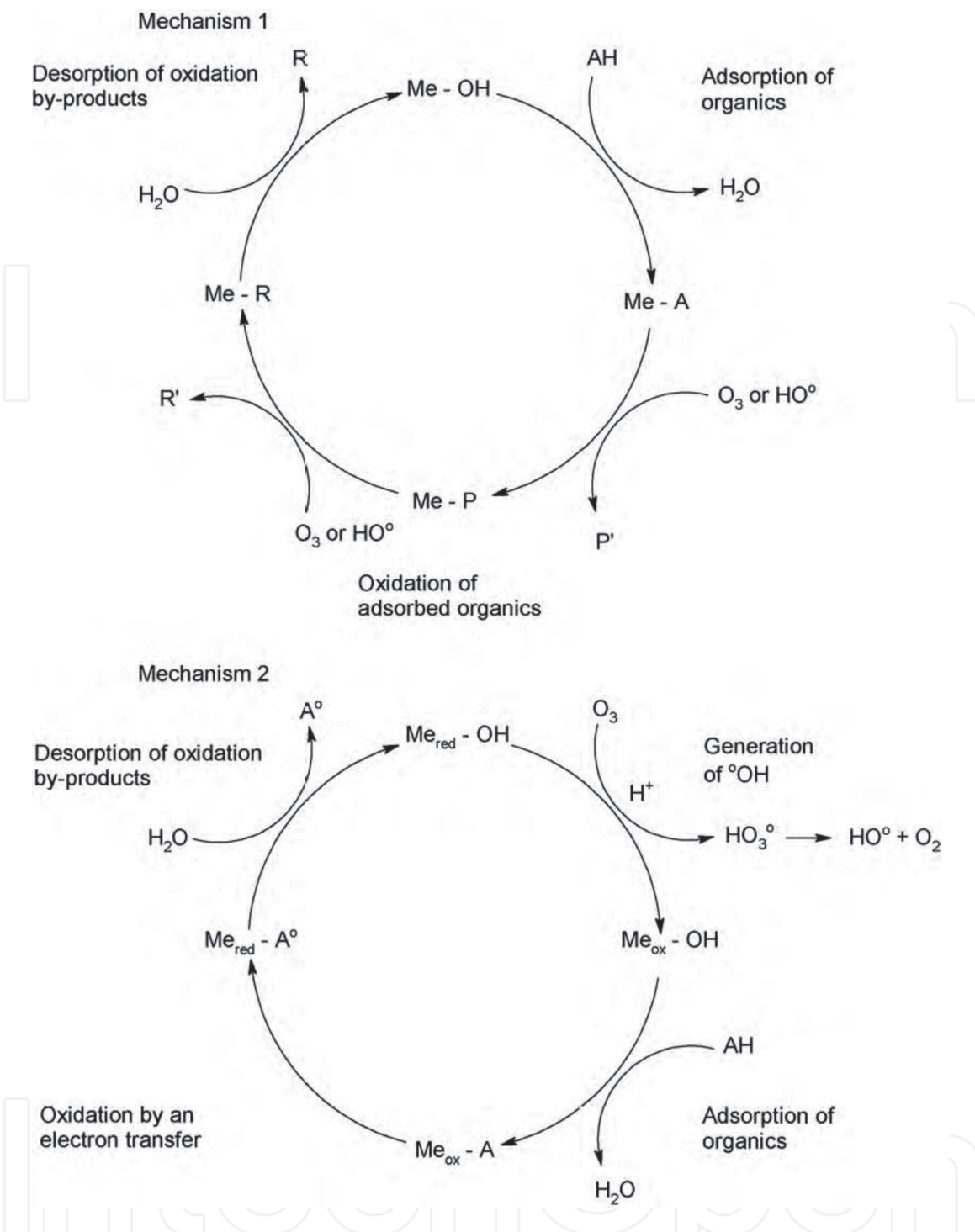
Figure 4.
Mechanisms of catalytic ozone oxidation in the presence of metals on supports (AH (organic acid); P, R (adsorbed primary and final by-products); P, R (primary and final)) [73].

2.2.3 Activated carbon

Activated carbon is also used as a catalyst for catalytic ozone oxidation as a relatively cheap and durable material. The surface properties of activated carbon are different from metals' and cannot coordinate with organic matter in water. So most of the research focused on how ozone decomposes on the surface of activated carbon. In general, there are two catalytic paths for activated carbon: (i) increasing the surface reaction area and (ii) decomposing ozone on the surface to produce •OH radicals.

3. Research on catalytic ozone oxidation in petrochemical secondary effluent

The mechanism described above is part of the research progress on the mechanism of catalytic ozone oxidation in recent years and plays a decisive role in the theoretical development of the process. However, the main research ideas of these studies are to use target pollutants to explore the mechanism of related catalysts. Whether it is possible to maintain high treatment efficiency in the face of actual wastewater with complex water quality is not clear at present; moreover some catalysts have high cost which restrains to implement in practical engineering applications.

In China, ozonation/catalytic ozone oxidation has been widely used in the advanced treatment of petrochemical wastewater. The proportion of applications is estimated to be as high as approximately 64%. Thus, it is necessary to carry out research on the mechanism of catalytic ozone oxidation which is instructive for practical engineering.

The research team of the author is based on a petrochemical wastewater treatment plant (WWTP) which uses catalytic ozone oxidation process as an advanced treatment in the north of China. All the water samples and catalysts in the experiment are obtained from the WWTP, instead of choosing the target pollutants to do in-depth researches, which break through the traditional ways of exploring the mechanism and mean a lot to the practical engineering applications.

In terms of the petrochemical secondary effluent (PSE) treatment, the research on the mechanism of catalytic ozone oxidation and existing problems in the treatment of petrochemical wastewater when using catalytic ozone oxidation process has achieved certain results, which is at the domestic leading level. The research will be generally introduced below.

3.1 Research ideas

The catalysts used in the WWTP are commercial material which mainly comprises alumina-supported copper oxide (ACO). It has been demonstrated that the adsorption of organics on alumina was associated with hydrophilicity of organics [74]. The catalytic activity of dissolved organic matters (DOM) is extremely correlative to their physicochemical properties (e.g., aromaticity, polarity, hydrophobicity-hydrophilicity, acidity-alkaline, molecular weight) [31, 75–77]. Due to the differences of hydrophobicity-hydrophilicity and acidity-alkaline, resin fraction can be an appropriate way to isolate DOM from wastewater [78]. Moreover, the specific effects of ozonation/catalytic ozone oxidation on DOM with different characteristics can be observed from the changes of different DOM fraction. Therefore, the research team innovatively used the resin classification method to divide the DOM in PSE into four components: hydrophobic acids (HoA), hydrophobic bases (HoB), hydrophobic neutrals (HoN), and hydrophilic substances (HI). Herein, HI included hydrophilic acid (HiA), hydrophilic base (HiB), and hydrophilic neutral (HiN). The effect of the three common ozone treatment processes, single ozonation, ozone/H_2O_2 (representing homogeneous catalytic oxidation technology), and catalytic ozone oxidation with a commercial ACO (representing heterogeneous catalytic oxidation technology), on different fractions, was investigated. Then the catalytic ozone oxidation mechanism of the major fractions is systematically elaborated.

3.2 Results and discussion

3.2.1 The characteristic of catalyst

In the study, as the catalyst is commercial and obtained from the practical industrial application, we only investigate the characteristics related to the mechanism proposed. SEM images of commercial catalyst used were presented in **Figure 5**. The catalyst was spherule of 2–4 mm. It possessed mesoporous surface with packed lamellar layer. The structure is very important for the organic pollutant removal. The BET surface area, pore volume, and average size were listed in **Table 2**. The pHpzc of ACO was found to be (pHpzc) of 8.0 ± 0.2. The pH of sample was about 7.5 (pH < pHpzc = 8.0). ACO will be positively charged and adsorb anions from aqueous solution. The surface hydroxyl group density was 2.7×10^{-5} M/m^2. The FTIR spectra of catalyst before and after catalytic ozone oxidation were shown in **Figure 6**. The adsorption peaks at 3450 and 1635 cm^{-1} attributed to the surface hydroxyl groups of catalyst and adsorbed water, respectively. The bands at 1525 and 1385 cm^{-1} were likely to attribute to surface acid functional group of catalyst. After catalytic ozone oxidation, the hydroxyl groups at 3450 cm^{-1} broadened may be formed from adsorbed water by hydrogen binding because the catalyst interacted with ozone.

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique that detects information on the composition and content of various compounds, chemical state, molecular structure, and chemical bonds. As shown in **Figure 7**, obvious O 1s and Al 2p and weak Cu 2p signals are observed in the survey region. The signal corresponding to Al 2p was found at 73.7 eV. The content of Cu was minor. The weak signal related to Cu 2p at around 932 eV could be identified in the narrow region. The signal of O 1s was displayed at 530.3 eV corresponding to the adsorbed hydroxyl.

3.2.2 The effect of ozonation and catalytic ozone oxidation on fraction distribution of the PSE

For the selection study of the optimal wastewater treatment method, Fu et al. compared the reactivity characteristics of DOM in single ozone, ozone/H$_2$O$_2$, and
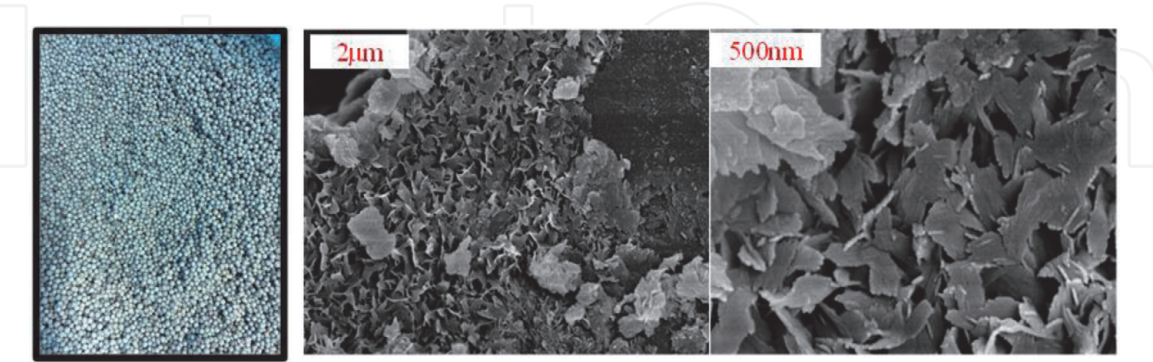

Figure 5.
SEM images for catalyst.

Items	BET surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)	pH$_{pzc}$	Surface hydroxyl group density (M/m^2)
Average value	169.28	0467	11.0	8.0 ± 0.2	2.7×10^{-5}

Table 2.
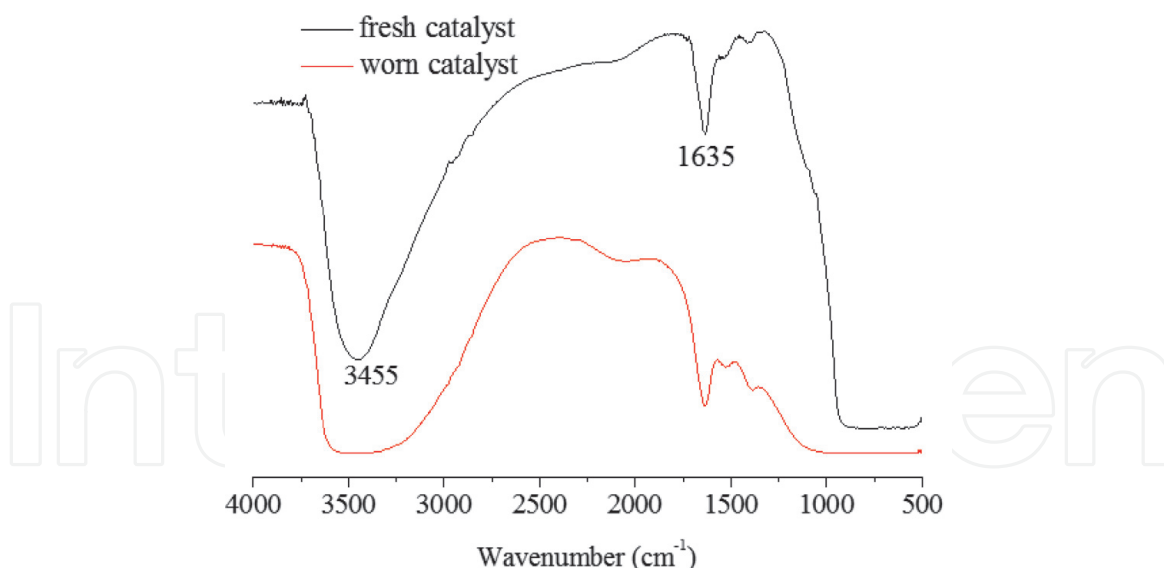*Surface characteristics e of commercial catalyst.*

Figure 6.
The FTIR spectra of original and worn catalyst.

ozone/catalyst systems [79]. The highest removal efficiency (42.8%) of TOC was achieved in the ozone/catalyst system, followed by the ozone/H_2O_2 (23.8%) and single ozone (4.7%) systems. This implied that homogeneous catalysis (ozone/H_2O_2) has obvious lower DOM removal rate (~20%) than heterogeneous catalysis when the ozone dosage and contact time were the same treating PSE.

In order to investigate the specific changes of each component, Sun et al. [80] first isolated four fractions (HiA, HiB, HiN, and HI) and operated the ozonation experiment on separate fraction system. They measured the values of DOC and $SUVA_{254}$ of raw water and its fractions before and after ozonation and catalytic ozone oxidation, which present in **Figure 8**. As shown in **Figure 8a**, HI and HoA were the dominated fractions in PSE with relatively high percentage of total DOC. SUA_{254}, the value of UV_{254} divided by itself DOC, has been reported to act as an indicator of active aromatic structure and unsaturated bonds (carbon-carbon and carbon-oxygen) from organic matters [81]. In **Figure 8b**, HoA had the largest $SUVA_{254}$ value among other fractions, indicating HoA had the most containing aromatic and unsaturated bond organic matters, while the $SUVA_{254}$ of HI is the smallest. The results are entirely in accordance with the results of the previous studies [77, 78].

The fraction distribution changed significantly after ozonation and catalytic ozone oxidation. **Figure 8a** manifested that the DOC of HoA remarkably decreased by ozonation. However, the DOC of HI had slight reduction after ozonation. This result indicated that ozonation could be more readily to oxidize HoA than HI. Under the same condition, catalytic ozone oxidation exhibited higher DOC removal than ozonation for all fractions, in particular HI. It is well known that ozone is prone to react with compounds containing electrophilic groups [82]. As can be seen in **Figure 8b**, ozonation decreased significantly the $SUVA_{254}$ of all fractions. On the contrary, catalytic ozone oxidation showed less changes on the reduction of $SUVA_{254}$ than ozonation for all fractions. This suggested UV-absorbing matters are susceptible to electrophilic groups which are easily attacked by ozone. Thus, ozonation reacting easily with HoA is likely to be the highest $SUVA_{254}$.

In a high complex circumstance, Fu et al. evaluated specific changes; six fractions in both raw wastewater and ozonized wastewater instead separate isolated fractions in previous study [80]. Fu et al. specified that HiN (belongs to HI) were one dominant DOM fractions with the highest TOC contents in the effluent of the three ozonation systems, accounting for 24.8–53.6% of the total TOC contents (**Figure 9a**). From the changes in TOC distributions ($TOC_{effluent} - TOC_{influent}$)

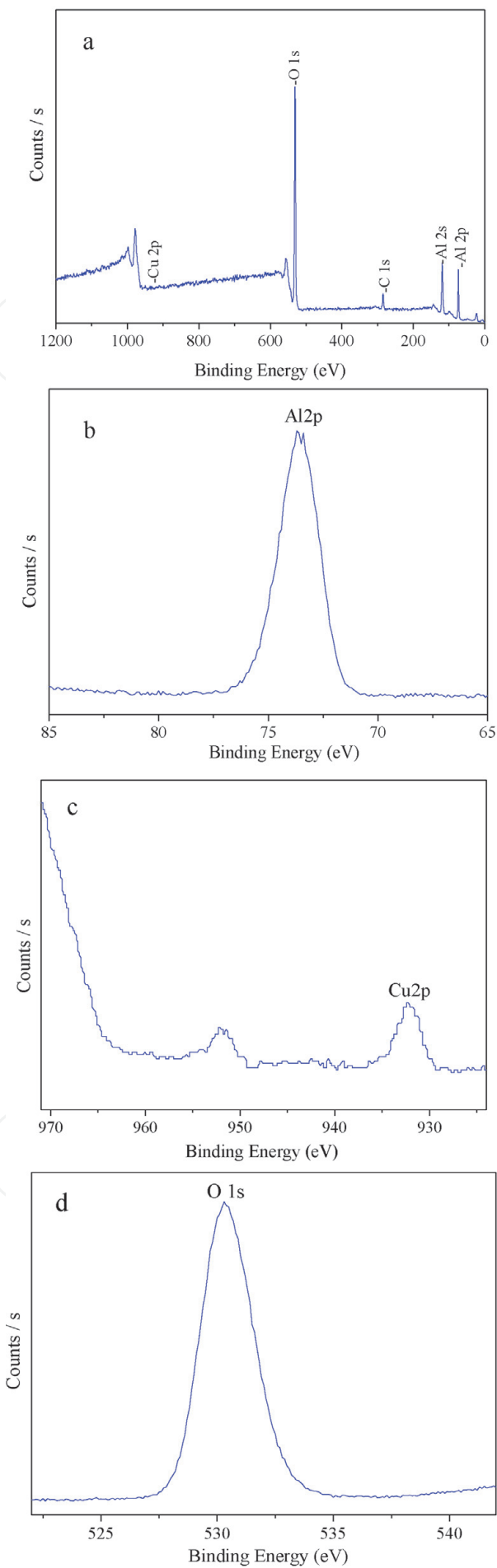**Figure 7.**
XPS spectra of catalyst: (a) wide-range survey, (b) Al 2p region, (c) Cu 2p region, and (d) O 1s.

Figure 8.
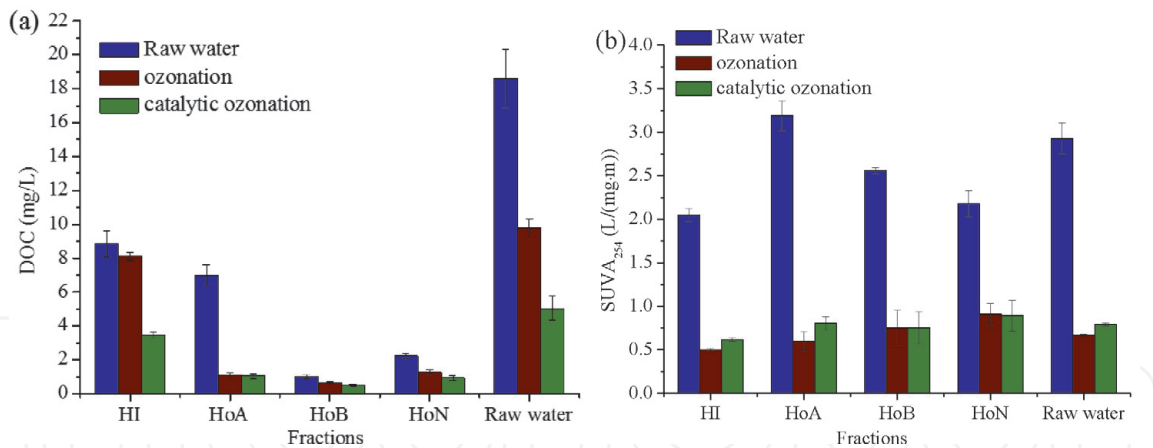*The DOC (a) and SUVA$_{254}$ (b) of raw water and its fractions before and after ozonation and catalytic ozone oxidation. Experiment conditions: initial concentration, 19.0 ± 2.0 mg/L; initial pH, 7.5; ozone dose, 1.0 mg/min; reaction time, 120 min; catalyst dose, 500 g.*
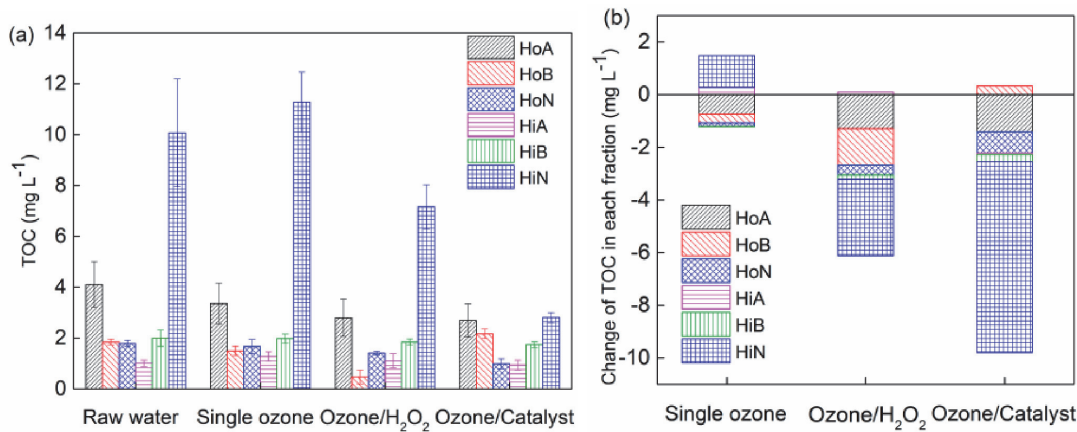

Figure 9.
TOC distribution of the DOM fractions before and after ozonation via single ozone, ozone/H$_2$O$_2$, and ozone/catalyst treatment: (a) TOC content and (b) change in TOC content.

(**Figure 9b**), for the single ozone system, the mass balance of TOC content was maintained after single ozone treatment (**Figure 9b**), and the sum of the increased TOC content (contributed by HiA and HiN) was 38.8%, which approximately equaled the sum of the decreased TOC content contributed by the other four fractions (44.8%). In the single ozone system, HoA showed the highest TOC removal, decreasing by 18.1%, whereas HiN exhibited the lowest TOC removal content, increasing by 12.0% in the effluent conversely. Thus, it is reasonable to think that the single ozone system transformed hydrophobic components (e.g., HoB, HoN, and HoA) into hydrophilic compounds (e.g., HiA and HiN). In addition, for ozone/H$_2$O$_2$ treatment, HiA was hard to remove, while HoB was easy to remove.

3.2.3 Transformation of DOM fractions during the ozonation process

The specific fluorescence excitation-emission matrix (EEM) spectroscopy volume could be used to rapidly identify the fluorescent compounds present in the DOM and reflect the compositional and structural characteristics of DOM. The ratio of the cumulative volume (Φ_i) to the TOC (Φ_i/TOC) of the DOM fractions is further compared (**Figure 10**) [79]. HiA and HiN had the lowest Φ_i/TOC ratios among other fractions in raw water, indicating that non-fluorescent compounds contributed a large portion of TOC in these two fractions. The FTIR adsorption spectrum of HiA and HiN also suggested that the spectral fine structure and

adsorption patterns of the reactive functional groups, such as the stretching vibration of $C\!\!=\!\!O$, $O\!\!-\!\!H$ of the carboxylates, were not as significant as those for the other fractions. The HiN presented the smallest changes in $\Phi i/TOC$ ratio after single ozone treatment, implying that the portion of non-fluorescent and fluorescent substances did not change much when reacted with single ozone, and HiN may mainly consist of ozone-resistant compounds.

After treatment by the ozone/H_2O_2 and ozone/catalyst systems, the $\Phi i/TOC$ ratios of HiN in raw water increased significantly (**Figure 10**), showing that compounds with little fluorescence but large TOC contents were removed. Therefore, it could be assumed that the HiN in the raw water may consist of compounds with unsaturated bonds and low molecular weights, which have short conjugation lengths and could readily react with H_2O_2 or catalyst in the presence of ozone [83, 84]. As shown in **Figure 10**, $\Phi i/TOC$ ratio of HiN did not change substantially in the single ozone system, but increased gradually in the ozone/ H_2O_2 and ozone/catalyst systems. This also demonstrated that HiN was principally responsible for the DOM removal in the ozone/ H_2O_2 system and especially in ozone/catalyst system. Because HiN is the dominant fraction in the sample and was ozone resistant, for the better treatment of petrochemical wastewater, efficient HiN removal is necessary.

3.2.4 The proposed mechanism of catalytic ozone oxidation

1. *HoA removal and transformation*. Sun et al. have proven that HoA is a group of DOM which contains activated aromatic rings or double bonds in their research (**Figure 11**). Those electrophilic groups easily react with ozone molecule [85]. It benefits the contact of HoA and ozone molecule. The study also confirmed that HoA transformed into HI with ozonation. •OH quenching test also proved that ozone molecule and partial •OH reaction are the main pathways.

2. *HI removal*. Higher adsorption rate (22% for HI) on the catalyst of alumina-supported copper oxide (ACO) was observed than that of other studies [74]. The adsorption of catalyst plays a key role during catalytic ozone oxidation. Higher adsorption rate led to the enrichment of organics on ACO, and concentration of HI adsorbed is much higher than that of in the bulking solution. In addition, that adsorbed ozone decomposed into •OH on the surface of
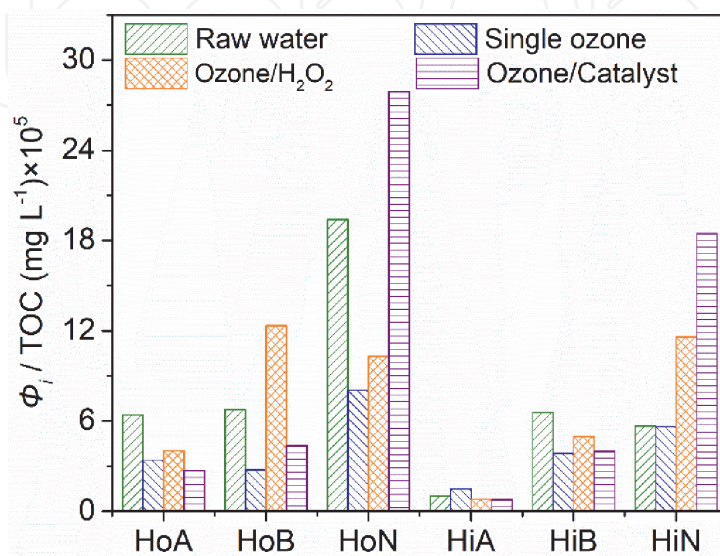

Figure 10.
Ratio of Φi to TOC in the wastewater fractions ($\Phi i/TOC$ (mg/L) $\times 10^4$ for HiN).
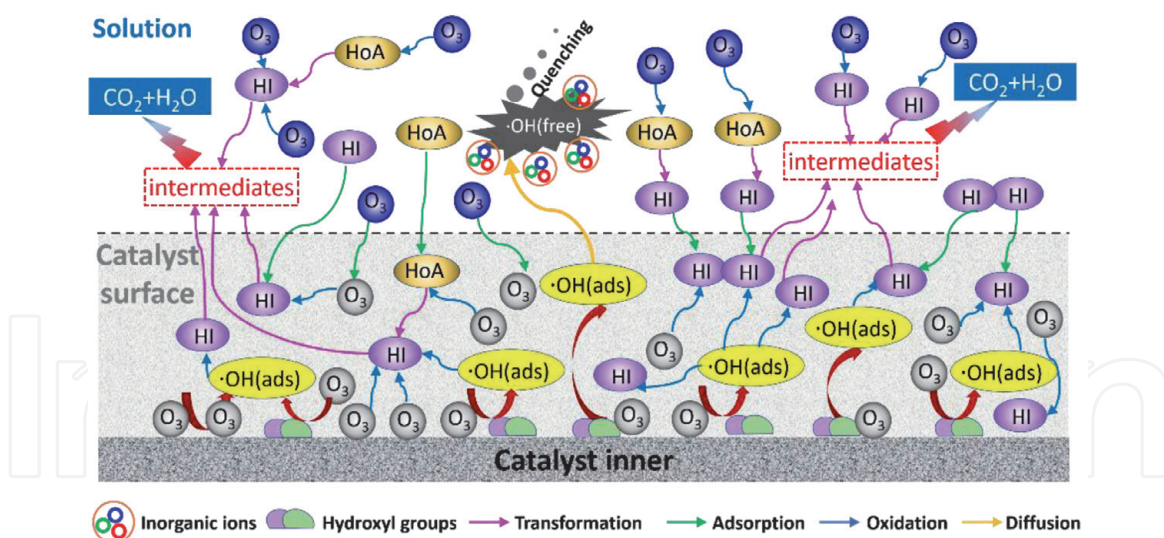
Figure 11.
The proposed reaction mechanism of HoA and HI during catalytic ozone oxidation treating PSE.

catalyst accelerated the mineralization of adsorbed HI, and the reduction of HI on the catalysts' surface would promote the further adsorption of HI from the bulking. Thus, the adsorption role on catalytic ozone oxidation kept a dynamic balance process between ozonation and re-adsorption, triggering a cyclic reaction to reduce the concentration of HI.

3. *OH quenching protection*. Survival time of •OH is just about 10 ms [86]. If the generated •OH on the surface of catalyst are spread into the bulking solution, it can be immediately consumed by high concentration of inorganic salts, such as Cl^- (359.5–380.0 mg/L) and SO_4^{2-} (908.0–955.9 mg/L) with their low affinity for adsorption on the surface of catalyst [87]. Our previous study also found that homogeneous catalysis (H_2O_2/O_3) has obvious lower DOM removal rate (~20%) than heterogeneous catalysis when the ozone dosage and contact time were the same treating PSE [79, 88]. It is proven that the quenching of •OH cannot be ignored during catalytic ozone oxidation of PSE. The adsorption of organic on the surface of catalyst and simultaneous •OH generation in the solid-liquid interface can guarantee the high consumption of •OH reacting with HI, preventing the emission of •OH into the bulking solution. Solid–liquid interface provides dominant reaction site between ozone molecule and •OH with organics. It is the •OH quenching protection.

3.3 Problems on catalytic ozone oxidation in the PSE

3.3.1 The effect of flocs on catalytic ozone oxidation

The toxicity of petrochemical wastewater is higher than that of ordinary urban sewage, which has an adverse effect on the biological treatment system of wastewater, causing the concentration of suspended solids (SS) (mainly organic flocs) in effluent generally beyond 25 mg/L [89]. Generally, SS and colloidal substances in PSE account for 15–20% of the total organic matter in the wastewater. The main components are microbial residues, microbial secretions (such as extracellular polymeric substances, EPSs), soluble microbial metabolites (SMPs), adsorbed proteins, sugars, and other macromolecular organics or inorganic substances such as heavy metals [90]. The presence of flocs in PSE system will have the following adverse effects on the catalytic ozone oxidation unit:

1. An increase in ozone consumption: According to the research, more than 75% of SS in the PSE are small pieces of activated sludge that does not completely separate from the water. The average particle size is about 30–60 μm [91]. Researches discover when catalytic ozone oxidation process is adopted to treat the PSE, the removal of per unit COD will consume more ozone with the increase of SS. The reason is bioflocs in the wastewater can react with O_3, causing the grow of ozone consumption [89]. The research of Zucker et al. [92] shows O_3 has a tendency to react with particulate matter at a high rate even in the first second of the reaction. Our researchers used catalytic ozone oxidation process to treat the PSE. It was found that when the influent SS concentration ranged from 0 to 10 m/L, the depletion of COD was 1.17 gO$_3$/g COD. When the concentration range of SS rose to 30–35 mg/L, the depletion of COD grew to 2.31 gO$_3$/g COD. Zhang et al. [90] suggested that when the ozone dosage was less than 10 mg/L, the ozone basically did not react with the flocs in the PSE. Once the dosage was beyond 10 mg/L, ozone can react rapidly with flocs, following the order of dissolved organic matter, outer layer loosely bound EPS (LB-EPS), and inner layer tightly bound EPS (TB-EPS).

2. The flocs covering the catalyst surface hinder the mass transfer of ozone and dissolved organic matters to the catalyst surface, thereby reducing the reaction efficiency. Studies have shown that catalytic ozone oxidation can affect the distribution of the floc particle size in wastewater. It can enhance the flocculation of the flocs, causing the particles to aggregate as larger flocs [92], which are trapped in the catalyst bed. In actual engineering application, if there are no actions being taken to the SS in the PSE before discharging into the unit of catalytic ozone oxidation, the treatment effect will be significantly reduced even within 7 h. Backwashing can effectively improve the situation; however, frequent backwashing strengthens the friction and shear between the catalysts, resulting in the loss of active components of the catalyst, reducing the service life of the catalyst, and invisibly increasing the application cost of the process.

3. Detrimental effects on the removal of characteristic organic matter in the PSE. The research of Zhang et al. [93] indicates that esters, alcohols, olefins, ketones, and nitrogen-containing organic compounds in the PSE can be effectively removed by catalytic ozone oxidation. Twelve main characteristic organic pollutants are detected in the influent, about six kinds of them can be degraded by catalytic ozone oxidation. But the target characteristic pollutants in the effluent can be reduced to three, if the PSE is filtered by 0.45 μm membrane before catalytic ozone oxidation.

3.3.2 The effect of colloidal macromolecular organic matters

Due to the characteristics of small size, light weight, and large specific surface area, the colloidal substance adsorbs a large amount of ions on the surface so that the colloids are mutually repulsive to keep stable state. Colloidal macromolecular substances cannot be settled by their own gravity. So it is necessary to add chemicals in water to make the colloids destabilize and for sedimentation. Studies have shown that colloidal organic matters accounted for about 9%–15% of COD in the PSE [94]. Because of the large molecular weight, such substances will affect the treatment of catalytic ozone oxidation. Adding 25 mg/L poly-aluminum chloride (PAC) coagulant to the PSE to remove the colloidal organic matters before performing catalytic ozone oxidation, compared with the direct use of catalytic

ozone oxidation for the PSE, the removal rate of COD can be increased by about 11%. This is because the presence of colloidal macromolecular organics in the PSE affects the rate of ozone decomposition in the initial stage (t < 30 s), thereby reducing the production efficiency of hydroxyl radicals (•OH) [95]. Many studies have also shown that in the advanced treatment of sewage, colloidal macromolecular organic matters mainly had effect on the removal of characteristic organic matters during the catalytic ozone oxidation.

3.3.3 The effect on the mass transfer of ozone

Ozone oxidation of organic pollutants in water depends on ozone transferring from the gas phase to the liquid phase, reacting with the target pollutants after diffusion. The mass transfer efficiency of ozone shifting into the liquid phase directly affects the effect of ozone oxidation [96]. The total ozone mass transfer coefficient is mainly influenced by many factors, for example, the degree of gas-liquid two-phase turbulence, the scale and quantity of ozone bubbles, the area of the two-phase contact, and the kinetics of ozonation reaction. The process rate is usually limited by the procedure in which ozone is transferred from the gas phase to the liquid phase [97]. At the same gas flow rate, the smaller bubble size is, the larger phase boundary area will be. Broadening the gas–liquid two-phase boundary area is beneficial not only to increase the total mass transfer rate of the process but also to improve the utilization of ozone [98]. At present, there is still a lack of relevant reports at home and abroad.

4. Conclusions

Flocs and colloidal macromolecular organic matter in the PSE increase the consumption of ozone as well as make the operation unstable. The configuration and operation mode of the catalytic ozone oxidation reactor are not optimized enough, causing the gas-liquid-solid three-phase mass transfer efficiency relatively low. These problems are common problems in the WWTP that are already operating catalytic ozone oxidation processes in China. As a kind of advanced oxidation process, catalytic ozone oxidation has attracted much attention because of its green, high-efficiency and energy-saving characteristics.

People have never stopped exploring its catalytic mechanism; the main research ideas of these studies are to use target pollutants and mixed water to explore the mechanism of related catalysts. Whether it is possible to maintain high treatment efficiency in the face of actual wastewater with complex water quality is not clear at present.

This manuscript first reviews and summarizes the progress and current status of ozonation/catalytic ozone oxidation mechanism research and secondly provides a relatively unique research idea: the DOM in raw water is divided into four fractions, HI, HoA, HoN, and HoB, according to the difference in chemical characteristics. The possible mechanism of ozonation/catalytic ozone oxidation is studied by observing the changes of each fraction. What's more, the common problems that may exist in the actual ozonation/catalytic ozone oxidation process are proposed and summarized. The matching point between mechanism research and practical engineering application is found, which provides direction for future research.

Future research should be carried on further with actual wastewater in the following aspects: (1) Fractional. It is a marvelous research idea to divide the substances in the water into different fractions for the specific research. (2) Microscopic. Future research should focus on microscopic scales, such as phase interface;

it can be combined with orbital theory to discuss the catalytic dynamics in-depth. (3) Whole process. The horizon of researches should be extended to the entire process to explore the effects of the surrounding environment on the catalytic process and mechanism, such as the specific effects of flocs and colloidal molecules on the process. In other words, although we have achieved some results in the study of catalytic ozone oxidation, there is still a lot of work that we need to continue.

Author details

Yu Tan[1], Liya Fu[1], Changyong Wu[1*], Yanan Li[1], Xiumei Sun[1,2] and Yuexi Zhou[1*]

1 State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing, China

2 College of Water Science, Beijing Normal University, Beijing, China

*Address all correspondence to: changyongwu@126.com and zhouyuexi@263.net

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References

[1] Liao LH. Application of advanced oxidation technology in water supply and wastewater treatment. Chemical Engineering and Equipment. 2018;**08**: 279-281 +259

[2] Beltran FJ, Rivas FJ, Montero-de-Espinosa R. Iron type catalysts for the ozonation of oxalic acid in water. Water Research. 2005;**39**:3553-3564

[3] PIi Y, Ernst M, Schrotter J-CH. Effect of phosphate buffer upon CuO/Al_2O_3 and $Cu(II)$ catalyzed ozonation of oxalic acid solution. Ozone: Science and Engineering. 2003;**25**:393-397

[4] Abd El-Raady AA, Nakajima T. Decomposition of carboxylic acids in water by O_3, O_3/H_2O_2, and $O_3/catalyst$. Ozone: Science and Engineering. 2005; **27**:11-18

[5] Gracia R, Aragues JL, Ovelleiro JL. Study of the catalytic ozone oxidation of humic substances in water and their ozonation Byproducts. Ozone: Science and Engineering. 1996;**18**:195-208

[6] Piera E, Calpe JC, Brillas E, Domenech X, Peral J. 2,4-Dichlorophenoxyacetic acid degradation by catalyzed ozonation: $TiO_2/UVA/O_3$ and $Fe(II)/UVA/O_3$ systems. Applied Catalysis B: Environmental. 2000;**27**:169-177

[7] Sauleda R, Brillas E. Mineralization of aniline and 4-chlorophenol in acidic solution by ozonation catalyzed with Fe^{2+} and UVA light. Applied Catalysis B: Environmental. 2001;**29**:135-145

[8] Pines DS, Reckhow DA. Effect of dissolved cobalt (II) on the ozonation of oxalic acid. Environmental Science and Technology. 2002;**36**:4046-4051

[9] Beltran FJ, Rivas FJ, Montero-de-Espinosa R. Ozone-enhanced oxidation of oxalic acid in water with cobalt catalysts. 2. Heterogeneous catalytic ozone oxidation. Industrial & Engineering Chemistry Research. 2003; **42**:3210-3217

[10] Logager T, Holeman J, Sehested K, Pedersen T. Oxidation of ferrous ions by ozone in acidic solutions. Inorganic Chemistry. 1992;**31**:3523-3529

[11] Nawrocki J, Kasprzyk-Hordern B. The efficiency and mechanisms of catalytic ozone oxidation. Applied Catalysis B: Environmental. 2010;**99**:27-42

[12] Nawrocki J. Catalytic ozone oxidation in water: Controversies and questions. Discussion paper. Applied Catalysis B: Environmental. 2013; **142-143**:465-471

[13] Beltrán Fernando J, Rivas FJ, Montero-de-Espinosa R. Ozone-enhanced oxidation of oxalic acid in water with cobalt Catalysts.1. Homogeneous catalytic ozone oxidation. Industrial & Engineering Chemistry Research. 2003;**42**(14):3210-3217

[14] Ma J, Graham NJD. Degradation of atrazine by manganese-catalysed ozonation: Influence of humic substances. Water Research. 1999;**33**(3):785-793

[15] Sánchez-Polo M, Rivera-Utrilla J. Ozonation of 1,3,6-naphthalenetrisulfonic acid in presence of heavy metals. Journal of Chemical Technology & Biotechnology. 2004; **79**(8):8

[16] Ma J, Graham NJD. Preliminary investigation of manganese-catalyzed ozonation for the destruction of atrazine. Ozone Science & Engineering. 1997;**19**(3):227-240

[17] Andreozzi R, Casale MSL, Marotta R, et al. N-methyl-p-aminophenol(metol) ozonation in aqueous solution:Kinetics,mechanism

and toxicological characterization of ozonized samples. Water Research. 2000;**34**(18):4419-4429

[18] Cooper C, Burch R. Mesoporous materials for water treatment processes. Water Research. 1999;**33**(18):3689-3694

[19] Kasprzyk-Hordern B, Raczyk-Stanisławiak U, S'wietlik J, Nawrocki J. Catalytic ozone oxidation of natural organic matter on alumina. Applied Catalysis B: Environmental. 2006;**62**: 345-358

[20] Ernst M, Lurot F, Schrotter JC. Catalytic ozone oxidation of refractory organic model compounds in aqueous solution by aluminum oxide. Applied Catalysis B: Environmental. 2004;**47**(1): 15-25

[21] Yunrui Z, Wanpeng Z, Fudong L, et al. Catalytic activity of $Ru/A_{l2}O_3$ for ozonation of dimethyl phthalate in aqueous solution. Chemosphere. 2007; **66**(1):145-150

[22] Ni CH, Chen JN. Heterogeneous catalytic ozone oxidation of 2-chlorophenol aqueous solution with alumina as a catalyst. Water Science & Technology. 2001;**43**(2):213

[23] Beltrán FJ, Rivas FJ, Montero-De-Espinosa R. Catalytic ozone oxidation of oxalic acid in an aqueous TiO slurry reactor. Applied Catalysis B: Environmental. 2002;**39**(3):221-231

[24] Rosal R, Rodríguez A, Gonzalo MS, et al. Catalytic ozone oxidation of naproxen and carbamazepine on titanium dioxide. Applied Catalysis B: Environmental. 2008;**84**(1):48-57

[25] Rosal R, Gonzalo MS, Rodríguez A, et al. Ozonation of clofibric acid catalyzed by titanium dioxide. Journal of Hazardous Materials. 2009;**169**(1): 411-418

[26] Rosal R, Gonzalo MS, Boltes K, et al. Identification of intermediates and assessment of ecotoxicity in the oxidation products generated during the ozonation of clofibric acid. Journal of Hazardous Materials. 2009;**172**(2): 1061-1068

[27] Zhang T, Lu J, Ma J, et al. Fluorescence spectroscopic characterization of DOM fractions isolated from a filtered river water after ozonation and catalytic ozone oxidation. Chemosphere. 2008;**71**(5):911-921

[28] Park JS, Choi H, Ahn KH. The reaction mechanism of catalytic oxidation with hydrogen peroxide and ozone in aqueous solution. Water Science & Technology. 2003;**47**(1):179

[29] Park JS, Choi H, Ahn KH, et al. Removal mechanism of natural organic matter and organic acid by ozone in the presence of goethite. Ozone Science & Engineering. 2004;**26**(2):141-151

[30] Park JS, Choi H, Cho J. Kinetic decomposition of ozone and para-chlorobenzoic acid (CBA) during catalytic ozone oxidation. Water Research. 2004;**38**(9):2285-2292

[31] Zhang T, Lu J, Ma J, et al. Comparative study of ozonation and synthetic goethite-catalyzed ozonation of individual NOM fractions isolated and fractionated from a filtered river water. Water Research. 2008;**42**(6): 1563-1570

[32] Trapido M, Veressinina Y, Munter R, et al. Catalytic ozone oxidation of m-dinitrobenzene. Ozone Science & Engineering. 2005;**27**(5): 359-363

[33] Andreozzi R, Insola A, Caprio V, et al. The use of manganese dioxide as a heterogeneous catalyst for oxalic acid ozonation in aqueous solution. Applied Catalysis A: General. 1996;**138**(1):75-81

[34] Muruganandham M, Wu JJ. Synthesis, characterization and catalytic activity of easily recyclable zinc oxide nanobundles. Applied Catalysis B: Environmental. 2008;**80**(1):32-41

[35] Gracia R, Cortés S, Sarasa J, et al. Heterogeneous catalytic ozone oxidation with supported titanium dioxide in model and natural waters. Ozone Science & Engineering. 2000;**22**(5): 461-471

[36] Gracia R, Cortés S, Sarasa J, et al. Catalytic ozone oxidation with supported titanium dioxide. The stability of catalyst in water. Ozone Science & Engineering. 2000;**22**(2): 185-193

[37] Gracia R, Cortes S, Sarasa J, et al. TiO_2-catalysed ozonation of raw Ebro river water. Water Research. 2000; **34**(5):1525-1532

[38] Volk C, Roche P, Joret JC, et al. Comparison of the effect of ozone, ozone-hydrogen peroxide system and catalytic ozone on the biodegradable organic matter of a fulvic acid solution. Water Research. 1997;**31**(3): 650-656

[39] Beltrán FJ, Rivas FJ, Montero-De-Espinosa R. A TiO_2/Al_2O_3 catalyst to improve the ozonation of oxalic acid in water. Applied Catalysis B: Environmental. 2004;**47**(2):101-109

[40] Ma J, Sui MH, Chen ZL, et al. Degradation of refractory organic pollutants by catalytic ozone oxidation —Activated carbon and Mn-loaded activated carbon as catalysts. Ozone Science & Engineering. 2004;**26**(1):3-10

[41] Álvarez PM, Beltrán FJ, Pocostales JP, et al. Preparation and structural characterization of Co/Al_2O_3 catalysts for the ozonation of pyruvic acid. Applied Catalysis B: Environmental. 2007;**72**(3):322-330

[42] Chen L, Qi F, Xu B, et al. The efficiency and mechanism of γ-alumina catalytic ozone oxidation of 2-methylisoborneol in drinking water. Water Science & Technology: Water Supply. 2006; **6**(3):43

[43] Qi F, Xu B, Chen Z, et al. Catalytic ozone oxidation for degradation of 2,4,6-trichloroanisole in drinking water in the presence of gamma-AlOOH. Water Environment Research. 2009; **81**(6):592

[44] Dong Y, Yang H, He K, et al. β-MnO_2 nanowires: A novel ozonation catalyst for water treatment. Applied Catalysis B: Environmental. 2009;**85**(3): 155-161

[45] Faria PCC, Monteiro DCM, Órfão JJM, et al. Cerium, manganese and cobalt oxides as catalysts for the ozonation of selected organic compounds. Chemosphere. 2009;**74**(6): 818-824

[46] Faria PCC, Órfão JJM, Pereira MFR. Activated carbon and ceria catalysts applied to the catalytic ozone oxidation of dyes and textile effluents. Applied Catalysis B: Environmental. 2009;**88**(3): 341-350

[47] Qu J, Li H, Liu H, et al. Ozonation of alachlor catalyzed by Cu/Al_2O_3 in water. Catalysis Today. 2004;**89**(3):291-296

[48] Udrea I, Bradu C. Ozonation of substituted phenols in aqueous solutions over CuO-Al_2O_3 catalyst. Ozone Science & Engineering. 2003; **25**(4):335-343

[49] Xu ZZ, Chen ZL, Joll C, et al. Catalytic efficiency and stability of cobalt hydroxide for decomposition of ozone and-chloronitrobenzene in water. Catalysis Communications. 2009;**10**(8): 1221-1225

[50] Jie Z, Lee KH, Cui L, et al. Degradation of methylene blue in aqueous solution by ozone-based processes. Journal of Industrial & Engineering Chemistry. 2009;**15**(2): 185-189

[51] Avramescu SM, Bradu C, Udrea I, et al. Degradation of oxalic acid from aqueous solutions by ozonation in presence of Ni/Al_2O_3 catalysts. Catalysis Communications. 2008;**9**(14): 2386-2391

[52] Qin W, Li X, Qi J. Experimental and theoretical investigation of the catalytic ozone oxidation on the surface of $NiO-CuO$ nanoparticles. Langmuir: The ACS Journal of Surfaces & Colloids. 2009;**25**(14):8001-8011

[53] Yang L, Hu C, Nie Y, et al. Catalytic ozone oxidation of selected pharmaceuticals over mesoporous alumina-supported manganese oxide. Environmental Science & Technology. 2009;**43**(7):2525-2529

[54] Moussavi G, Mahmoudi M. Degradation and biodegradability improvement of the reactive red 198 azo dye using catalytic ozone oxidation with MgO nanocrystals. Chemical Engineering Journal. 2009;**152**(1):1-7

[55] Hu C, Xing S, Jiuhui Qu A, et al. Catalytic ozone oxidation of herbicide 2,4-D over cobalt oxide supported on mesoporous zirconia. Journal of Physical Chemistry C. 2008;**112**(15):5978-5983

[56] Sui M, Sheng L, Lu K, et al. FeOOH catalytic ozone oxidation of oxalic acid and the effect of phosphate binding on its catalytic activity. Applied Catalysis B: Environmental. 2010;**96**(1):94-100

[57] Rui CM, Quinta-Ferreira RM. Catalytic ozone oxidation of phenolic acids over a Mn-Ce-O catalyst. Applied Catalysis B: Environmental. 2009;**90**(1): 268-277

[58] Tong S-P, Liu W-P, Leng W-H, Zhang Q-Q. Characteristics of MnO_2 catalytic ozone oxidation of sulfosalicylic acid and propionic acid in water. Chemosphere. 2003;**50**:1359-1364

[59] Ma J, Sui M, Zhang T, et al. Effect of pH on MnO_x/GAC catalyzed ozonation for degradation of nitrobenzene. Water Research. 2005;**39**(5):779-786

[60] Kasprzyk B, Nawrocki J. Preliminary results on ozonation enhancement by a perfluorinated bonded alumina phase. Ozone: Science and Engineering. 2002;**24**:63-68

[61] Kasprzyk-Hordern B, Nawrocki J. The feasibility of using a perfluorinated bonded alumina phase in the ozonation process. Ozone: Science and Engineering. 2003;**25**:185-194

[62] Kasprzyk-Hordern B, Andrzejewski P, Dąbrowska A, Czaczyk K, Nawrocki J. MTBE, DIPE, ETBE and TAME degradation in water using perfluorinated phases as catalysts for ozonation process. Applied Catalysis B: Environmental. 2004;**51**:51-66

[63] Han F, Kambala VSR, Srinivasan M, Rajarathnam D, Naidu R. Tailored titanium dioxide photocatalysts for the degradation of organic dyes in wastewater treatment: A review. Applied Catalysis A: General. 2009;**359**:25-40

[64] Gaya UI, Abdullah AH. Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems. Journal of Photochemistry and Photobiology C: Photochemistry Reviews. 2008;**9**:1-12

[65] Chatterjee D, Dasgupta S. Visible light induced photocatalytic degradation of organic pollutants. Journal of Photochemistry and Photobiology C: Photochemistry Reviews. 2005;**6**:186-205

[66] Suty H, de Traversay C, Cost M. Applications of advanced oxidation processes: Present and future. Water Science and Technology. 2004;**49**: 227-233

[67] Bhatkhande DS, Pangarkar VG. Photocatalytic degradation for environmental applications-a review Journal of Chemical Technology and Biotechnology. 2002;**77**:102-116

[68] Chong MN, Jin B, Chow Christopher WK, Saint C. Recent developments in photocatalytic water treatment technology: A review. Water Research. 2010;**44**(10): 2997-3027

[69] Yang Y, Ma J, Qin Q, Zhai X. Degradation of nitrobenzene by nano-TiO_2 catalyzed ozonation. Journal of Molecular Catalysis A: Chemical. 2007; **267**:41-48

[70] Ye M, Chen Z, Liu X, Ben Y, Shen J. Ozone enhanced activity of aqueous titanium dioxide suspensions for photodegradation of 4-chloronitrobenzene. Journal of Hazardous Materials. 2009;**167**: 1021-1027

[71] Zhang T, Ma J. Catalytic ozone oxidation of trace nitrobenzene in water with synthetic goethite. Journal of Molecular Catalysis A: Chemical. 2008; **279**:82-89

[72] Ma J, Zhang T, Chen ZL. The mechanism of ozone decomposition and oxidation of trace nitrobenzene catalyzed by ferric hydroxide in water. Environmental Science. 2005;**26**(2): 78-82

[73] Legube B, Karpel Vel Leitner N. Catalytic ozone oxidation: A promising advanced oxidation technology for water treatment. Catalysis Today. 1999; **53**(1):61-72

[74] Ikhlaq A, Brown DR, Kasprzyk-Hordern B. Catalytic ozone oxidation for the removal of organic contaminants in water on alumina. Applied Catalysis B: Environmental. 2015;**165**:408-418

[75] Qi F, Chen ZL, Xu BB, Shen JM, Ma J, AnnaHeitz CJ. Influence of surface texture and acid-base properties on ozone decomposition catalyzed by aluminum (hydroxyl) oxides. Applied Catalysis B: Environmental. 2008;**84**: 684-690

[76] Qian FY, Sun XB, Liu YD. Effect of ozone on removal of dissolved organic matter and its biodegradability and adsorbability in biotreated textile effluents. Ozone Science & Engineering. 2013;**35**:7-15

[77] Li CM, Wang DH, Xu X, Wang ZJ. Formation of known and unknown disinfection by-products from natural organic matter fractions during chlorination, chloramination, and ozonation. Science of the Total Environment. 2017;**587-588**:177-184

[78] Gong JL, Liu YD, Sun XB. O_3 and UV/O_3 oxidation of organic constituents of biotreated municipal wastewater. Water Research. 2008;**42**:1238-1244

[79] Fu LY, Wu CY, Zhou YX, Zuo JE, Song GQ, Tan Y. Ozonation reactivity characteristics of dissolved organic matter in secondary petrochemical wastewater by single ozone, ozone/H_2O_2, and ozone/catalyst. Chemosphere. 2019;**233**:34-43

[80] Sun XM, Wu CY, Zhou YX, Han W. Using DOM fraction method to investigate the mechanism of catalytic ozonation for real wastewater. Chemical Engineering Journal. 2019; **369**:100-108

[81] Ratpukdi T, Siripattanakul S, Khan E. Mineralization and biodegradability enhancement of

natural organic matter by ozone—VUV in comparison with ozone, VUV, ozone—UV, and UV: Effects of pH and ozone dose. Water Research. 2010;**44**: 3531-3542

[82] Hoigné J, Bader H. Rate constants of reactions of ozone with organic and inorganic compounds in water—I: Non-dissociating organic compounds. Water Research. 1983;**17**:173-183

[83] Baker A. Fluorescence excitation–emission matrix characterization of some sewage-impacted rivers. Environmental Science & Technology. 2001;**35**:948-953

[84] Chen W, Westerhoff P, Leenheer JA, Booksh K. Fluorescence excitation–emission matrix regional integration to quantify spectra for dissolved organic matter. Environmental Science & Technology. 2003;**37**:5701-5710

[85] Van Sonntag C, Van Gunten U. Chemistry of Ozone in Water and Wastewater Treatment. London, UK: IWA Press; 2012

[86] Wu JF, Su TM, Jiang YX, Xie XL, Qin ZZ, Ji HB. In situ DRIFTS study of O_3 adsorption on CaO, γ-Al_2O_3, CuO, γ-Fe_2O_3 and ZnO at room temperature for the catalytic ozone oxidation of cinnamaldehyde. Applied Surface Science. 2017;**412**:290-305

[87] Petre AL, Carbajo JB, Rosal R, Garcia-Calvo E, Perdigón-Melón JA. CuO/SBA-15 catalyst for the catalytic ozone oxidation of mesoxalic and oxalic acids: Water matrix effects. Chemical Engineering Journal. 2013;**225**:164-173

[88] Fu LY. The study of the operation and mechanism of an integrated ozone and biological aerated filter (BAF) advanced treatment for petrochemical wastewater [PhD dissertation]. Beijing, China: Tsinghua University; 2017

[89] Wu C, Li Y, Zhou Y, Li Z. Upgrading the Chinese biggest petrochemical wastewater treatment plant: Technologies research and full scale application. Science of the Total Environment. 2018;**633**:189-197

[90] Zhang SY, Wu CY, Zhou YX. Effects of bioflocs on advanced treatment of petrochemical secondary effluent by ozone catalytic oxidation. Proceedings of the Annual Meeting of the Chinese Society of Environmental Sciences. 2017:2869-2877

[91] Wu C, Zhou Y, et al. Pretreatment of petrochemical secondary effluent by micro-flocculation and dynasand filtration: Performance and DOM removal characteristics. Water Air & Soil Pollution. 2016;**227**(11):415

[92] Zucker I, Lester Y, Avisar D, et al. Influence of wastewater particles on ozone degradation of trace organic contaminants. Environmental Science and Technology. 2015;**9**:301-308

[93] Zhang S, Wu C, Zhou Y, et al. Effect of wastewater particles on catalytic ozone oxidation in the advanced treatment of petrochemical secondary effluent. Chemical Engineering Journal. 2018;**345**:280-289

[94] Rickert DA, Hunter JV. Colloidal matter in wastewaters and secondary effluents. Journal of Water Pollution Control Federation. 1972;**44**(1):134-139

[95] Wert EC, Gonzales S, Dong MM, et al. Evaluation of enhanced coagulation pretreatment to improve ozone oxidation efficiency in wastewater. Water Research. 2011; **45**(16):5191-5199

[96] Qin YJ, Qin WZ, Yang PF. Advances in enhanced ozone mass transfer. Journal of Process Engineering. 2017; **17**(2):420-426

[97] Li X, Lin C, Jiang Y. Effect of microporous distributor on mass transfer in photocatalytic ozonation reactor. Journal of Environmental Engineering. 2011;**5**(5):1101-1105

[98] Chu JY, Wu CD, Chen WJ. Ozone technology and its application. Beijing: Chemical Industry Press; 2002