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The Application and Reaction Mechanism of Catalytic Ozonation in Water Treatment

Yifei Guo¹, Li Yang¹, Xiaoliang Cheng² and Xiangtao Wang^{1*}

¹Institute of Medicinal Plant Development, Chinese Academy Of Medical Sciences, Peking Union Medical College, 151 Malianwa North Road, Beijing 100094, P. R. China ²Mailstop 977-180A, Life Sciences Division, Lawrence Berkeley National Lab, 717 Potter St, Berkeley, CA 94710

Abstract

Pharmaceuticals and personal care products (PPCPs) are considered as the emerging environmental problem in the recent years. The elimination of PPCPs during water treatment are investigated at lab through different advanced oxidation processes (AOPs), which are the technologies based on the intermediacy of hydroxyl and other radicals to oxidize pollutants. Catalytic ozonation is proved as an effective technology for the removal of organics from wastewater. The paper presents a short review about the introduction of the ozonation catalysts and the reaction mechanism of the catalytic ozonation. The main aim is to provide a new and effective method in the removal of PPCPs in the aqueous solution.

Keywords: Pharmaceuticals; Ozone; AOPs; Catalyst; Catalytic ozonation

Introduction

The demand for fresh water is increasing with the growth in world population, and obtaining an adequate supply of clean water has likely been the challenge for many countries. To solve this problem, using water from unconventional sources is the best method from economic point of view. To make wastewater reuse safety, all the pollutants including biodegradable organic matter [1,2], pathogens [3], and micropollutants [4] presented at wastewater should be removed completely.

Every year the large number of pharmaceuticals and personal care products (PPCPs) enter the environment by the incomplete sewage treatment. PPCPs are now recognized as a new class of emerging environmental contaminants and brings increasing concern and scientific interests [5-7]. In recent years, there are numerous reports about the occurrences of PPCPs in wastewater, surface water, groundwater, and drinking water [8-11]. Even though the concentration of detected PPCPs in aqueous environment are low and often range from ng/L to μ g/L levels, the potential dangers of PPCPs and their metabolites to human and ecological health exist due to many of them for some persistence in the body [12-14].

According to present knowledge, the elimination of PPCPs is mainly by the biological method [15], adsorption on activated carbon [16], reverse osmosis [17], and separation by membranes [18], ozonation [19,20], photocatalysis [21], photo-Fenton [22,23], UV radiation [24]. Biological treatment is an environmentally friendly way with reasonable costs, but they are not adequate to treat non-biodegradable wastewaters and, usually, require a long period for micro-organisms to degrade the pollutants [25]. Thermal treatment at high temperature, although effective, is not economically feasible. Chemical treatments are not resolving requiring a post-treatment [26]. Advanced oxidation processes (AOPs) were frequently selected as a water treatment option to remove refractory and toxic organic compounds present in water, however, the traditional AOPs, including photocatalysis and photo-Fenton can hardly meet the requirements of the practical applications, because the high cost and the low mineralization efficiency [27].

Ozone is used widely in water treatment technology because of its powerful oxidation [28-30]. However, it has been reported, in most cases, the ozonation cannot completely degrade organic compounds and sometimes produce toxic intermediates. In such cases, the efficiency of oxidation can be improved by employing ozone together with H_2O_2 or UV irradiation to generate free radicals, mainly hydroxyl radicals (HO•) with high oxidation potential [24,31], however they present some drawbacks such as the residual of H_2O_2 [32], the shorter life and higher energy consumption of UV lamp [33].

As a new and the most promising development in the research of advanced oxidation water treatment, heterogeneous catalytic ozonation has been attracting the increasing interest due to its potentially higher effectiveness in the degradation, and mineralization of refractory organic pollutants and lower negative effect on water quality [34-37]. So far, metals oxide (e.g. MgO [38], Co₃O₄ [39,40], ZnO [41], TiO₂ [42], Al₂O₂ [43]), metal or metal oxides on supports (e.g. Pr/Al₂O₂ [44], Co/Al₂O₃ [45], Au/Bi₂O₃ [46], MnO₂/MWCNT [37], TiO₂/silicagel [47], TiO₂/Al₂O₃ [48]) have been reported as effective catalysts for ozonation processes. According to the previous investigation, two possible pathways of the heterogeneous catalytic ozonation can be speculated [49]: (1) enhancing HO• generation from aqueous ozone and (2) forming surface complexes between the carboxylic groups of the pollutants and the surface metal sites of the catalyst, which renders the coordinated pollutants more reactive towards molecular ozone. This paper gives a short review about the introduction of the ozonation catalysts and the mechanism of the catalytic ozonation.

Ozonation

The organic pollutants can be oxidized with ozone by direct or indirect pathways. The direct oxidation $(M + O_3)$ of organic pollutants by ozone is a selective reaction with slow reaction rate constants. The ozone molecule can directly react with the organic pollutants through

*Corresponding author: Xiangtao Wang, Institute of Medicinal Plant Development, Chinese Academy of Medical Sciences, Peking Union Medical College, 151 Malianwa North Road, Beijing 100094, P. R. China, E-mail: xtwang@implad.ac.cn

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1,3 dipolar cycloaddition, electrophilic, and nucleophilic reaction [50]. In water, only the former two reactions have been identified with many organics [51]. On the contrary, the nucleophilic reaction has been proposed in only a few cases in non-aqueous systems [52].

The indirect type of ozonation is due to the reactions of free radical species, especially the hydroxyl radical (HO \bullet), with the organic matter present in water. These free radicals come from reaction mechanisms of ozone decomposition in water that can be initiated by the hydroxyl ion or, to be more precise, by the hydroperoxide ion.

The mechanism of ozone decomposition in water is pretty complicated, so far the most popular reaction model to explain the decomposition of ozone is the chain mechanism of Weiss, which the procedure is combined with initiation, propagation, and termination as follows [53,54] (Table 1).

Supportive of this chain model, Bühler et al. proved experimentally that the HO radicals are dominant decomposition products of ozone in aqueous solutions, and accelerate the decomposition of ozone [55].

The rate of ozone decomposition in water is affected by pH, which is accelerated in basic aqueous solution. Actually, several compounds could be the initiator, promoter, or inhibitor in nonpure water [56,57]. The Initiator (OH⁻, H₂O₂/HO₂⁻, Fe²⁺) can lead to the formation of •O₂ in the decomposition of ozone. The promoters (R₂–CH–OH, aryl– (R), formate, humic substances, O₃) are responsible for the regeneration of the •O₂⁻ ion from the hydroxyl radicals. The inhibitors (CH₃–COO⁻, alkyl– (R), HCO₃⁻/CO₃²⁻, humic substances) are compounds capable of consuming hydroxyl radicals without the regeneration of the superoxide anion.

In summary, the ozone reactions could be acted with unsaturated aromatic compounds, unsaturated aliphatic compounds, and some special functional groups. If the radical reaction is inhibited, the direct ozone reaction becomes more important. Ozone reaction is more inclined to direct reaction with increasing the inhibitor concentration. Therefore, inorganic carbon and organics show the substantial impact during these reactions.

Due to its high oxidation efficiency and environmentally friendly, ozone is widely used to oxidize the organic pollutants in water, however, it still remain problems. First, the utilization of ozone is low during the ozonation procedure, the solubility of ozone in water is poor, and there is a part of soluble ozone can be changed to HO•, which is nonselective oxidants [58,59]. Besides, comparing with other wastewater treatment methods, ozone is high cost to produce. Second, it is difficult to remove TOC and COD in water completely by ozonation. All these limit the development of ozonation.

Catalytic Ozonation

Catalytic ozonation has received increasing attention during past decades, due to its higher effectiveness in the degradation of organic pollutants. Organics can be oxidized by catalytic ozonation in the ambient temperature and pressure, which are difficult to dissociate by single ozonation. Catalytic ozonation shows great advantages in refractory organics in water, and is expected to be the powerful and valuable technology in water treatment. According to the different catalysts, catalytic ozonation can be divided to two kinds: one is the homogeneous catalytic ozonation, which is the metal ions as the catalysts present in the reaction system; the other is heterogeneous catalytic ozonation, the main catalysts are metal oxide and metal or metal oxide on supports.

Homogeneous catalytic ozonation

Transition metal ions (Fe²⁺, Mn²⁺, Ni²⁺, Co²⁺, Cd²⁺, Cu²⁺, Ag⁺, Cr²⁺, Zn²⁺) are usually used as the catalysts in homogeneous catalytic procedure, to degrade the organic pollutants in water [60-65]. During this procedure, metal ions decide the rate of reaction system, the selectivity of ozone oxidation system, and the efficiency of ozone utilization.

The mechanism of homogeneous catalytic ozonation is based on an ozone decomposition reaction followed by the generation of hydroxyl radicals. The metal ions accelerate the decomposition of ozone to produce the $\bullet O_2^{-1}$, and then electron of $\bullet O_2^{-1}$ transfer to O_3 to gain $\bullet O_3$, HO• is accepted successfully [66]. In addition, as proposed by Pines and Reckhow [60], for a cobalt (II) oxalate/ozone system at pH 6, it is proposed that the first step in the reaction pathway is the formation of a cobalt (II) -oxalate complex. Cobalt (II) oxalate is then oxidized by ozone to form cobalt (III) oxalate. It is suspected that the site of attack is the metal center. The partial donation of electron density from oxalate to cobalt (II) may increase the reactivity of cobalt (II) oxalate as compared to free cobalt (III). The catalytic cycle is completed with the decomposition of cobalt (III) complex to form an oxalate radical and cobalt (II). The proposed reaction pathway for the ozonation of cobalt (II) -monooxalate complex is shown in Figure 1.

Homogeneous catalytic ozonation can effectively improve the efficiency of removal of organic pollutants in water, but the disadvantage of this technology is to introduce ions and result in the secondary pollution, which lead to increase the costs of water treatment.

Heterogeneous catalytic ozonation

Heterogeneous catalysts with higher stability and lower loss can improve the efficiency of ozone decomposition, and be recycled and reused without further treatment. Due to these advantages, the heterogeneous catalytic ozonation is used widely in water treatment. The efficiency of the catalytic ozonation process depends to a great extent on the catalyst and its surface properties as well as the pH of the solution that influences the properties of the surface active sites and ozone decomposition reactions in aqueous solutions [57]. The most important factor for heterogeneous system is the choice of catalysts. Now, the catalysts studied by researcher widely are metal oxides, and metals or metal oxides on supports.

Initiation

Termination

Propagation

 $\begin{array}{l} \mathsf{O}_3 + \mathsf{HO}_2 \bullet \to \mathsf{HO} \bullet + 2\mathsf{O}_2\\ \mathsf{2HO}_2 \bullet \to \mathsf{H}_2\mathsf{O}_2 + \mathsf{O}_2\\ \end{array}$ Table 1

 $O_3 + H_2O \rightarrow 2HO + O_2$

 $O_3^- + OH^- \rightarrow \bullet O_2^- + HO_2^-$

 $O_3 + HO \rightarrow HO_2 + O_2$





Metal oxides: The catalytic efficiency of metal oxides is decided by their physical and chemical properties. Physical properties include surface area, pore size, and surface charge. The main chemical properties include chemical stability, and active surface sites. Several researches claim that, some metal oxides, such as Al_2O_3 [67-69], MnO_2 [70,71], TiO₂ [72,73], ZnO [41,74], and FeOOH [75,76] show excellent catalytic activity as the heterogeneous catalysts in degrading the organic pollutants in aqueous solution.

Metal or metal oxides on supports : The activity of supported catalysts is affected by the factors as follows: (1) the choice of the supports. The function of the catalyst supports is able to provide effective surface area and suitable pore structure, make the catalysts to obtain the excellent mechanical strength, thermal stability, and play the role of active center. In addition, the ordered mesoporous materials with larger surface area are suitable for catalyst supports. At present, the catalyst supports used widely are TiO₂, Al₂O₃, activated carbon, and ceramic honeycomb and so on. (2) The active components of the catalysts. In general, the noble metal catalysts have the better catalytic activity than transition metal. However, due to the transition metal is relatively inexpensive, has higher thermal stability, and moderate mechanical strength, which lead to transition metal used widely in catalysts. (3) Preparation of the catalysts. The structure and dispersion of the catalysts are affected by the preparation method, so good catalyst preparation process can significantly improve the catalytic activity. Currently, the supports for heterogeneous system are including Al₂O₃, TiO₂, active carbon, and clay; the active components are Fe, Co, Mn, Cu, Ni and so on [35,37,44,77-86]. The results show that the supported catalysts give excellent activity during the ozone decomposition.

Mechanism of heterogeneous catalytic ozonation: The three phases, including gaseous, liquid, and solid, are involved in aqueous heterogeneous catalytic ozonation. In addition, the catalytic process is affected by the kinds of catalysts, the target pollutants, and the pH value of solution, therefore, it is difficult to establish effective methods to track the process of reactive intermediates. Although some researchers have conducted several studies about the heterogeneous catalytic system, there is undefined conclusion. Two representative mechanisms are as follows:

(1) Interfacial reaction mechanism. In this mechanism, the main function of catalysts is to act as adsorptive material. First, using its large surface to adsorb and then remove the organic pollutants. Second, provide active adsorptive site and combine with aim molecules to form active complexes with lower activation energy, all of these make the pollutants could be oxidized simply by gaseous ozone and ozone or HO• in solution. And then, the intermediates can be further oxidized in the surface of catalysts, or desorbed to the aqueous solution to be oxidized by ozone or HO•. The procedure is shown in Figure 2 [59].

Legube et al. [59] proposed that, the catalyst would behave only as adsorbent (Me-OH); ozone and hydroxyl radical would be the oxidant species. Firstly, initial organic acid would be adsorbed on the surface of catalyst. Secondly, a strong negative charge would appear into the six or five-membered chelate ring at the surface. Lastly, the ozone or hydroxyl radical would oxidize the surface complex to give oxidation by-products either desorbed in solution or still adsorbed at the surface of catalyst (Figure 2).

Essentially, catalysts act as adsorptive materials in this mechanism, combine with organics to form the chelate that can be degraded by ozone or HO radical easier. This mechanism can explain the catalytic ozonation system with the good adsorptive properties. However, some heterogeneous catalytic process with poor adsorptive ability is difficult to be explained by this mechanism.

(2) HO• mechanism. This mechanism proposes that the metal oxide catalysts can increase the solubility of ozone and initiates the ozone decomposition. This mechanism speculates that surface hydroxyl groups of metal oxides play a vital role in the formation of HO•. Soluble ozone in aqueous solution is adsorbed to the surface of the catalyst, a series of radical chain transfer are occurred to generate much HO•, which hold a high oxidation potential and can oxide the organic pollutants in wastewater. The catalytic ozonation system with poor adsorptive ability can be explained by this mechanism, the procedure is shown in Figure 3.

Legube et al. [59] also propose that in this mechanism, the catalyst would react with both ozone and adsorbed organics. Starting to the reduced catalyst, ozone would oxidize metal. The reaction of ozone on reduced metal could lead to HO radical. Organic acids would be adsorbed on oxidized catalyst and then oxidized by an electron-transfer reaction to give again reduced catalyst. The organic radical species A• would be then easily desorbed from catalyst and subsequently oxidized by HO or O₃ either in bulk solution, or more probably, into the thickness of electric double layer (Figure 3).



Figure 2: The mechanism for adsorption on catalyst and oxidation by ozone or HO radical of adsorbed organic.







Ernst et al. [68] proposed, the adsorption of organics on the catalyst's surface would not be necessary to provide the catalytic effect, moreover, DOC adsorption would probably inhibit the effect due to an overlaying of hydroxyl groups. As can be seen from Figure 4, dissolved ozone adsorbs first on the catalyst's surface and then decomposes rapidly due to presence of hydroxyl surface groups. Due to the decomposition of ozone, active atomic oxygen is produced and reacted with alumina hydroxyl surface groups to form O_2H^- anions which subsequently can react very fast with another O_3 to form O_2H^- and the oxide or the O_3^- radical can be produced directly. This radical reacts subsequently with another ozone molecule to generate an O_3^- radical. The O_3^- radical decomposes into oxygen and a free HO radical which can oxidize organic compounds either in solution or on the surface or in a thin film layer above the surface of the catalyst (Figure 4).

Thus, during the process of pollutants degraded by heterogeneous catalytic ozonation, when the interfacial reaction occurs, and the characteristics of organics play the decisive role. The pH of solution affects the adsorption of organic pollutants on the catalyst surface, the adsorption is the rate controlling step of the interfacial reactions, which determines the removal degree of organic pollutants. For HO• mechanism, the activity of catalysts is related with the surface properties of metal oxides, especially the surface Lewis acid sites playing the important role in the catalytic reaction.

Conclusions

Ozone is an environmentally friendly oxidant, since it decomposes to O_2 without producing self-derived byproducts in the oxidation reactions. The application of ozone in water treatment systems has experienced rapid growth in the past decades, including homogeneous and heterogeneous catalytic ozonation. Recent research has shown that heterogeneous catalytic ozonation are useful tools for studying fundamental problems, both the active components and the support play important roles in this system due to their desirable structure and surface characteristics that affect the properties of the surface active sites and the decomposition of pharmaceuticals and personal care products (PPCPs). Besides, in order to explain the process of heterogeneous catalytic ozonation, the reaction mechanisms are summarized in this paper.

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