

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

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Abstract

This study investigates the ozonation of 2-naphthalenesulfonate (2-NS) combined with UV radiation in the electroplating solution. 2-NS is commonly used as a brightening and stabilization agent in the electroplating solution. Semibatch ozonation experiments were conducted under various reaction conditions to study the effects of ozone dosage and UV radiation on the oxidation of 2-NS. The concentrations of 2-NS were analyzed at specified time intervals to elucidate the decomposition of 2-NS. Total organic carbon (TOC) is chosen as a mineralization index of the ozonation of 2-NS. In addition, values of pH and oxidation reduction potential were continuously measured in the course of experiments. As a result, the nearly complete mineralization of 2-NS via the ozonation treatment can be achieved. The mineralization of 2-NS is found accelerated by the introduction of UV radiation and has a distinct relationship with the consumption of applied ozone. These results can provide useful information for the proper removal of 2-NS in the electroplating solution by the ozonation with UV radiation.

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Keywords: Ozone; Ozonation; UV radiation; 2-Naphthalenesulfonate; Electroplating solution

1. Introduction

Discarded aged electroplating solution is one of the major wastewater sources in the printed wiring board (PWB) industry. The substrates (the major chemical species) of solution recipe are inorganics such as sulfuric acid, copper sulfate, hydrochloric acid, etc., while the minor substances are organics such as 2-naphthalenesulfonate (2-NS), which is commonly used as a brightening and stabilization agent [1]. Consequently, the characteristics of wasted electroplating solution exhibit high acidity (pH = 0.18–0.42) and ionic strength. All of the above features make the solution hard to be treated by the conventional treatment processes [1,2]. The current major method used to treat the waste electroplating solution of PWB is chemical coagulation, which produces hazardous

chemical sludge because of its high heavy metal content such as copper.

In Taiwan, the yield of the waste electroplating solution of PWB is approximately 1.23 m³/s, resulting in about 2.1 × 10⁷ kg waste and hazardous sludge per year with 78 wt.% water content [3]. Furthermore, in view of the resource recycling, the aged electroplating solution of PWB has high reclamation and recycling potentials with high copper concentration and electric conductivity. Note that the qualities of the organics in the electroplating solution become low and unreliable to the process after a certain period of time of operations of the electroplating and electrophoresis. For this reason, removal of the spent organic additives with the replacement by adding new additives is one of the key steps for the reutilization of process solution. Ozonation is an effective way to remove organics and reduce the total organic carbons (TOCs). The compounds may be attacked via two different reaction mechanisms: (1) the direct ozonation

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Nomenclature

C_{AGi}	gas concentration of ozone of inlet gas (mg/L or M)
C_{AGe}	gas concentration of ozone of discharged gas (mg/L or M)
C_{AL}	concentration of ozone in bulk liquid (mg/L or M)
C_{ALS}	dissolved ozone concentration of liquid at gas–liquid interface (M)
C_{BL}	concentration of 2-NS in bulk liquid (mg/L or M)
C_{BL0}	initial concentration of 2-NS in bulk liquid (mg/L or M)
C_e	experimental data
\bar{C}_e	average value of all experimental data
C_p	predicted values
C_{TOC}	concentration of total organic carbon (TOC) (mg/L or M)
C_{TOC0}	initial concentration of TOC (mg/L or M)
H_A	dimensionless Henry's constant of ozone (MM^{-1})
H_e	Henry's law constant of ozone, p_{Ai}/C_{ALS} (atm L/mol)
$[I_{UV}]$	photon flux of UV entering the reactor (W/m^2)
k_B	pseudo-first-order reaction rate constant of 2-NS (min^{-1})
m_{O_3R}	ozone consumption (mol)
2-NS	2-naphthalenesulfonate
ORP	oxidation reduction potential
p_{Ai}	partial pressure of ozone of gas (atm)
Q_G	gas flow rate (L/min)
R^2	determination coefficient, $1 - \frac{\sum (C_e - C_p)^2}{\sum (C_e - \bar{C}_e)^2}$
TOC	total organic carbon
V_F	volume of free space (L)
V_L	volume of solution (L)
t	ozonation time (min)

Greek symbol

η_{TOC}	removal efficiency of TOC defined by Eq. (1) (%)
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by the ozone molecule and (2) the radical oxidation by the highly oxidative free radicals such as hydroxyl free radicals, which are formed by the decomposition of ozone in the aqueous solution [4]. The radical oxidation is non-selective and vigorous.

Recently, Chen et al. [5] investigated the decomposition of 2-NS in the aqueous solution by ozonation with ultraviolet (UV) radiation. Their results indicated that the combined process of ozonation with UV radiation is an effective way for the removal of 2-NS in the aqueous solu-

tion. However, the information about the ozonation of 2-NS in the electroplating solution, which has distinct properties from the aqueous solution, is still scarce but desirable for evaluating the practicability of removal of 2-NS via ozonation treatment. Thus, the aim of the present study is to employ ozonation combined with UV radiation to eliminate 2-NS in the electroplating solution. The purpose of introducing UV radiation in the ozonation processes is to enhance the ozone decomposition yielding more free radicals for achieving a higher ozonation extent [6,7].

Semibatch ozonation experiments are proceeded under various reaction conditions. The decomposition of 2-NS accompanies with the variations of TOC, gas and liquid ozone concentrations and oxidation reduction potential (ORP). The results obtained can provide useful information about the proper application of the process for the removal of 2-NS via ozonation with UV radiation in the electroplating solution.

2. Materials and methods

2.1. Chemicals

The substrate recipe of the electroplating solution is: $[CuSO_4 \cdot 5H_2O] = 200$ g/L, $[H_2SO_4] = 60$ g/L, and $[Cl^-] = 0.03$ g/L. The concentration of target organic compound of 2-NS is 200 mg/L according to the prescription of electroplating solution [1]. The 2-NS with chemical formula as $C_{10}H_7SO_3Na$, which was purchased from Aldrich (Milwaukee, WI, USA) and used without any further purification, has molecular weight of 230.22. The molecular structure of 2-NS is shown in Fig. 1. All experimental solutions were prepared with deionized water without other buffers. The initial values of pH and TOC of experimental solution are about 0.25 and 104 mg/L, respectively. The dimensionless Henry's law constant (H_A) of ozone in the electroplating solution was determined as 4.18 [8]. Accordingly, the dimensional Henry's law constant of ozone (H_e) defined by $p_{Ai} = H_e C_{ALS}$ is 102.1 atm L/mol.

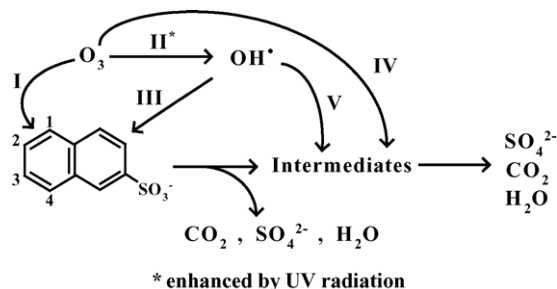


Fig. 1. The molecular structure and simplified scheme of the decomposition pathways of the ozonation of 2-naphthalenesulfonate (2-NS) with UV radiation.

2.2. Instrumentation

The airtight reactor of inside diameter of 17.2 cm was 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 was based on the criteria of the shape factors of a standard six-blade turbine [9]. The gas diffuser in cylindrical shape with pore size of 10 μm was located at the bottom of reactor. Two quartz tubes of outside diameter of 3.8 cm installed symmetrically inside the reactor were used to house the UV lamps. The low-pressure mercury lamps emitted principally at 254 nm supplied the UV radiation. The radiation intensity was measured by a digital radiometer (Ultra-Violet Products (UVP), Upland, CA, USA) with a model UVP-25 radiation sensor. About 3.705 L solution was used in each experiment, while the total sampling volume was within 5% of solution. The stirred speed was as high as 800 rpm to ensure the complete mixing of liquid and gas phases according to previous tests [10,11]. The generation of ozone gas was controlled by the power input of ozone generator (model SG-01A, Sumitomo, Tokyo, Japan) with constant gauge pressure (0.968 atm). The ozone generator used in this study employed two steel plate electrodes and ceramic dielectric. Ozone-containing gas generated by pure oxygen was introduced into the reactor with a gas flow rate of 1.94 L/min. A circulation pump was used to transport the liquid from the reactor to the sensors of monitors with a flow rate of 0.18 L/min, and to re-flow it back during the ozonation.

The concentrations of 2-NS (C_{BL}) were analyzed using high-performance liquid chromatography (HPLC) system with column of 250 mm × 4.6 mm of model BDS C18 (5 μm) (Thermo Hypersil-keystone, Bellfonte, PA, USA),

and UV–vis detector (model 1706, Bio-Rad, Hercules, CA, USA) at 254 nm. The ratio of water:CH₃CN of composition of effluent with flow rate of 1.0 mL/min was 83:17. The injection volume of analytic solution was 20 μL. The TOC concentrations (C_{TOC}) of samples were analyzed by a TOC analyzer (model 700, OI Corporation, Texas, USA). The instrument applies 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 300T, Suntext, Taipei, Taiwan) and ORP (model 900C, Apogee, Taipei, Taiwan) meters with sensors were used to measure the values of pH and ORP of solution. All fittings, tubings and bottles were 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 ozonation of 2-NS were performed to examine the variations of C_{BL} , C_{TOC} , pH, and ORP. Before starting the ozonation experiments, the ozone-containing gas was bypassed to the photometric analyzer (model SOZ-6004, Seki, Tokyo, Japan) to assure the stability and ozone concentration. A part of gas stream at the preset flow rate was directed into the reactor when the ozonation system was ready to start. In addition, the concentrations of inlet (C_{AGi}) and discharged (C_{AGe}) gas ozone were measured. Liquid samples were drawn out from the reactor at desired time intervals in the course of ozonation of 2-NS. The photon flux of UV, $[I_{UV}]$ entering the reactor with value of 60.35 W/m² was employed to test the effect of UV radiation on the ozonation.

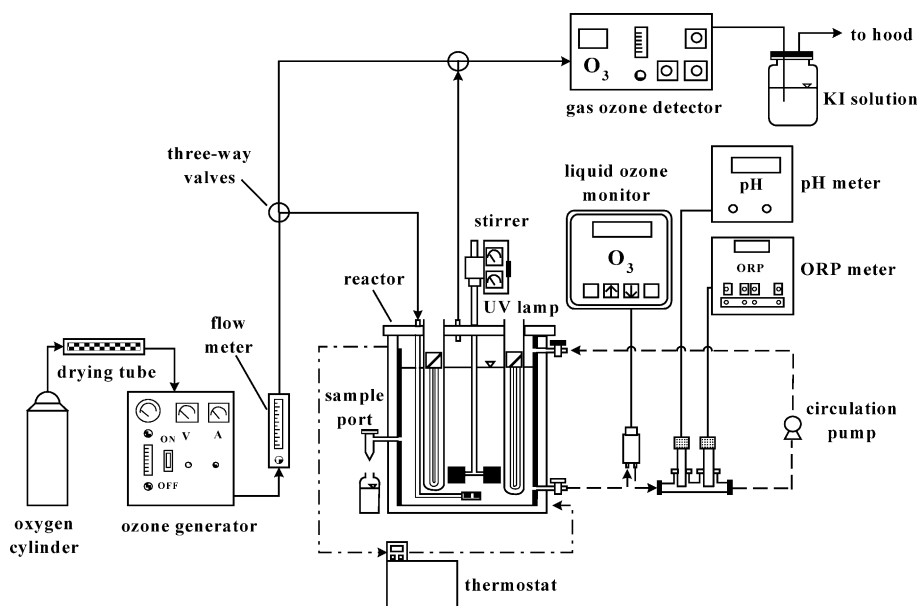


Fig. 2. The experimental apparatus sketch: (—) ozone gas stream, (---) experimental solution, and (---) isothermal water.

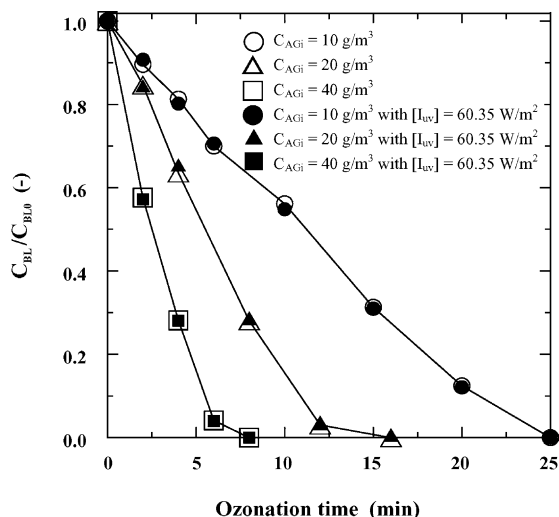


Fig. 3. Variation of C_{BL}/C_{BL0} with time for the ozonation of 2-NS in semi-batch system. $C_{BL} = C_{BL0}$ at $t = 0$.

3. Results and discussion

3.1. Decomposition of 2-NS during ozonation with UV radiation

The time variations of the decomposition of 2-NS via the ozonations with and without UV radiation are shown in Fig. 3. The effect of the ozone concentration of feed gas on the decomposition of 2-NS is remarkable. The time required for the complete decomposition of 2-NS with $C_{AGi} = 40$ mg/L is about one-third and half of those with $C_{AGi} = 10$ and 20 mg/L, respectively. However, comparing the results of the cases with and without UV radiation indicates that the UV radiation affects the decomposition extent of 2-NS slightly.

In order to illustrate the possible roles of O_3 and UV radiation on attacking the 2-NS and its intermediates, a simplified scheme of the decomposition pathways of 2-NS via the ozonation with UV radiation is proposed as shown in Fig. 1. The major contribution of UV is to generate OH^\bullet via reaction II. This can enhance the radical reaction of hydroxyl free radicals with 2-NS noted as reaction III, which is more vigorous than the direct reaction of O_3 with 2-NS via reaction I. However, the decrease of dissolved ozone concentration then decreases the extent of reaction I. As the result, the overall decomposition extent of 2-NS in ozonation is only slightly accelerated by the UV radiation. Further, the pseudo-first-order kinetics for the elimination of 2-NS, $C_{BL}/C_{BL0} = \exp^{-k_B t}$, can be obtained from Fig. 3 with k_B (min^{-1}) = $0.0107 \pm 0.0042 C_{AGi}$ for a 95% confidence interval, where C_{AGi} is in mg/L.

The decomposition of 2-NS accompanies a diminution of TOCs. The removal efficiencies of TOCs (η_{TOC}) defined by Eq. (1) at time about 8–25 min, for the complete elimination of 2-NS are between 1 and 4% as shown in Fig. 4. The intermediates produced from the decomposi-

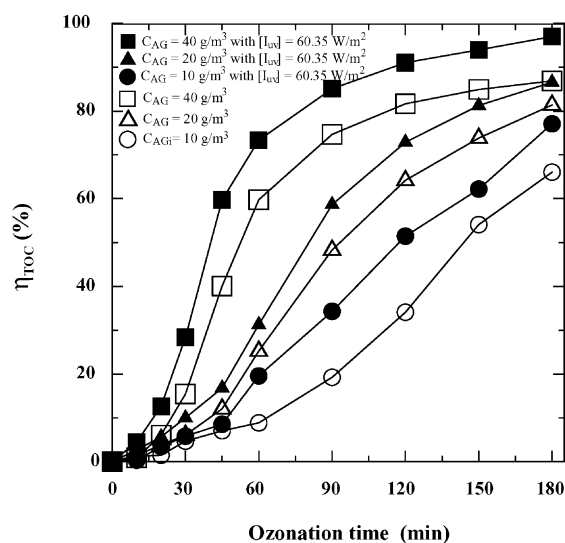


Fig. 4. Variation of η_{TOC} with time for the ozonation of 2-NS in semi-batch system.

tion of 2-NS contribute over 96% TOC relative to the initial value.

$$\eta_{TOC} = \frac{C_{TOC0} - C_{TOC}}{C_{TOC0}} \quad (1)$$

where C_{TOC0} and C_{TOC} are values of C_{TOC} at $t = 0$ and t , respectively. The decrease of decomposition extent of 2-NS with ozonation time also counts for the generation of by-products, which are also competitors for oxidation. The initial attacks of ozone on 2-NS may be proceeded via (1) an ozone dipolar cycloaddition on the 1,2 bond or (2) an electrophilic substitution of ozone on carbon 1 [5].

3.2. Variations of removal efficiency of TOC and ozone concentration

Fig. 4 shows the variation of removal efficiency of TOC (η_{TOC}) under various experimental conditions. The value of η_{TOC} increases with the ozonation time continuously. Apparently, the C_{AGi} significantly contributes the mineralization extent of 2-NS for both sole O_3 and O_3/UV systems. Moreover, the UV radiation in the ozonation of 2-NS also improves the removal of TOC. The OH^\bullet induced by the presence of UV radiation proceeds with higher η_{TOC} via the reaction noted as reaction V [12,13]. Limiting values of η_{TOC} seem to appear for the sole ozonation of intermediates. The lower value of $d\eta_{TOC}/dt$ in the early stage of ozonation is due to the cause that ozone is first consumed for the opening of benzene rings and the oxidation of the sulfonic substituent, thus accompanying with the low diminution of TOCs. In addition, the lower value of $d\eta_{TOC}/dt$ in the later ozonation stage (higher η_{TOC}) is caused by the ozonation of resistant intermediates such as oxalic acid, phthalic acid, and formic acid, which have low reactivity towards ozone molecules [14,15].

Note that the cause for the apparent contribution of UV radiation on the mineralization of 2-NS during ozonation is attributed to the vigorous attack of hydroxyl radicals, for which the generation is enhanced by the UV radiation, on the intermediates that are more resistant to ozone than hydroxyl radicals. On the other hand, the insignificant effect of UV radiation on the decomposition of 2-NS is due to the high reactivity of 2-NS toward ozone. Similar phenomena were also observed during the ozonation of 2-NS in the aqueous solution [5]. Furthermore, the decomposition rates of 2-NS and TOC via sole ozonation in the electroplating solution seems to be faster in comparison with those in the aqueous solution. It may be caused by the catalytic effect of copper ions in the electroplating solution [16,17]. On the other hand, the enhancement of UV radiation on the mineralization of 2-NS during ozonation in the electroplating solution is weaker than that in the aqueous solution because of the lower transmission of UV radiation in the electroplating solution. In addition, the pH value of the electroplating solution is about 0.25. The variation of pH during the ozonation experiments was found to be very slight due to the high acid concentration.

Moreover, the variations of dimensionless liquid ($C_{AL}/(C_{AGi}/H_A)$) and gas (C_{AGe}/C_{AGi}) ozone concentrations with η_{TOC} for various cases are shown in Fig. 5. In the first stage (with $\eta_{TOC} \leq 5\%$), the C_{AL} remains nearly undetectable (Fig. 5a). In this regime, the rate of ozonation reaction is very fast so that the ozone transferred from the gas phase is immediately consumed in the solution. Then the dissolved ozone starts to appear with $C_{AL}/(C_{AGi}/H_A)$ having a value of about 0.11 in the regime with $34\% \leq \eta_{TOC} < 5\%$. Later, the C_{AL} gradually increases with η_{TOC} when $\eta_{TOC} > 34\%$. The accumulation of dissolved ozone is attributed to the case that the consumption rate of dissolved ozone is lower than the gas–liquid mass transfer rate of ozone due to the lower reactivities of the refractory intermediates in the reacted solution. The variation of C_{AL} with η_{TOC} seems to be only slightly dependent on C_{AGi} . Obviously, the C_{AL} has the smaller value in the case of O_3/UV than that of sole O_3 . Fig. 5b shows that the C_{AGe}/C_{AGi} increases rapidly in the beginning and has a value of 0.36–0.56 when $\eta_{TOC} \leq 34\%$. The C_{AGe} apparently further increases with η_{TOC} corresponding to the increase of C_{AL} as $\eta_{TOC} > 34\%$.

3.3. Removal of TOC associated with ozone consumption and ORP

In addition, the relation between η_{TOC} and the ozone consumption per mol 2-NS, $m_{O_3R}/(C_{BL0} V_L)$ (mol mol^{-1}), is illustrated in Fig. 6. The ozone consumption (m_{O_3R}) is calculated by Eq. (2), where V_L and V_F are the volumes of solution and free space in the reactor, respectively.

$$m_{O_3R} = \int_0^t Q_G(C_{AGi} - C_{AGe}) dt - C_{AL} V_L - C_{AGe} V_F \quad (2)$$

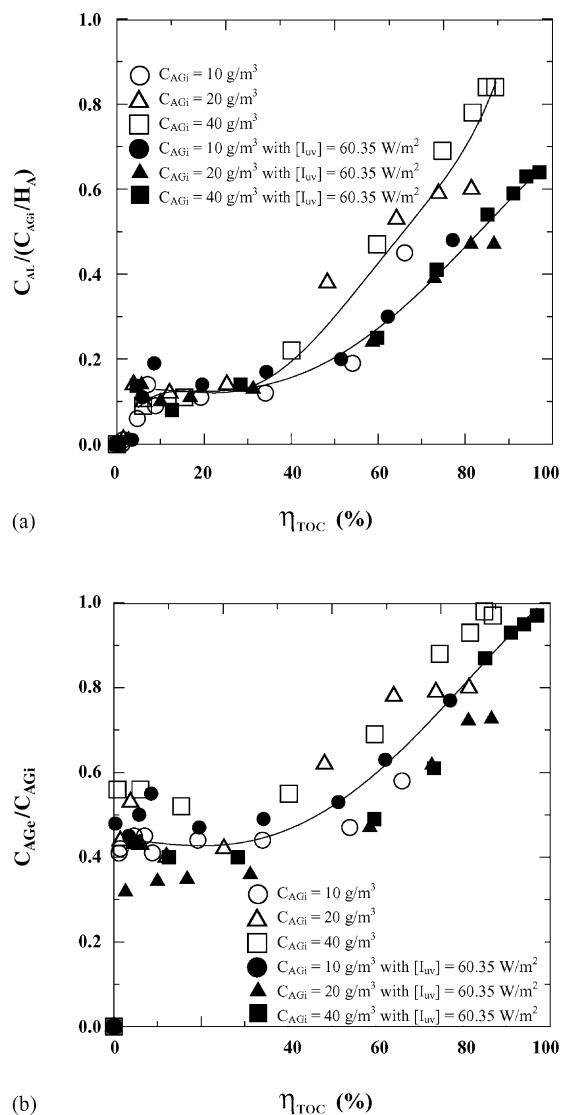


Fig. 5. $C_{AL}/(C_{AGi}/H_A)$ and C_{AGe}/C_{AGi} vs. η_{TOC} for the ozonation of 2-NS in semibatch system. Line: average and smooth curve of experimental data. (a) $C_{AL}/(C_{AGi}/H_A)$; (b) C_{AGe}/C_{AGi} .

As a result, η_{TOC} increases with $m_{O_3R}/(C_{BL0} V_L)$ apparently and agreeably in all cases examined, indicating a high correlation between the mineralization of 2-NS and the ozone consumption. It reveals that the value of ratio of $\eta_{TOC}/(m_{O_3R}/(C_{BL0} V_L))$ is about 4.3% during the ozonation treatments of 2-NS. The η_{TOC} approaches to 100%, which stands for the nearly complete mineralization of 2-NS, as the value of $m_{O_3R}/(C_{BL0} V_L)$ is greater than 23. It is worth noting that the higher mineralization extent of 2-NS in the O_3/UV treatment is resulted from the greater consumption efficiency of applied ozone.

Fig. 7 presents the variation of ORP of liquid with η_{TOC} . The value of ORP can be used as a supplementary ozonation index of ozonation system [5,18]. The experimental ORP data of the present study were further used to plot the average and smooth curve in Fig. 7, which shows the distinct

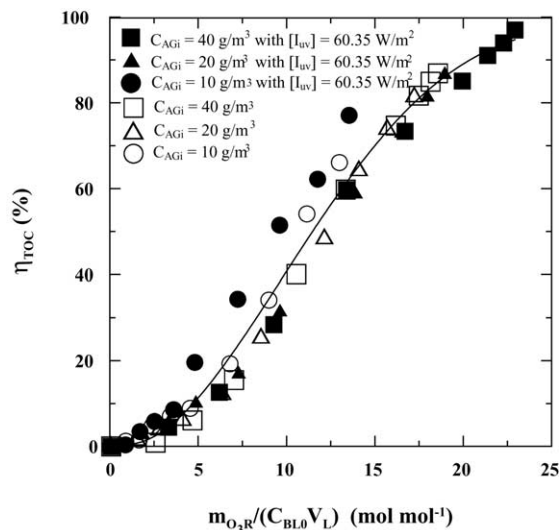


Fig. 6. η_{TOC} vs. $m_{\text{O}_3\text{R}}/(C_{\text{BLO}}V_L)$ for the ozonation of 2-NS in semibatch system. Line: average and smooth curve of experimental data with $R^2 = 0.980$.

variation of ORP with η_{TOC} . The value of ORP reveals a slight variation in the initial period while a significant increase in the later period for $10\% < \eta_{\text{TOC}} < 30\%$. The initial ORP value of the electroplating solution before ozonation is 426 mV. For $\eta_{\text{TOC}} \leq 10\%$, the values of ORP are between 700 and 785 mV. In this stage, the organics of TOCs in the solution are predominant for controlling the ORP of system with small variation. As the concentration of TOCs (C_{TOC}) decreases below 93.6 mg/L ($\eta_{\text{TOC}} > 10\%$), the ORP starts to increase with η_{TOC} as shown in Fig. 7. This regime may be called the transient stage. As the η_{TOC} is close to 50%, the value of ORP of system approaches to that of organic-free solution of about 1360 mV. Thus, ORP is a useful index associated with the oxidation state of the ozonation of 2-NS in terms of η_{TOC} .

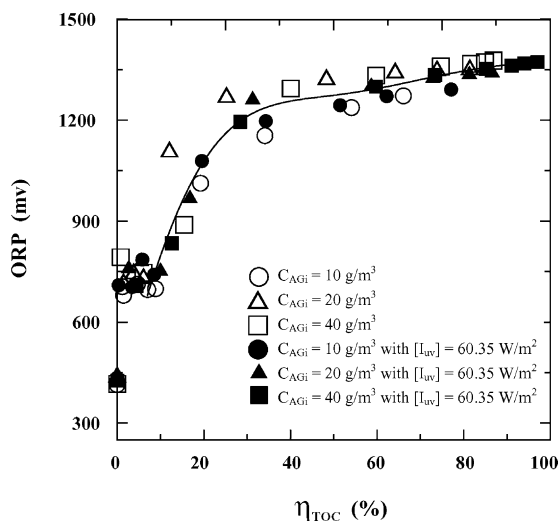


Fig. 7. ORP vs. η_{TOC} for the ozonation of 2-NS in semibatch system. Line: average and smooth curve of experimental data with $R^2 = 0.947$.

In summary, the difference in performance between O_3 and O_3/UV treatments regarding the destruction of 2-NS is not significant. However, the introduction of UV radiation combined with O_3 gives significant contribution for the subsequent oxidation of intermediates after the disappearance of 2-NS. The combination of ozone with UV radiation is recommended for treating the 2-NS in the electroplating solution as far as the TOC reduction is concerned, although the process with O_3 alone may be sufficient for destructing the 2-NS.

4. Conclusions

Ozonation combined with UV radiation was employed as an effective way for the removal of 2-naphthalenesulfonate (2-NS) in the electroplating solution. The nearly complete mineralization of 2-NS can be achieved under the experimental conditions of this study. The decomposition of 2-NS accompanies the diminution of total organic carbons (TOCs) and the consumption of ozone. The following conclusions may be drawn:

1. The decomposition extent of 2-NS increases with the ozone concentration of feed gas. However, it is not significantly enhanced by the presence of UV radiation. At the time when the decomposition of 2-NS is completed, the removal efficiency of TOC (η_{TOC}) is lower than 4%.
2. Both the ozone concentration of feed gas and UV radiation can improve the mineralization extent of 2-NS. Limiting values of η_{TOC} of 2-NS in the electroplating solution appear for the sole ozonation of intermediates. The explanation for the phenomena can be addressed with the mechanism of ozonation of 2-NS.
3. Both the liquid- and discharged-gas ozone concentration values remain low when $\eta_{\text{TOC}} \leq 34\%$, while they increase significantly with higher η_{TOC} afterwards. Furthermore, the clear-cut relationship between η_{TOC} and the ozone consumption was obtained in this study.
4. The oxidation reduction potential (ORP) can be used as a supplementary index of oxidation state of 2-NS in the electroplating solution. The ORP value varies with the residual TOC concentration during the ozonation of 2-NS.

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