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The mechanism of Fe (III)-catalyzed ozonation of phenol*

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Abstract: Fe (III)-catalyzed ozonation yielded better degradation rate and extent of COD (Chemical Oxygen Demand) or oxalic acid as compared with oxidation by ozone alone. Two parameters with strong effects on the efficiency of ozonation are pH of the solution and the catalyst (Fe^{3+}) dosage. The existence of a critical pH value determining the catalysis of Fe (III) in acid conditions was observed in phenol and oxalic acid systems. The best efficiency of catalysis was obtained at a moderate concentration of the catalyst. A reasonable mechanism of Fe (III)-catalyzed ozonation of phenol was obtained based on the results and literature.

Key words: Catalytic ozonation, Phenol, Oxalic acid, Fe (III), Mechanism
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INTRODUCTION

Ozonation is a promising alternative in water treatment for the removal of water pollutants, odors, color and tastes, or increasing the BOD_5-COD ratio through the degradation of big molecular weight contaminants to lower molecular weight acids as preparation for the subsequent biodegradation. But ozone is also well known as a highly selective oxidant without the potential to further oxidize intermediates. It is necessary to improve the efficiency of ozone mineralization of pollutants in order to overcome the disadvantage of expensive chemical oxidation reaction due to the high production cost of ozone, generated in-situ, and also because of the low solubility of ozone in aqueous solutions.

Pollutant substances may be degraded by direct oxidation with ozone alone and/or by indirect oxidation with hydroxyl radicals formed through ozone decomposition. These refractory intermediates are mainly oxidized by ozone as a promoter of radical mechanism. The rate of ozone decomposition increases with increase of solution pH because those hydroxyl ions are good catalysts for enhancing the reaction with ozone to form radicals. So ozonation in alkaline conditions could be regarded as a kind of advanced oxidation process. However, in acidic conditions, aqueous ozone has better stability due to the absence of initiators. AOPs (Advanced Oxidation Process), including ozone with UV, ozone with hydrogen peroxide, Fenton's reagents, and catalytic ozonation, for completely mineralizing all organic solutes are well developed. The presence of some transition metal ions (Fe, Mn, Ni, Zn, etc.) enhances the efficiency of ozonation for the removal of different organic compounds in aqueous solution (Legube *et al*., 1999).

In this work, Fe (III)-catalyzed ozonation for removing phenol and oxalic acid was investigated. The presence of iron ions improved the degradation efficiency of COD of phenol solution, and to simplify the experimental system for researching the

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formation mechanism of more powerful oxidants; oxalic acid was chosen as simulated pollutant, as oxalic acid may be converted to CO_2 and water without complicated intermediates.

EXPERIMENTAL DETAILS

Catalytic ozonation experiment

The experiments were performed in a semi-batch reactor (Fig.1), 1 L of an aqueous buffered solution containing 50 mg of phenol or 100 mg of oxalic acid at constant desired temperature controlled by the water bath. The reaction was started by bubbling a 36 L/h ozonized oxygen stream with ozone content of 3.0 g/L. Samples withdrawn by a glass syringe at different ozonation times were passed through 0.45 μm membrane filter, and analyzed for organic solutes, aqueous ozone concentration and COD, using HPLC.

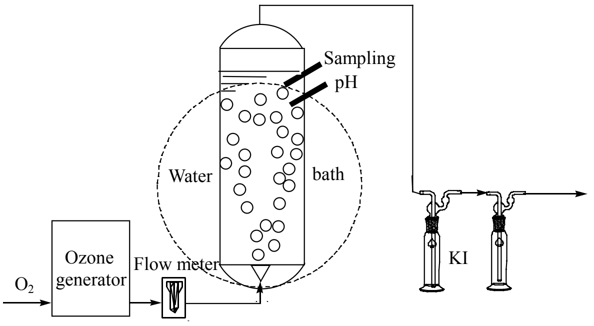

Fig.1 Schematic diagram of experimental reaction

Analysis procedures

Organic solutes (phenol, its ozonation by-products and oxalic acid) were analyzed using Shimadzu HPLC (LC-10ATvp), coupled to SPD-10Avp UV-Vis detector (214 nm), using 0.2% H_3PO_4 solution and pure methanol mixture (1:1 volume ratio) mobile phase at column temperature of 20 °C, and a total flow rate of 1 ml/min. The samples (20 μl) were injected manually through an injection port.

COD of the phenol solution was determined by standard method.

Concentration of aqueous ozone was determined by standard indigo method (Bader and Hoigne, 1981).

RESULTS AND DISCUSSION

Oxidation of phenol

The rate of direct ozonation of phenol was over three-order magnitude (Hoigne and Bader, 1983), which was much faster than that of ozone self-decomposition either in acidic or in alkaline conditions. Direct oxidation predominated the reaction of phenol and ozone in the presence or absence of catalysts. As shown in Fig.2, the concentration of phenol in aqueous solution almost linearly decreased, that is to say, the kinetics of reaction was pseudo-zero order to phenol concentration when there existed high phenol quantity of more than 10 mg/L in the sample water. It could be concluded that the mass transfer of gas phase ozone to the liquid was the limiting step of the whole process. So the possible catalysis effect of Fe^{3+} catalysis on the degradation of phenol might be masked by the slow mass transfer of ozone.

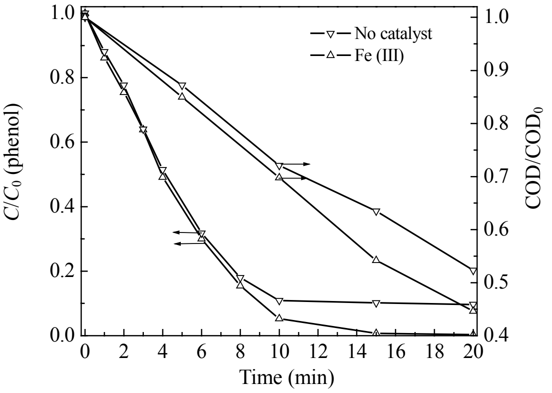

Fig.2 Comparison of catalytic ozonation with ozonation (T=20 °C, C_0=75 mg/L, C_{Fe}=10 mg/L, pH=2.9, Q_{O_3} =36 L/h)

Although the presence of catalyst (Fe^{3+}) did not promote the conversion of phenol, it was observed that iron ions accelerated the removal rate and increased the removal extent of COD in simulated wastewater after 10 min of reaction time as compared to ozone alone. The reaction time of 10 min seemed to be the turning point of the whole reaction, after which the concentration of aqueous ozone suddenly increased from 0.3 mg/L at 10 min to 3 mg/L at 20 min, the gas-off ozone content would increase, which not only needed more KI solution to remove residual ozone from the off-gas, but also meant that the mass transfer of ozone was strongly prevented due to the decrease of concentration differences; to overcome which, it was necessary to enhance the reactivity of ozone with stable organic solutes. Some authors (Legube *et al.*, 1999; Arslan, 2001; Abe and Tanaka, 1997) reported that higher degrading efficiency of TOC (Total Organic Carbon) was obtained in the presence of some transitional metallic ions or their complexes, possibly due to the catalyzed formation of secondary oxidants (hydroxyl radicals) by these substances.

COD should be chosen as a better indicator than phenol concentration, and described the whole, not partial degradation of all organic pollutants including not only phenol, but also its ozonized by-products in simulated wastewater.

The efficiency of COD removal was strongly affected by two parameters, pH value and iron ions concentration, as presented in Table 1. When pH=2.8, catalysis accelerated the velocity of COD removal, while at pH=3.9, the COD removal rates were similar to those by ozone alone. Catalysis was performed by more powerful oxidants, for example hydroxyl radicals or more reactive substances, such as Mn (III)-oxalic acid (AO) complexes, which were produced in sufficient quantity to oxidize the refractory organic solutes. In general, H^+ could participate or OH^- might be produced in the reaction formula of producing these more oxidized species (Colin and Robble, 1999; Villasenor *et al.*, 2002). So it seems that there is a critical pH value in acidic conditions, although the exact value was not determined in our study.

Table 1 Effects of pH and Fe (III) dosage on removal of COD

	pH	C_{Fe} (mg/L)	Removal efficiency of COD (%)	
			10 min	20 min
1	2.8	0	18.91	47.68
2	2.8	5	26	50.95
3	2.8	10	30.21	55.36
4	2.8	25	25.5	46.2
5	3.9	10	16.00	47.67

Higher efficiency of catalysis was achieved when Fe (III) concentration was 10 mg/L instead of 25 mg/L and 5 mg/L. At low Fe (III) concentration, only a small amount of catalysts participated in producing more powerful oxidants; so the amount of active substances formed was less than that needed, so the increase of the Fe (III) dosage increased significantly the degradation rate of organic solutes till a certain content. However, thereafter the best efficiency of catalytic ozonation was obtained at a moderate concentration of metallic iron ions, excess of Fe (III) had negative effect on conversion of low molecular weight acid, possibly because that would excessively consume O_2^- radicals formed in-situ during the reaction, leading to termination of the chain reaction to successfully produce hydroxyl radicals.

$$Fe^{3+}+\cdot O_2^- \rightarrow Fe^{2+}+O_2$$

Since Fe (III)-catalyzed ozonation was aimed at the refractory intermediaters, oxidation of oxalic acid was carried out to further prove the catalysis of Fe (III). Main parameters, pH values and Fe (III) dosages, had similar effects on mineralization of oxalic acid as compared to those of phenol solution (Fig.3). It was obvious that the catalysis efficiency of oxalic acid was much higher than that of phenol solution due to the greater stability of oxalic acid.

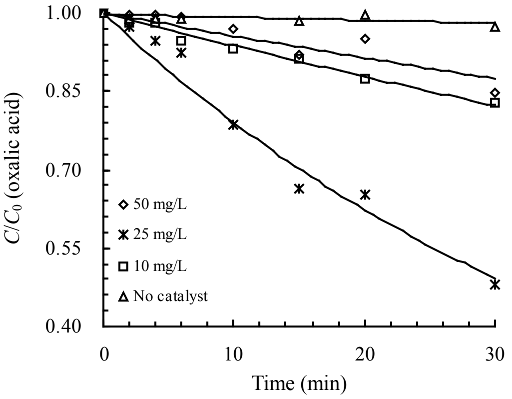

Fig.3 Effects of Fe (III) concentration on reactionsystem (T=20 °C, pH=3, C_0=100 mg/L, Q_{O_3} =0.6 L/min)

Mechanism of phenol degradation

The degradation products of phenol might in theory be classified as primary products (such as resorcinol, catechol and hydroquinone), more oxidized products (such as maleic acid, benquenze, pyruvic acid and oxalic acid), and the final products (CO_2 and water). In our study, only several main products were detected. The concentration of the different products varied with reaction time as shown in Fig.4. The primary products (such as resorcinol, catechol and hydroquinone) were not detected possibly because their concentrations were below the limiting detection value of HPLC after all ozone could very easily further oxidize them. Some other intermediate products, such as maliec acid and benquenze were unsaturated organic substances with double-carbon bonds easily attacked by ozone molecules. So these products that would be further oxidized to more steady species, such as oxalic acid. Oxalic acid should be a certain degradation product of phenol ozonation based on the electrophilic character of ozone molecules. The oxalic acid molecule is symmetrical, with each of its carbon atoms stabilized by carboxyl. A high quantity of oxalic acid was detected as expected; with the amount increasing with the reaction time.

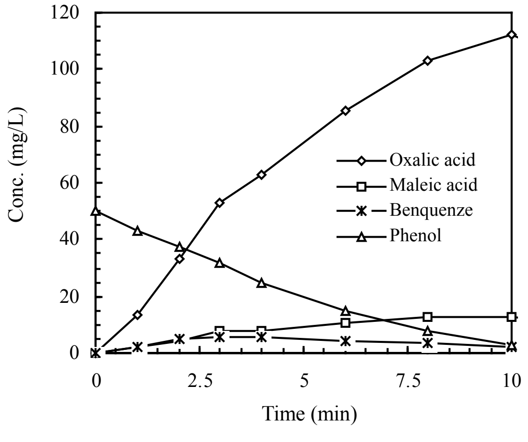

Fig.4 Conc. of phenol and its byproducts vs reaction time

From the above discussion, it was concluded that the degradation of phenol by ozonation occured via the following simple pathway in our study conditions (Fig.5).

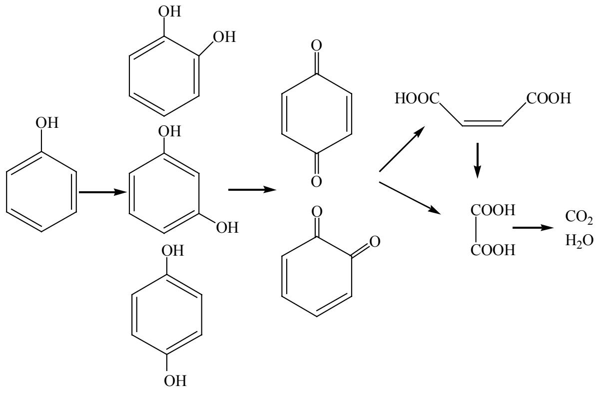

Fig.5 Reaction pathway in phenol degradation

Mechanism of Fe (III)-catalyzed ozonation

Complexes of Fe^{3+} with organic and inorganic ligands are much less reactive than uncomplexed forms. Certain Fe^{3+} complexes, especially the complex of Fe (III) $(AO)_n$ (AO: oxalic species) are very sensitive to sunlight that result in the reduction of iron and the production of $\cdot HO_2/\cdot O_2^-$. The formation reactions of these intermediates comprise the initiation step of the chain reaction mechanism.

Depending on the reaction system, ozonation may lead to a build-up of H_2O_2 (Hoigne and Bader, 1976). This may be due to reactions of superoxide ions that can also be the product of O_3 decomposition and of organic peroxide intermediates composition. Lower pH value of aqueous solution led to more amount generation of H_2O_2, whereas little H_2O_2 was formed at neutral and basic condition.

In our studied conditions, there existed a complicated oxidation system involving $O_3/H_2O_2/$ Fe (III) $(AO^{2-})_n$ during the catalytic ozonation of phenol and oxalic acid at pH=3, which might be regarded as the combination of O_3/H_2O_2 with similar Fenton's reagent. Many intermediates, such as Fe (II), AO^-, H_2O_2, etc., generated during the chain reaction of hydroxyl radicals in the role of initiator and/or promoter. Their constant interaction is too fast to be the limiting step of the oxidation reaction. In fact, the pH of solution and the concentration of Fe (III) exerted great effect on the reaction rate, which suggested that the amount of H_2O_2 and $\cdot O_2^-$ participating in the chain reaction governed the whole process. The excess Fe (III) reacted with $\cdot O_2^-$ competing with radicals' formation reaction, although its reduced products (Fe^{2+}) would improve H_2O_2 dissociation into hydroxyl radicals. This ultimately led to the negative effect of excess Fe (III) on the oxidation of organic mater.

CONCLUSION

Fe^{3+} dosage and pH of the solution have significant effects on the oxidation of phenol and oxalic acid by Fe (III)/O_3 system. The removal efficiency of phenol solution COD is improved in the presence of Fe (III), and the catalyst accelerated the removal of COD when pH=2.8, but at pH=3.9, the removal efficiency was similar to that by ozone alone. Better efficiency of the catalysis is obtained when the concentration of Fe (III) is 10 mg/L rather than 25 mg/L and 5 mg/L. Maliec acid, bequenze and oxalic acid are the main intermediates during the catalytic ozonation of phenol. In the end the reasonable mechanism of Fe (III)-catalyzed oxidation is deduced based on the results and literature.

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