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Effect of Ozonation of Naphthalene Derivatives on Their Elimination, TOC, and Biodegradability

Zhu S.,[1] Zhang Q.,[1] Wang L.,[1] Chen J.,[1] Lian H.[2]

[1] State Key Laboratory of Pollution Control and Resource Reuse, Department of Environmental Science and Engineering, Nanjing University, 210093, Nanjing, People's Republic of China
[2] Center of Materials Analysis, Nanjing University, 210093, Nanjing, People's Republic of China

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The main parameters to control the degree of pollution, like COD and BOD, could be reduced by biological oxidation, which is conventionally combined with ozone or other chemical oxidation processes. Ozone is a powerful oxidizing reagent and hence is used for purification of drinking water as well as wastewater. Ozonation of organic compounds in water with high ozone dosages usually produces oxygenated organic products that are more biodegradable. This was shown by investigations of ozonation of organic model compounds (Balcioglu and Getoff 1998; Gilbert 1983; 1988; Legube, et al. 1981; Narkis et al. 1984; 1980; Wang 1990; Hoigne and Bader 1978; 1983a; 1983b). This effect is used in water works where ozone is applied to wastewater and especially effluents from municipal biological treatment plants in order to improve the removal of organic material (Sonthermer, et al. 1978; Heinzle, et al. 1995; Uesaka, et al. 1997). Studies performed on a pilot plant scale showed that sometimes an increase in ozone dosage had no additional effect on COD removal (Janssens et al.1984; van Leeuwen et al.1984; Brunet et al.1982). In most of the investigations an improvement in biodegradability of refractive organic substances has been observed, However, the results vary considerably. Depending on the particular compounds studied, the effect of ozonation can be relatively small (Beltran, et al. 1997; Jones et al. 1985; Stover et al. 1982). These results are specific for the special wastewater investigated and; because the compounds of different waste waters vary significantly, they cannot automatically be extrapolated to the other waters to be treated.

Naphthalene compounds and many of their derivatives are widely used in a number of industrial operations such as the manufacture of chemical solvents, pesticides, polymers, explosives and many other products of everyday use. These derivatives can pose a health hazard and have been designated as priority pollutants. Most are toxic or inhibitory to biological activities and therefore present a serious problem in conventional wastewater treatment systems. Researchers have recently reported a possible alternative by showing that ozonation enhanced the anaerobic biodegradability of these materials (Stover et al.1982; Medley and Stover 1983; Gilbert 1983; 1988; Wang, et al. 1989;Wang 1990).

The aim of this study was to investigate the change of TOC, biodegradability and their concentrations of five naphthalene derivatives as model compounds treated by ozonation.

Correspondence to: Zhu S.

HPLC(high performance liquid chromatograph) was used to determine the degradation products. The values of TOC (total organic compound) and COD of the treated compounds were tested as well.

MATERIALS AND METHODS

Each experiment was performed two times. Ozonation was performed in the experimental set up shown in Figure 1. Ozone gas was continuously bubbled into a plexiglass reactor(9.5cm (ID) × 100cm (Height)). The agitation of reaction solution was accomplished by a multi porous diffuser in the bottom of the reactor which allows the gas (air and generated ozone)and the liquid (aqueous solutions of the compounds studied) to be mixed. Ozone was produced with an electrolytic laboratory type generator (Model NDC-02). Air was used for the generation feed gas. The piping materials were all glass and PTFE. The gas feed rate was 0.6 $m^3 \cdot nhr^{-1}$. The average productivity of the ozone generator was 210 mg $\cdot hr^{-1}$. Ozone in the gas phase both at the reactor inlet and outlet was measured by an ultraviolet photometer (Beijing Analysis Instrument Corp, Model BF-8810).

2-naphthol, 2-naphthylsulfric acid, 2-amino naphthalene, Tobias' acid, Peri acid were purchased from Shanghai Reagent Company and have purity of 98% or better. Their structures are listed in Figure2. These compounds were employed without further purification. They were dissolved in distilled water, which had been saturated with corresponding gas before irradiation with ozone. It is very difficult for Peri acid to be dissolved in the water. Its dissolve was accomplished with an ultrasonator. The reactions were allowed to occur without the addition of pH adjustment. The initial concentrations of all the naphthalene compounds studied were $1.4x10^{-3}$ mol $\cdot L^{-1}$. The experiments were conducted at room temperature(30.0 ± 0.5 °C). The target samples(5.0 liters) were treated with ozonated air.

The samples were taken at appropriate time intervals and tested by HPLC (Varian Corp, Model 5060, the analysis column is Lichrosorb RP-18, 150mm (Length)x 4mm(I.D.) with an ultra violet spectrophotometric detector, Model UV-100).

Biodegradability of the studied compounds was tested using a Warburg respiration meter (Shanghai Scientific Equipment Corp., Model SKW -3). The biomass were cultivated for ten to fifteen days and then for another twenty four hours aerated without the feed of the model compound. The biomass and the studied compound were employed in the Warburg respiration detector and studied for 8 hours. In this study, COD was performed with potassium dichromate. TOC was conducted with TOC-5000 analyzer (Shimadzu Corp.). The feed speed was 150 mL per minute.

RESULTS AND DISCUSSION

The effects of ozonation of the five naphthalene compounds are shown in Figure 2. All of the

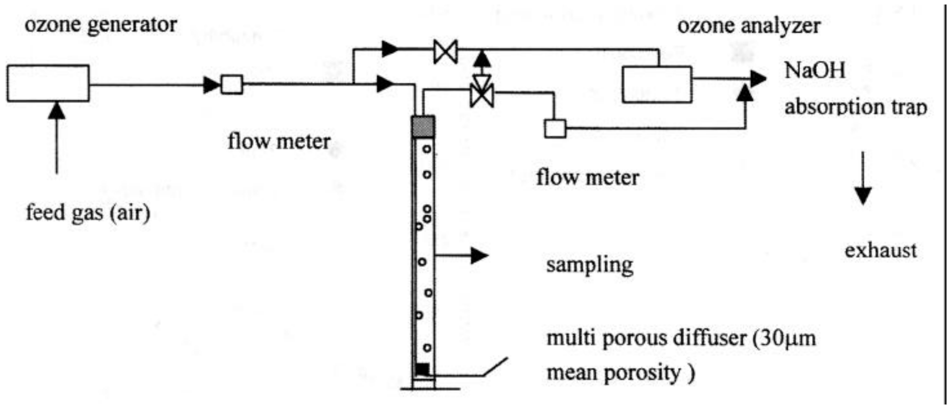

Figure 1. Scheme of experimental set up

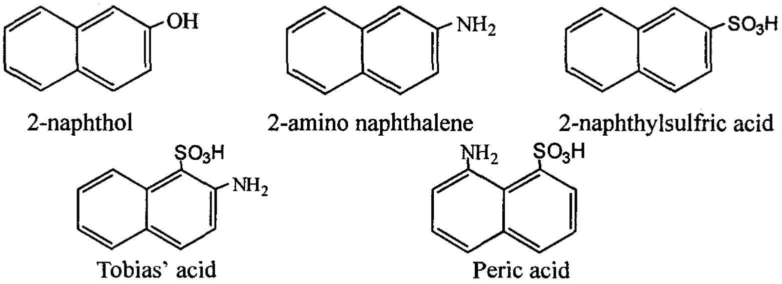

Figure 2. Molecule Structures of the five naphthalene derivatives

studied compounds can be eliminated by ozone. The colour of the solutions became gradually red. That is because ozonation of these derivatives has produced quinones and hydroxyl aromatic compounds (Yun G, et al. 1986). The compounds were eliminated in two ways: the direct attack by ozone molecules and the radical way by the generated hydroxyl and (or) other radicals. Radicals may first attack the substitute of the aromatic compound while ozone molecules is likely to attack aromatic nucleus (Razumovskii, 1984). So the reaction rate constants of different substituted naphthalene derivatives vary by many orders of magnitude. The reaction intermediates were very complex and many were still remain unidentified. Comparing the elimination ratio of these compounds corresponding to a specific ozonation time, naphthalene derivatives showed different reactivity during ozonation. Their differences during ozonation are due to different reacting sites with ozone. 2-naphthol (hydroxyl substitute) and 2-amino naphthalene (amino substitute) have electron contribution effects and the reaction with ozone can take place at the substitutes and the two rings. While the sulfuric substitute in 2-naphthylsulfric acid has an electrophilic effect, the reaction with ozone takes place at the ring without the sulfuric acid.

Figure 3 shows that the concentration of ozone in the exit gas changes with the reaction time.

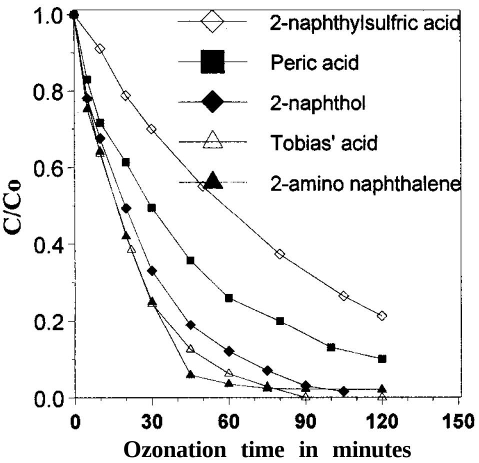

Figure 3. Plots of C/Co of the naphthalene derivatives verse ozonation time

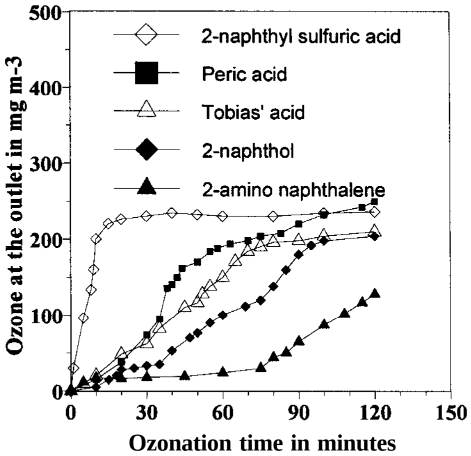

Figure 4. Plots of ozone concentration in the exit gas verse ozonation time

In this experiment, it was found that the concentration of ozone in the feed gas is (350 ± 10) $mg.m^{-3}$. For 2-naphthylsulfric acid ozone concentration in the exit gas is constant after a few minutes of ozonation. The ozone concentration of 2-naphthol was almost zero for the first twenty minutes and then increased gradually to 100 mg/m^3 and then kept constant for some time period. In Figure 4, it can be seen that $C_{o3,o}$, the exit ozone concentration, during ozonation of 2-naphthylsulfric acid was the highest in the five corresponding compounds; that of 2-amino naphthalene was the lowest. The curves of Peri acid and Tobias' acid were similar to each other. Their exit ozone concentrations increased gradually to a value of about 200 mg/m^3. A steady value of $C_{O3,o}$ means ozone utilization is constant. While a change of $C_{O3,o}$ indicates a reaction mechanism change in the ozonation process(Beltran, et al. 1994).

From the above two figures, it is known that different substitutes on the naphthalene ring exert a significant effect on ozonation. In this study, 2-naphthylsulfric acid is the last to be ozonated. Both the ozone consumption and the elimination ratio of Peri acid are lower than those of the three compounds and are higher than those of 1-naphthylsulfric acid in this study. Comparing the elimination ratios and ozone consumption of the derivatives, stoichiometric coefficients , η ,can be obtained. Ozone consumption, Wo_3,and η , are defined as follows:

$$Wo_3\,(mg) = \text{Ozone dose} - (\text{Volume of gas dose}) \times \int_0^t C_{O3,o}\,d\,t$$

$$\eta = \Delta\, Wo_3 / 48 / \{Co \times \Delta\,(C/Co)\}$$

Where, t is ozonation time; Δ Wo_3 and Δ (C/Co) are the difference of the ozone consumption and the elimination ratio of the studied time intervals, respectively. In this experiment assuming that ozone self-decomposition can be neglected the ozone dose rate is almost constant. Δ (C/Co) and $\int_0^t C_{O3,o}\,d\,t$ can be obtained from Figure 3 and Figure 4, respectively. The value of η corresponding to the first twenty minutes are listed in Table 1.

To investigate the effect of ozonation on TOC elimination, TOC of the aqueous solutions was studied. It was found that the naphthalene compounds, except for 2-amino naphthalene, showed little difference in TOC during the two hours of ozonation. That is because the ozone applied to the aqueous system was not high enough to produce many volatile oxidation compounds. TOC of the aqueous solution of 2-amino naphthalene decreased at first with an increase of ozone dose and increased after about 90 minutes in this study because the ozonation primary products of this compound are not dissolvable so they are removed by ultrafiltration before TOC analysis. Total organic dissolved in the aqueous solution is then decreased first. While as the reaction went on, the intermediate(s) was oxidized to some dissolvable compounds, which contribute to TOC increase.

In spite of the small difference of TOC is found between the initial solution and the ozonated samples, COD and the biodegradability during the reaction undergo changes. The results of ozonation of the aqueous solutions of the five compounds over 60 minutes are shown in Table 1 and Figure 5. In Table 1, the value of COD is in mg/L. COD_0 and COD_t are the values of COD before and after ozonation. Δ COD is value of (1- COD_t/COD_0). Wo_3 is the ozone consumption in one hour while η is within the above mentioned 0~20 minutes time interval..

Table 1. Stoichiometric coeffkients of the naphthalene derivatives in twenty minutes and effects of ozonation in an hour on COD

Compound	η	Wo_3 mg $(5\ L)^{-1}$	COD_0	COD_t	Δ COD %	mg O_3 per mg COD
2-naphthol	1~3	175	530	330	37.7	0.18
2-amino naphthalene	1~3	190	540	454	15.9	0.44
2-naphthylsulfric acid	2~4	85	490	457	6.7	0.52
Tobias' acid	1~3	162	540	380	29.6	0.20
Peri acid	2~4	140	510	349	31.6	0.17

Table 1 shows COD removal varied significantly. COD of 2-naphthol decreased most and COD of 2-naphthylsulfric acid was removed only by 6.7%. Ozone consumption per mg COD is from 0.17 mg to 0.52 mg.

The biodegradability between the water samples before and after ozonation are compared in Figure 5 and Table 2. During the experiments, the biomass of every compound studied was cultivated separately. Therefore the endogenous respiration curves of the samples before and after ozonation are different. Figure 5 shows the differences between the sample and endogenous respiration before and after ozonation. It can be seen that the difference of the oxygen utilization of the sample biodegradation and endogenous respiration increases with time. In order to compare the biodegradability of the derivatives in more detail, $\Delta W \cdot x / COD$ (Δ W here is the difference of oxygen utilization value between the sample biodegradation curve and the endogenous respiration curve ; x here is the biomass concentration, 0.0105

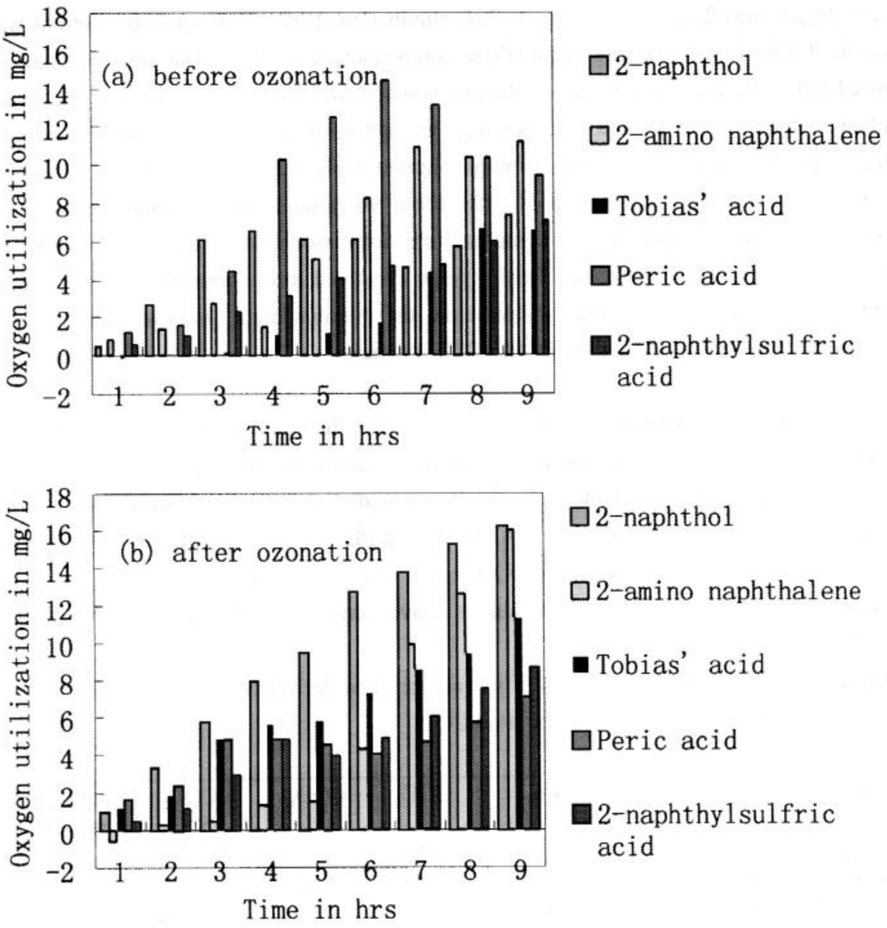

Figure 5. Biodegradability of the five naphthalene derivatives before and after ozonation

Table 2. Biodegradability of the five naphthalene derivatives before and after ozonation

Compound	ΔW (g/g)	ΔW x (mg/L)	ΔW x COD
2-naphthol before ozonation	7.4	77.3	0.15
2-naphthol after ozonation	16.2	169.7	0.51
2-amino naphthalene before ozonation	11.2	117.4	0.22
2-amino naphthalene after ozonation	16.0	168.4	0.37
2-naphthsulfric acid before ozonation	7.0	73.9	0.15
2-naphthsulfric acid after ozonation	8.7	91.0	0.20
Tobias' acid before ozonation	6.6	69.3	0.13
Tobias' acid after ozonation	11.3	118.6	0.31
Peric acid before ozonation	9.5	99.8	0.19
Peric acid after ozonation	7.1	74.6	0.21

g/L) at the time of the eighth hour has been calculated and listed in Table 2. It can be seen that Δ W·x/COD value of all the samples before ozonation is below 0.3. This indicates that before ozonation it is difficult to degrade the compounds biologically. The Δ W·x/COD value of each ozonated water sample was found increased. So the biodegradability of all the samples has increased after ozonation. This suggests that the reaction of the substrate studied with ozone has produced compounds of lower molecular weight that are more biodegradable. Thus the ozonation of water samples improved the biodegradability of the compounds. These are similar to the results of Wang(1990).

Table 2 shows that the Δ W·x /COD value of 2-amino naphthalene, Tobias' acid and 2-naphthol at the eighth hour are above 0.3. This suggests that it will be effective to use biological treatment for the wastewater containing such compounds. Because the two compounds have not been successfully eliminated(see Figure 3 and Table 1), the Δ W·x/COD value of Peri acid and 2-naphthylsulfric acid are still below 0.3. It is shown in Gilbert's work(1987) that with higher ozone dosage the biodegradability of the refractory compounds can be improved. In that case, higher ozone concentration and(or) longer contact time are needed.

It should be noted that in a real situation since it is impossible to know the full composition of a surface water or a special effluent, which was contaminated by naphthalene derivatives or a given pollutant, detailed work should be done to predict an appropriate ozone dose.

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