Decomposition of 2-naphthalenesulfonate in aqueous solution by ozonation with UV radiation

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Abstract

This study investigates the ozonation of 2-naphthalenesulfonate (2-NS) combined with ultraviolet (UV) radiation. Naphthalenesulfonic acids are of importance as dye intermediates for the dye and textile auxiliary industries. Its derivatives, such as 2-NS, have been found in rivers and tannery effluents causing pollution problems. Thus, the 2-NS is of concern for the aquatic pollution control especially in the surface and waste waters. Ozonation combined with UV radiation is employed for the removal of 2-NS in the aqueous solution. Semibatch ozonation experiments were proceeded under different reaction conditions to study the effects of ozone dosage and UV radiation on the oxidation of 2-NS. The concentrations of 2-NS and sulfate are analyzed at specified time intervals to elucidate the decomposition of 2-NS. In addition, values of pH and oxidation reduction potential are continuously measured in the course of experiments. Total organic carbon is chosen as a mineralization index of the ozonation of 2-NS. The mineralization of 2-NS via the ozonation is remarkably enhanced by the UV radiation. These results can provide useful information for the proper removal of 2-NS in the aqueous solution by the ozonation with UV radiation. © 2002 Published by Elsevier Science Ltd.

Keywords: Ozone; Ozonation; UV radiation; 2-Naphthalenesulfonate; Wastewater

1. Introduction

Aromatic sulfonates, which are produced in large amounts in chemical industry since the end of 19th century, have been widely applied in many industrial processes, including the various steps of industrial textile procedure [1]. Among them, naphthalenesulfonic acids (NSAs) are of importance as dye intermediates and commonly used in the textile auxiliary industry employing many azo dyes and pigments, which are the major outlets of naphthalenesulfonates. In addition, the uses of 2-naphthalenesulfonic acid (2-NSA) include flotation collector, initiator for the catalytic polymerization of

caprolactam, stabilizer of maleic anhydride-olefin copolymers, condensation with formaldehyde and alcohol product to form surface-active agents, and tanning materials [2]. Its salt is also used as a brightening and stabilization agent in the electroplating solution of printed wiring board industry.

The aquatic toxicity of aromatic sulfonates appears to be small and the risk of bioaccumulation is limited since the octanol-water partition coefficients (log K_{ow} values) typically range below 2 [3]. Low log K_{ow} values are indication of high mobility within the aquatic system. Furthermore, many of them were reported to be persistent to microbial degradation [4]. Consequently, aromatic sulfonates would be expected to be discharged from wastewater treatments, and have been found in wastewater as well as surface water. For instance,

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<table>
<tr><td colspan="2">Nomenclature</td></tr>
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C_{AGi0}	gas concentration of ozone of inlet gas (mg/L)
C_{BLb}	concentration of 2-NS in bulk liquid (M or mg/L)
C_{BLb0}	initial concentration of 2-NS in bulk liquid (M or mg/L)
$\underline{C_e}$	experimental ORP data (mV)
$\overline{\mathbf{C_e}}$	average value of all experimental ORP data (mV)
C_p	predicted ORP values (mV)
$C_{SO_4^{2-}}$	concentration of sulfate in bulk liquid (M or mg/L)
C_{TOC}	concentration of total organic carbon (TOC) (M or mg/L)
C_{TOC0}	initial concentration of TOC (M or mg/L)
$[I_{uv}]$	light intensity of UV lamp (W/m^2)
NL	volume of gas in liter at 273 K, 1 atm (L)
R^2	determination coefficient, $1 - [\Sigma(C_e - C_p)^2/\Sigma(C_e - \overline{\mathbf{C_e}})^2]$
t	ozonation time (min)
$t_{f,NS}$	ozonation time for complete elimination of C_{BLb} (min)
$t_{f,TOC}$	ozonation time for complete elimination of C_{TOC} (min)
η_{TOC}	removal efficiency of TOC defined by Eq. (2) (%)

Alonson and Barceló [2] detected that the values of 2-NSA concentration were 50 μg/L in Llobregat River in Spain, and varied from several μg/L to several mg/L in different untreated tannery effluents in Sweden, Spain, and Portugal. Accordingly, 2-NSA is thqs of concern as aqueous pollutant in wastewater treatment.

Ozonation is an effective way to reduce the chemical oxidation demand (COD) and total organic carbons (TOCs) by oxidizing the stream solutions with ozone [5]. Ozone may attack on the pollutants via two different reaction pathways: (1) the direct ozonation by the ozone molecule, and (2) the radical ozonation by the highly oxidative free radicals such as hydroxyl free radicals, which are formed by the decomposition of ozone in the aqueous solution [6,7]. The radical ozonation is non-selective and vigorous. The ozonation process in the acid condition mainly takes place through the direct oxidation reaction, which is selective [8,9]. Ozonation combined with ultraviolet (UV) radiation is deemed as a more effective process to remove organics comparing to the sole ozonation. UV radiation is commonly employed to enhance the ozone decomposition yielding more free radicals resulting in a higher ozonation rate [10]. The degradation of less reactive compounds may be accelerated with the presence of free radicals.

Studies on the ozonation of NSA have been quite few among aromatic compounds. Shin and Lim [11] found that the biodegradability (BOD$_5$/COD) of oxidation products can be improved by preozonation of NSA. It was shown that the rate of NSA elimination at pH 3 is faster than that at pH 7, while the yield of sulfate is higher at pH 7 than that at pH 3. However, the effect of pH is insignificant on the rate of COD reduction and on the improvement of biodegradability. In general, ozonation of aromatic compounds may proceed with either the aromatic ring via decyclization or one of the side-chain substituents [12]. The ozonation of naphthalene investigated by Legube et al. [13] indicated 1,3-dipolar cyclo-addition of ozone on the 1,2 bond of naphthalene. The intermediates of naphthalene in ozonation were found to contain cyclic peroxide, oxalic acid, oxoma-lonic acid, formic acid, hydrogen peroxide, ortho-phthaldialdehyde, phthalic acid, and phthaladehydic acid. The above results provide referable information about the destruction of aromatic ring. However, the role of sulfonic substituent and the effect of UV radiation on the ozonation of 2-naphthalenesulfonate (2-NS) still need to be elucidated.

The objective of this study is to investigate the ozonation of 2-NS with UV radiation. Semibatch ozonation experiments are proceeded under different reaction conditions. The concentrations of 2-NS and sulfate are analyzed at specified time intervals to study the decomposition of 2-NS. TOC is chosen as a mineralization index of the ozonation of 2-NS, while the values of pH and oxidation reduction potential (ORP) are measured continuously in the course of experiments. The decomposition of 2-NS accompanies the production of sulfate, diminution of TOC, and variations of pH and ORP. These phenomena during the ozonation of 2-NS are studied. All these results can provide useful information about removing 2-NS in the aqueous solution by the ozonation with UV radiation.

2. Experimental

2.1. Chemicals

The concentration of 2-NS as the sole organic target is 200 mg/L according to the prescription of electroplating solution [14]. The 2-NS with chemical formula as $C_{10}H_7SO_3Na$, which is purchased from Aldrich (Mil-wankee, WI, USA) and used without any further
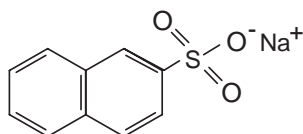
Fig. 1. The molecular structure of 2-NS.

purification, has molecular weight of 230.22. The molecular structure of 2-NS is shown as Fig. 1. All experimental solutions are prepared with deionized water without other buffers. The initial values of pH and TOC of experimental solution are about 5.20 and 104 mg/L, respectively.

2.2. Instrumentation

The airtight reactor of 17.2 cm inside diameter is made of Pyrex glass with an effective volume of 5.5 L, and equipped with water jacket to maintain a constant solution temperature at 25°C in all experiments. The design of reactor is based on the criteria of the shape factors of a standard six-blade turbine [15]. The gas diffuser in cylindrical shape with pore size of 10 μm is located at the bottom of reactor. Two quartz tubes of 3.8 cm outside diameter symmetrically installed inside the reactor are used to house the UV lamps. The low-pressure mercury lamps emitted principally at 254 nm supply the UV radiation. The radiation intensity is measured by a digital radiometer (ultra-violet products (UVP), Upland, CA, USA) with a model UVP-25 radiation sensor. About 3.705 L solution is used in each experiment, while the total sampling volume is within 5% of solution. The stirred speed is as high as 800 rpm to ensure the complete mixing of liquid and gas phases according to previous tests [16,17]. The generation of ozone is controlled by the power input of ozone generator (model SG-01A, Sumitomo, Tokyo, Japan) with constant gas pressure (1 kgf/cm²). The ozone generator used in this research employs two steel plate electrodes and ceramic dielectric. Ozone-containing gas generated by pure oxygen is introduced into the reactor with a gas flow rate of 1.78 NLPM. A circulation pump is used to transport the liquid from the reactor to the sensors of monitor with a flow rate of 0.18 L/min, and to reflow it back during the ozonation. Samples are drawn out from the reactor at desired intervals in the course of experiments. The residual dissolved ozone in the sample is removed by stripping with nitrogen.

The concentrations of 2-NS (C_{BLb}) are analyzed using high performance liquid chromatography system with $250 \times 4.6 \, mm^2$ model BDS C18 (5 μm) column (Thermo Hypersil-keystone, Bellfonte, PA, USA), and UV/Visible detector (model 1706, Bio-Rad, Hercules, CA, USA) at 254 nm. The effluent with flow rate of 1.0 mL/min has the composition with water: CH_3CN of 83:17.

The injection volume of analytic solution is 20 μL. The ionic chromatography employed to analyze the concentration of sulfate ($C_{SO_4^{2-}}$) is equipped with $150 \times 5.5 \, mm$ AN300 column (MetaChem, Lake forest, CA, USA) and model conductivity series IV detector (LabAlliance, Lemont, PA, USA). The effluent with flow rate of 2.0 mL/min has the composition with $NaHCO_3/Na_2CO_3$ of 1.7/1.8 mM. The TOC concentration (C_{TOC}) of samples is analyzed by a TOC analyzer (model 700, OI Corporation, TX, USA). The instrument utilizes the UV-persulfate technique to convert the organic carbon for the subsequent analysis by an infrared carbon dioxide analyzer calibrated with the potassium hydrogen phthalate standard. The pH (model 300 T, Suntex, Taipei, Taiwan) and ORP (model 900C, Apogee, Taipei, Taiwan) meters with sensors are used to measure the values of pH and ORP of solution. All fittings, tubings and bottles are made of stainless steel, Teflon, or glass. The experimental apparatus employed in this work is shown in Fig. 2.

2.3. Experimental procedures

The semibatch experiments of 2-NS ozonation are performed to examine the variations of C_{BLb}, $C_{SO_4^{2-}}$, C_{TOC}, pH, and ORP. Before starting the ozonation experiments, the ozone-containing gas is bypassed to the photometric analyzer (model SOZ-6004, Seki, Tokyo, Japan) to assure the stability and ozone concentration. Light intensity ($[I_{uv}]$) of 60.35 W/m² is employed to test the effect of UV radiation on the ozonation. A part of gas stream at preset flow rate is directed into the reactor when reaching the set conditions.

3. Results and discussion

3.1. Variations of C_{BLb}, $C_{SO_4^{2-}}$, C_{TOC}, pH, and ORP in ozonation of 2-NS

The mineralization reaction between O_3 and 2-NS can be stoichiometrically expressed as follows.

$$C_{10}H_7SO_3Na + 8O_3 \rightarrow 10CO_2 + SO_4^{2-} + H^+ + 3H_2O + Na^+. \tag{1}$$
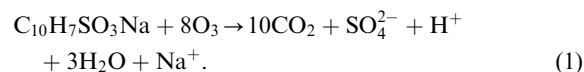
The variations of C_{BLb}, $C_{SO_4^{2-}}$, C_{TOC}, pH, and ORP with ozonation time under experimental conditions of sole O_3 and O_3/UV are shown in Fig. 3. There are two important characteristic times of concern during the ozonation of 2-NS. One is the time for the complete elimination of 2-NS signed as $t_{f,NS}$; the other is that for the complete mineralization of TOCs denoted as $t_{f,TOC}$. Comparison of ozonation results at $t_{f,NS}$ and $t_{f,TOC}$ under different experimental conditions is given in Table 1 for four cases. The differences of the values of
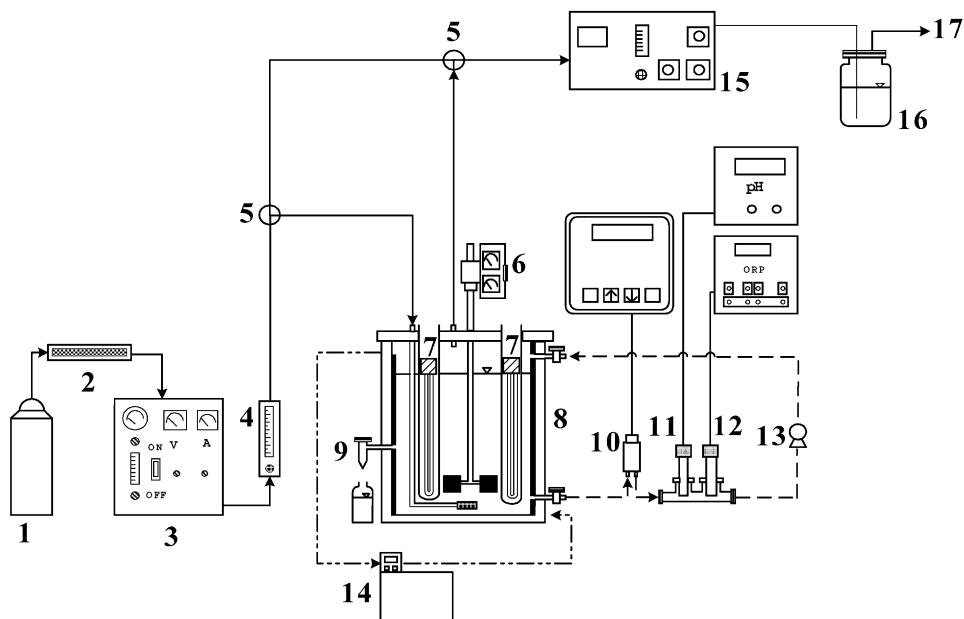
Fig. 2. The experimental apparatus sketch. ——, — —, —·--—: ozone gas stream, experimental solution, isothermal water. Components: (1) oxygen cylinder, (2) drying tube, (3) ozone generator, (4) flow meter, (5) three-way valves, (6) stirrer, (7) ultra-violet (UV) lamps, (8) reactor, (9) sample port, (10) liquid ozone sensor, (11) pH sensor, (12) ORP sensor, (13) circulation pump, (14) thermostat, (15) gas ozone detector, (16) KI solution, (17) vent to hood.

$C_{SO_4^{2-}}/C_{BLb0}$ under the conditions of sole O_3 and O_3/UV at $t_{f,NS}$ are remarkable. The yield of sulfate (about 43%, average of Cases 3 and 4) with O_3/UV is greater than two times of that (about 19%, average of Cases 1 and 2) with O_3 alone. This may be contributed to the cause that the aromatic compound with the sulfonic substituent, which is electron withdrawing, has low reactivity with O_3 molecules in ozonation [12]. Therefore, the initial attack of ozone on 2-NS is not mainly toward the generation of sulfate [11]. However, all the decomposition of 2-NS accompanies with moderate diminution of TOC. The removal efficiencies of TOC (η_{TOC}) defined by Eq. (2) at $t_{f,NS}$ range from 12.61% to 15.98%, indicating only slight difference. Thus the intermediates produced from the decomposition of 2-NS still contribute over 84% TOC relative to the initial value.

$$\eta_{TOC} = (C_{TOC0} - C_{TOC})/C_{TOC0}. \qquad (2)$$

The pH value of solution decreases rapidly in the early period and then gradually approaches to a constant as ozonation time increases. The decrease of pH at $t_{f,NS}$ under the condition of O_3/UV is more significant than that of sole O_3, indicating that O_3/UV induces the formation of intermediates with acidity higher than sole O_3. The increase of acidity (decrease of pH) is consistent with the increase of the yield of sulfate as noted in the preceding paragraph. Correspondingly, the proportion of the intermediates with the substituent of sulfonic

group under the condition of sole O_3 is greater than that of O_3/UV.

As the ozonation is further proceeded, the final pH values (at $t_{f,TOC}$) are close to the theoretical value of 3.06 calculated from Eq. (1). The values of ORP approach to constants of 990, 1070, 956, 1010 mV for the four cases in Table 1, which are close to that of organic-free solution, about the complete elimination of TOC.

Based on the above discussion on the variations of C_{BLb}, $C_{SO_4^{2-}}$, C_{TOC}, pH, and ORP, and noting that the reaction rates and intermediates of the ozonation of 2-NS are affected by the presence of UV radiation, one may then propose a simplified scheme of the decomposition pathways of the ozonation of 2-NS with UV radiation as shown in Fig. 4. The major contribution of UV is to generate OH$^\bullet$ via Reaction II.

3.2. Decomposition of 2-NS and formation of sulfate

The times required for the complete decomposition of 2-NS ($t_{f,NS}$) in the present experiments as shown in Table 1 are between 10 and 30 min. The effect of the ozone concentration of feed gas on the decomposition of 2-NS observed from Fig. 5 is remarkable. The value of $t_{f,NS}$ with $C_{AGi0} = 44$ mg/L is about one-third of that with $C_{AGi0} = 11$ mg/L under the condition of sole O_3. That with $C_{AGi0} = 40$ mg/L is about half of that with $C_{AGi0} = 20$ mg/L under the condition of O_3/UV.
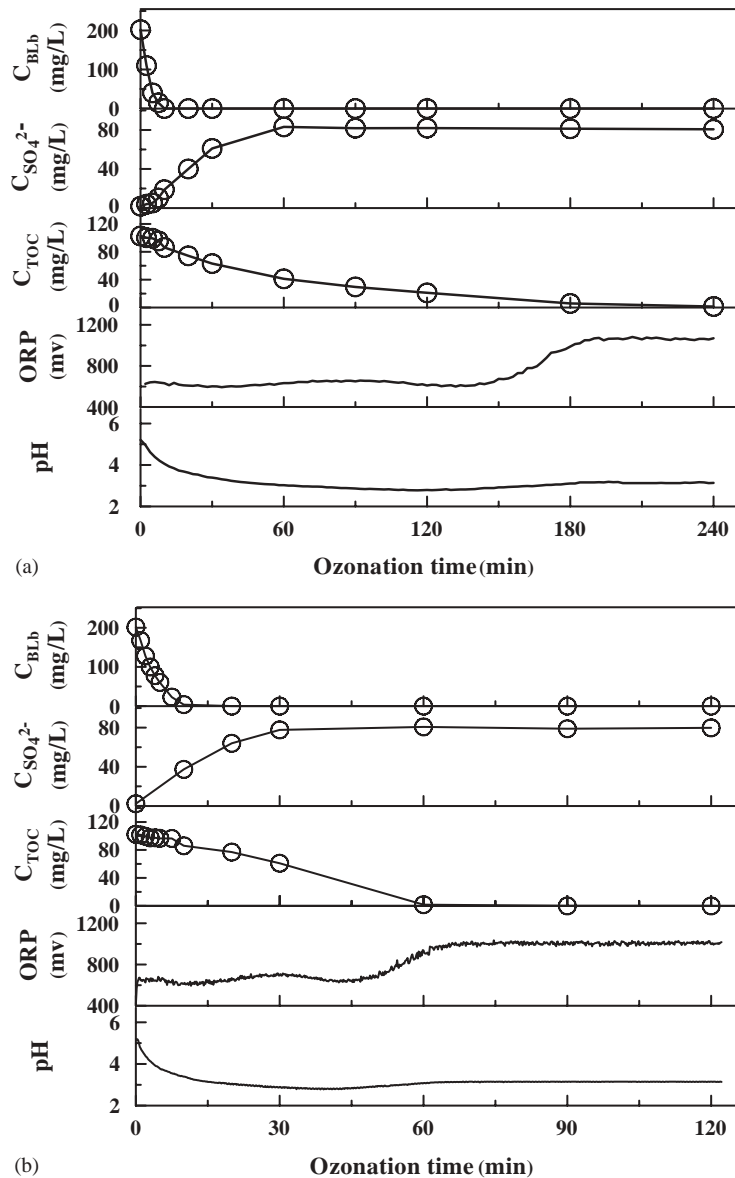
Fig. 3. Concentrations profile of 2-NS, SO_4^{2-}, and TOCs (C_{BLb}, $C_{SO_4^{2-}}$, C_{TOC}), pH, and ORP when ozonation of 2-NS occurred in semibatch system. (a) Concentration of ozone gas $C_{AGi0} = 44.0 \, g/m^3$; (b) $C_{AGi0} = 40.0 \, g/m^3$ with intensity of UV $[I_{uv}] = 60.35 \, W/m^2$.

However, comparing the results of $C_{AGi0} = 44 \, g/m^3$ (O_3 alone) and $40 \, g/m^3$ (O_3/UV) indicates that the UV radiation affects the decomposition rate of 2-NS slightly. As depicted in the decomposition pathways of 2-NS by the ozonation with UV, Reaction II is enhanced by the presence of UV radiation. The pathways via hydroxyl free radicals noted as Reactions III and IV would then be promoted while the contribution of Reaction I would decrease due to the decrease of dissolved ozone concentration. As the result, the overall decomposition rate of 2-NS in ozonation is only slightly accelerated by the UV radiation.

Noting the deactivation of benzene ring toward electrophilic substitution caused by the sulfonic substituent and steric hindrance of the sulfonic substituent [18] and referring to the mechanism of the sole ozonation of naphthalene reported by Legube et al. [13], one may propose the possible mechanism of Reaction I as shown in Fig. 6. The preferred site for electrophilic attack by ozone molecule is 1-position [19]. Indeed, Fig. 6 is similar to the ozonation pathways of naphthalene proposed by Legube et al. [13] who identified the ozonation products of naphthalene by GC/MS. However, 2-NS has the sulfonic substituent on

Table 1
Comparison of ozonation results at times for complete eliminations of 2-NS ($t_{f,\text{NS}}$) and mineralization of TOCs ($t_{f,\text{TOC}}$) under different experimental conditions

Experimental condition[a]	$t_{f,\text{NS}}$ (min)	$C_{\text{SO}_4^{2-}}/C_{\text{BLb0}}$[b] (%)	η_{TOC}[b] (%)	$t_{f,\text{TOC}}$ (min)	pH[b]	pH[c]	ORP[b] (mV)
Case 1 $C_{\text{AGi0}} = 11$ mg/L	30	15.36	13.70	NM[d]	3.88	NM[d]	534.4
Case 2 $C_{\text{AGi0}} = 44$ mg/L	10	22.87	15.98	240	4.06	3.14	623.1
Case 3 $C_{\text{AGi0}} = 20$ mg/L, $[I_{\text{uv}}] = 60.35$ W/m^2	20	40.82	12.61	120	3.26	3.01	596.9
Case 4 $C_{\text{AGi0}} = 40$ mg/L, $[I_{\text{uv}}] = 60.35$ W/m^2	10	46.04	15.97	90	3.39	3.14	613.4

[a] Initial values of pH, C_{BLb0} are 5.20, 104 mg/L.
[b] Values at $t_{f,\text{NS}}$.
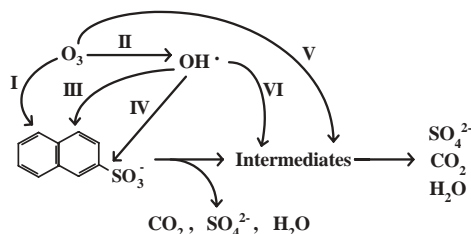[c] Values at $t_{f,\text{TOC}}$.
[d] NM: not measured.

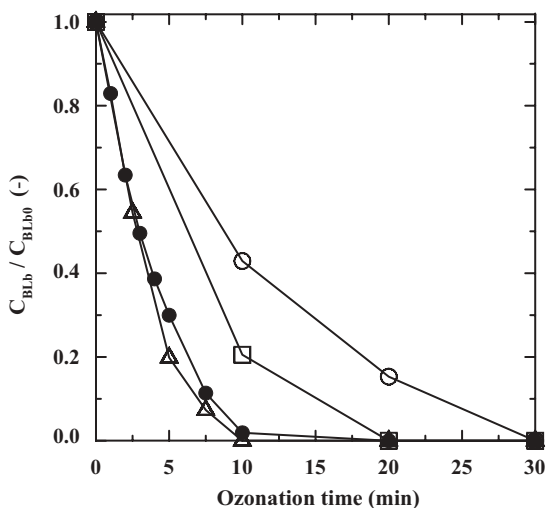Fig. 4. Simplified scheme of the decomposition pathways of the ozonation of 2-NS with UV radiation.

Fig. 5. Variation of $C_{\text{BLb}}/C_{\text{BLb0}}$ with time for the ozonation of 2-NS in semibatch system. $\bigcirc$, $\triangle$, $\square$ and $\bullet$: $C_{\text{AGi0}} = 11$ g/m^3, 44 g/m^3, 20 g/m^3 with $[I_{\text{uv}}] = 60.35$ W/m^2, 40 g/m^3 with $[I_{\text{uv}}] = 60.35$ W/m^2. $C_{\text{BLb}} = C_{\text{BLb0}}$ at $t = 0$.

the ring, which has deactivating effect by withdrawing electron density and directs incoming electrophiles to specific positions [20]. The byproducts of ozonated 2-NS were not analyzed in this study. Consequently, Fig. 6 is postulated simply to depict that ozone attacks the

substituted naphthalene with the consideration of the occurrence of subsequent possible reactions at preferred positions around the ring. The initial attacks of ozone on 2-NS may be proceeded via (a) ozone dipolar cycloaddition on the 1,2 bond or (b) an electrophilic substitution of ozone on carbon 1 [21]. The intermediates include 4-sulfo-o-phthalaldehyde (denoted as A in Fig. 4), peroxycyclic benzenesulfonic acid (C), 4-sulfo-o-phthalaldehydic acid (E). Some peroxides such as hydroperoxy ethanal (B) and hydrogen peroxide (D) also appear during the ozonation. The decomposition rate of 2-NS decreases with ozonation time accounting for the generation of byproducts, which are also competitors for oxidation.

As shown in Fig. 7, which presents the variation of $C_{\text{SO}_4^{2-}}/C_{\text{BLb0}}$ with ozonation time, the yield of sulfate reaches nearly 100% in 60–180 min for the cases examined. It is found that the effects of the ozone concentration of feed gas and UV radiation are all important on the generation of sulfate. The generation of sulfate is consistent with the increase of η_{TOC} for both sole O_3 and O_3/UV treatments as shown in Fig. 8. It is seen that the more sulfates are formed via O_3/UV than sole O_3 for $\eta_{\text{TOC}} < 40\%$. The enhancing effect of O_3/UV over sole O_3 on the generation of sulfate may be attributed to the cause that O_3/UV treatments generates more hydroxyl free radicals than sole O_3, which are non-selective and highly oxidative, thus increasing the opportunity of the release of sulfonic substituent via Reaction IV. As η_{TOC} increases to about 40–50%, the yields of sulfate for the four cases in Fig. 8 all approach to 100%.

3.3. Removal of TOC associated with variation of OPR

During the decomposition of 2-NS, the solution still contains byproducts of high TOC contents as shown in Fig. 3. Fig. 9 shows the variation of TOC under different experimental conditions. The treatments with O_3/UV take 60–120 min to completely eliminate TOCs. However, it takes more than 240 min via the treatments with
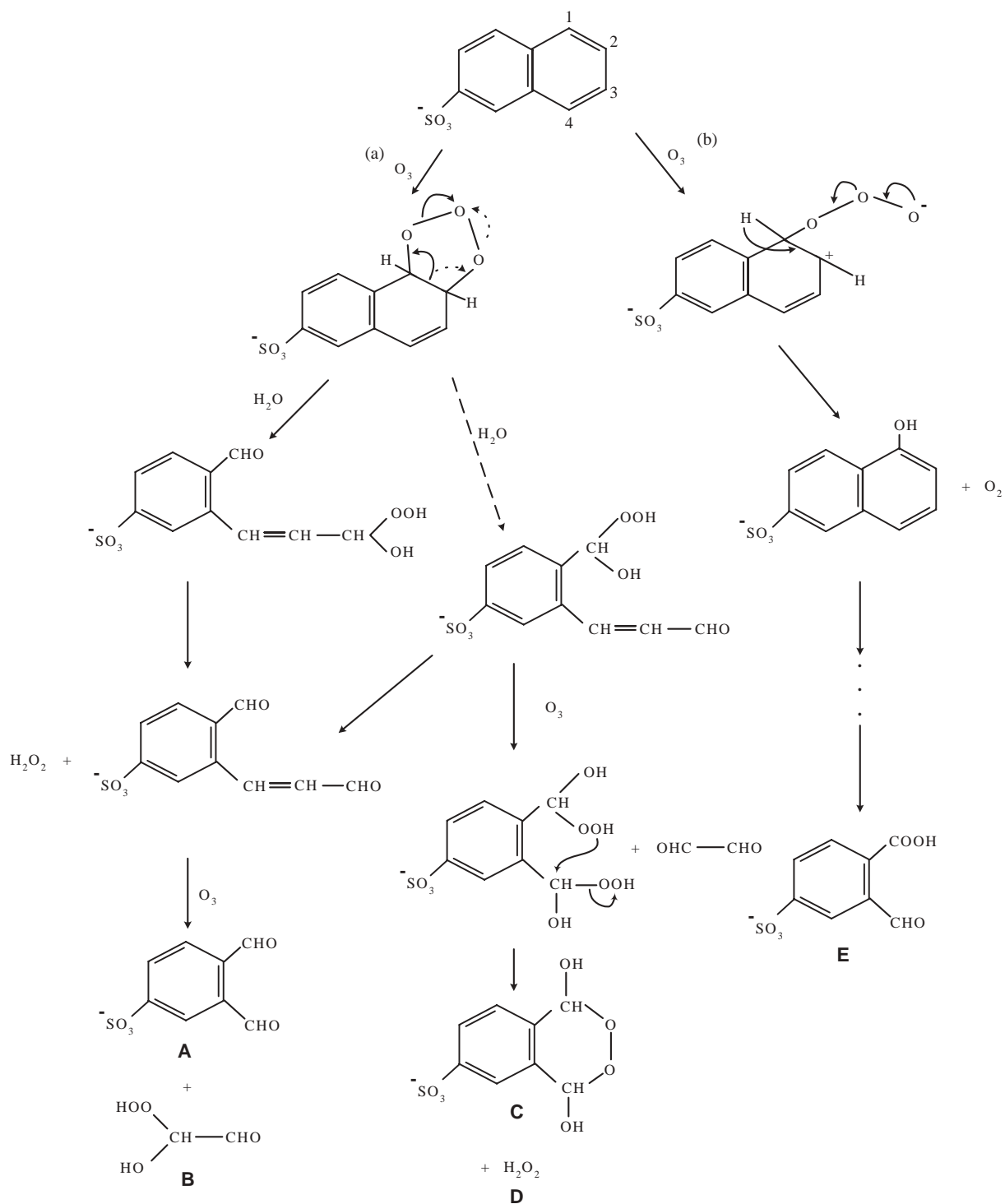
Fig. 6. Ozonation mechanism of 2-NS with ozone molecule. The cases of initial attack by (a) ozone dipolar cyclo-addition on the 1, 2 bond, (b) an electrophilic substitution of ozone on carbon 1.
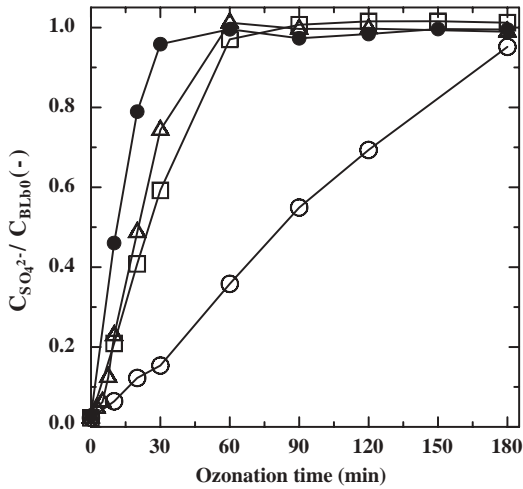
Fig. 7. Variation of $C_{SO_4^{2-}}/C_{BLb0}$ with time for the ozonation of 2-NS in semibatch system. Notations are the same as specified in Fig. 5.
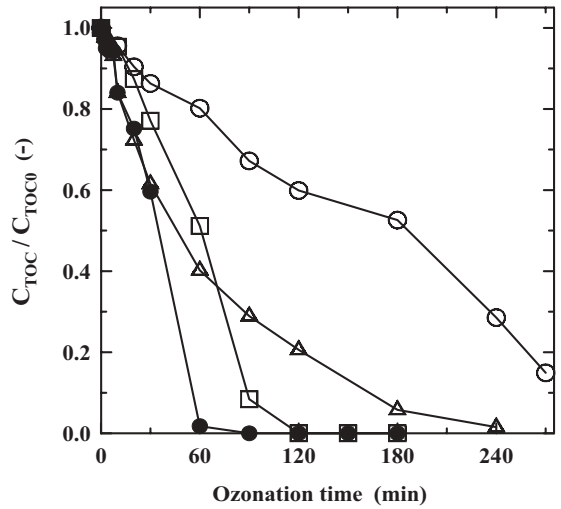

Fig. 9. Variation of C_{TOC}/C_{TOC0} with time for the ozonation of 2-NS in semibatch system. Notations are the same as specified in Fig. 5.
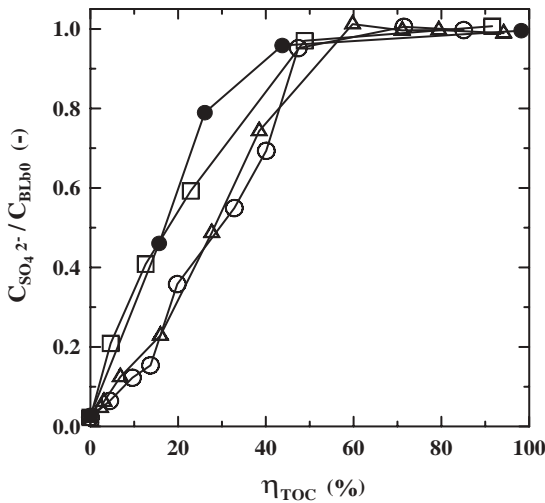

Fig. 8. $C_{SO_4^{2-}}/C_{BLb0}$ vs. η_{TOC} for the ozonation of 2-NS in semibatch system. $\eta_{TOC} = (C_{TOC0} - C_{TOC})/C_{TOC0}$, $C_{TOC} = C_{TOC0}$ at $t = 0$. Other notations are the same as specified in Fig. 5.
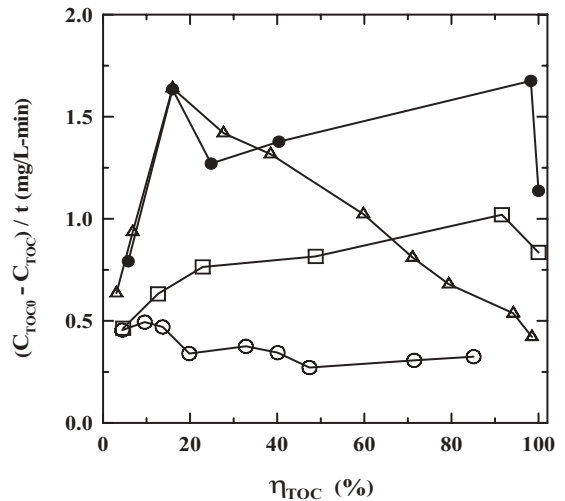

Fig. 10. $(C_{TOC0} - C_{TOC})/t$ vs. η_{TOC} for the ozonation of 2-NS in semibatch system. Notations are the same as specified in Fig. 5.

sole O_3. Therefore, the introduction of UV radiation in 2-NS ozonation makes significant contribution for the mineralization. Moreover, the ozone concentration of feed gas also improves the removal of TOC for both sloe O_3 and O_3/UV systems. For further illustrating the effects of C_{AGi0} and UV radiation on the elimination of TOC, Fig. 10 shows the variation of mean mineralization rate, $(C_{TOC0} - C_{TOC})/t$, with η_{TOC}. It is seen that the effect of UV radiation is not significant on enhancing the mean mineralization rate when

$\eta_{TOC} < 40\%$. Instead, C_{AGi0} affects the mineralization rate remarkably. However, in the later ozonation stage (higher η_{TOC}), the values of $(C_{TOC0} - C_{TOC})/t$ via O_3/UV are still high while those via sole O_3 become low. This is because the intermediates in the later stage of the ozonation of 2-NS such as oxalic acid, phthalic acid, and formic acid, have low reactivity toward ozone molecule [13,22,23]. The occurrence of the acidic group causes the deactivation of the molecule.

According to the previous studies on the oxidation of protocatechuic acid [24] and 4-chlorobenzaldehyde [25], the process of O_3/UV has better performance for the degradation of protocatechuic acid and 4-chlorobenzaldehyde than ozonation alone. Thus, the oxidation reaction via hydroxyl free radicals is predominant to proceed in the regime with higher η_{TOC}. These results then support the recommendation of employing O_3/UV process in the treatment of 2-NS. Noting that the value of $(C_{TOC0} - C_{TOC})/t$ in the early stage of ozonation is low due to the cause that the ozone is mainly consumed for ring opening accompanying with the low diminish of TOCs.

Fig. 11(a) presents the variation of ORP of liquid with η_{TOC}. The use of ORP as a supplementary ozonation index of ozonation system has been introduced by Yu and Yu [26]. The experimental ORP data of the present study are further used to plot the average and smooth curve in Fig. 11(b) which shows the distinct variation of ORP with η_{TOC}. The value of ORP reveals slight variation in the initial period while increases significantly in the later period with higher η_{TOC}. For $\eta_{TOC} < 60\%$, the values of ORP are between 500 and 700 mV. In this stage, the organics of TOCs in the solution are predominant for controlling the ORP of system with small variation. While the concentration of TOCs (C_{TOC}) decreases below 16 mg/L ($\eta_{TOC} > 85\%$), the ORP becomes > 800 mV as shown in Fig. 11(b). As the η_{TOC} approaches to 100%, the value of ORP of system is close to the value of organic-free solution under the same condition. Thus, indeed, ORP is a useful index associated with the oxidation state of the ozonation of 2-NS in terms of η_{TOC}.

In summary, the difference between O_3 and O_3/UV treatments regarding the destruction rate of 2-NS is not significant, however, the condition of O_3/UV gives significant contribution for the subsequent oxidation after the disappearance of 2-NS. Thus, the combination of ozone with UV radiation is recommended for treating the 2-NS solution as far as the TOC reduction is concerned, although the process with O_3 alone may be sufficient for removing the 2-NS.

It should be noted that, for treating the 2-NS in the wastewater containing other chemicals, the TOC value would be the lump of different organic sources. Therefore, the relations of $C_{SO_4^{2-}}/C_{BLb0}$, $(C_{TOC0} - C_{TOC})/t$, and ORP with η_{TOC}, and of C_{TOC}/C_{TOC0} with time obtained above for the case with 2-NS only may not be applicable to those with mixed chemicals. However, some comments may be noted. The removal percentage of TOC contributed by 2-NS in the wastewater during ozonation may be estimated by the value of $C_{SO_4^{2-}}/C_{BLb0}$ according to Fig. 8 in the cases that the increasing $C_{SO_4^{2-}}$ is mainly generated from the oxidation of 2-NS. In addition, the trends of mineralization rates contributed by 2-NS under different cases as shown in
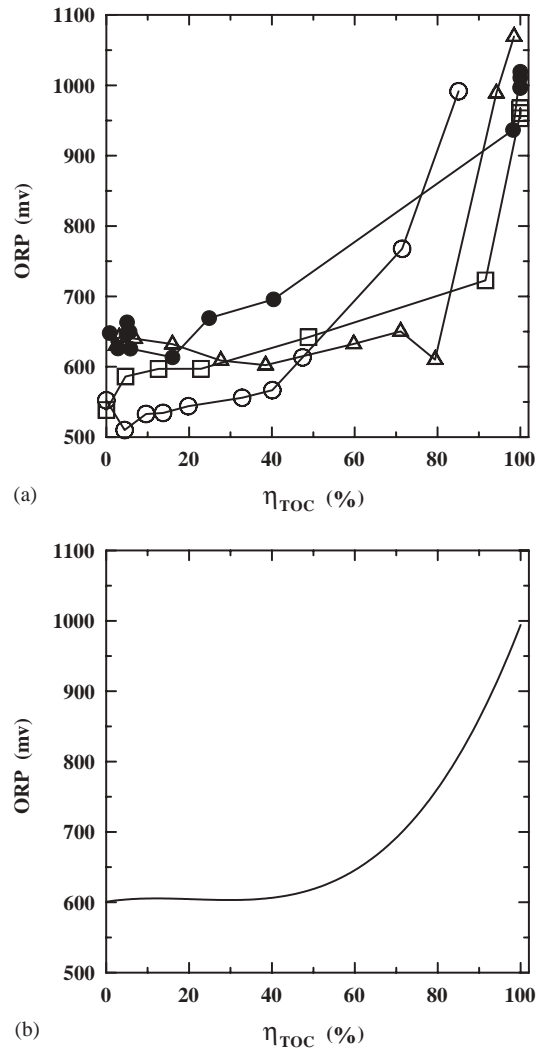

Fig. 11. ORP vs. η_{TOC} for the ozonation of 2-NS in semibatch system. Notations are the same as specified in Fig. 5. (a) Experimental data; (b) average and smooth curve of experimental data with $R^2 = 0.867$.

Fig. 9 may be referable for oxidizing the 2-NS in the wastewater. Of course, further work is needed for the detailed information of treating the 2-NS mixed with other chemicals by the ozonation in various wastewaters.

4. Conclusions

2-NS is an aqueous pollutant of environmental concern in the surface and wastewaters. Ozonation combined with UV radiation is employed as an effective way for the removal of 2-NS in the aqueous solution. The decomposition of 2-NS accompanies with the

diminish of TOCs and generation of sulfate. The following conclusions may be drawn:

1. The decomposition rate of 2-NS increases with the ozone concentration of feed gas, while is not significantly enhanced by the presence of UV radiation. When the decomposition of 2-NS is completed, the removal efficiency of TOC (η_{TOC}) is between 12.61% and 15.98%.
2. Both the ozone concentration of feed gas and UV radiation can improve the generation rate of sulfate. When η_{TOC} is $> 50\%$, the yield of sulfate is nearly 100%.
3. In the early stage of ozonation with $\eta_{TOC} < 40\%$, the elimination of TOC is remarkably enhanced by the ozone concentration of feed gas while slightly by the UV radiation. However, in the later stage, the O_3/UV system significantly gives higher mineralization rate than the sole O_3 system.
4. The ORP can be used as a supplementary index of oxidation state. Its value varies with the residual TOC concentration for the ozonation of 2-NS.

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