



Degradation of linuron by UV, ozonation, and UV/O₃ processes—Effect of anions and reaction mechanism

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ABSTRACT

A comprehensive study of the degradation of linuron, one of the phenylurea herbicides, was conducted by using different treatment processes including UV, ozonation and UV/O₃. The effect of various anions on the performance of ozonation has been examined. *N*-terminus demethoxylation, photohydrolysis with or without dechlorination, and *N*-terminus demethylation have been found to be the major mechanisms in the linuron decay under the irradiation of UV at 254 nm while *N*-terminus demethoxylation, dechlorination and hydroxylation on benzene ring was observed to be involved in the ozonation process. Eight new intermediates were identified in UV process in this study compared with previous studies. Different decay pathways were proposed based on the identified intermediates in the three studied processes. UV/O₃ has demonstrated the best performance among these three processes in terms of LNR decay, mineralization, dechlorination and de-nitrogenation.

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1. Introduction

Linuron (*N*-(3, 4-dichlorophenyl)-*N'*-methoxy-*N'*-methylurea) (LNR), one of the most commercialized phenylurea herbicides, has been broadly used to control annual and perennial broadleaf and grassy weeds by inhibiting photosynthesis upon absorption in the roots of a wide range of crops. LNR is moderately persistent in soil with a half-life ranging from 38 to 67 days [1]. LNR has been reported to inhibit the activity of 5 α -reductase which is one of the key enzymes of human androgen metabolism [2]; Wilson et al. have observed that LNR reduces testosterone production from the fetal rat testis [3]; furthermore, some of its naturally decayed intermediates (such as chloroaniline) have also been suspected as endocrine disruptors [4], which stimulate the demand of developing treatment techniques to eliminate LNR and its intermediates in aqueous phase. Therefore, LNR has suffered a demanding examination of its treatability by various treatment techniques, such as biological methods [5,6], O₃/H₂O₂ [7], UV/O₃ [8], direct photolysis [9], photo-Fenton procedure [10], ultrafiltration/nanofiltration process [11], and photocatalysis [12]. A major part of the investigation, however, focuses on the removal or decomposition of LNR. If the fate of the resulting products remains unanswered, the treatment process cannot be proposed as a trouble-free method since the decay of the parent compounds may result in the generation

of more toxic organics than parent compounds. The intermediates from the transformation of LNR vary with treatment methods since different methods offer differed reaction mechanisms. Even if LNR is treated by the same process, the identification and fate of intermediates can still be varied depending on the reaction conditions. As a result, a careful investigation of the resulting products is necessary in each process.

In earlier study, only four intermediates have been identified during the phototransformation of LNR in aqueous phase under the irradiation of UV at 254 nm [9] and the evolution and destination of these compounds still remain unanswered. In addition, the information about the reaction mechanism of LNR by UV/O₃ process and the fate of intermediates generated during this process is scanty so far. Therefore, in this study, the degradation intermediates of LNR by UV, O₃, and UV/O₃ were investigated and the decay pathways were proposed accordingly for these three processes, respectively. The influence of various anions on the decomposition of LNR by ozonation has also been examined. Some major products which escaped from identification in the earlier studies are presented in this paper.

2. Experimental

Linuron (*N*-[3,4-(dichlorophenyl)-*N'*-methoxy-*N'*-methylurea]) (99%) was obtained from SUPELCO. *N*-(3, 4-dichlorophenyl)-*N'*-methylurea (DCPMU) and 1-(3, 4-dichlorophenyl) urea (DCPU) were purchased from Sigma–Aldrich. Na₂CO₃, Na₂SO₄, and Na₂HPO₄ were obtained from BDH while NaCl was purchased from

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Table 1
Identified degradation products and their main fragments determined by LC/ESI-MS.

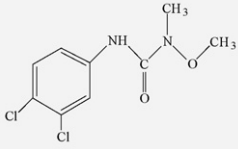
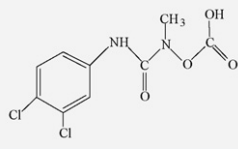
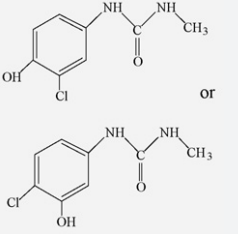
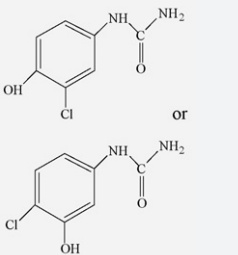
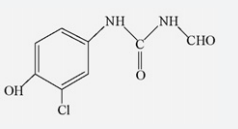
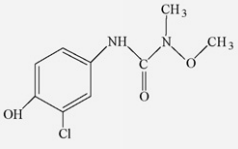
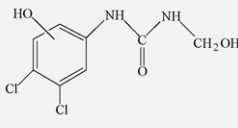
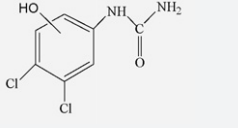
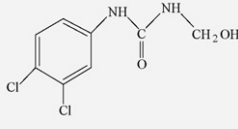
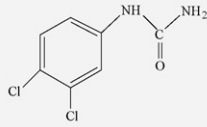
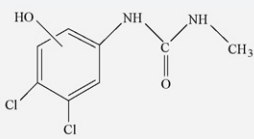
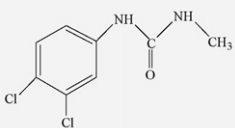
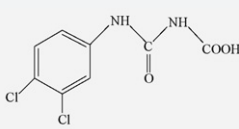
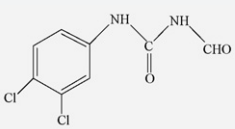
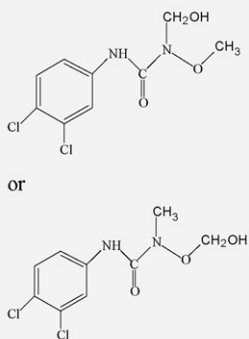
Compound	Retention time	Molecular weight	Molecular ion and main fragments	Structural formula	Detected in		
					UV	O ₃	UV/O ₃
LNR	20.93	248	247, 217, 188, 160, 109		✓	✓	✓
1	10.25	278	277, 250, 233, 217, 119				✓
2 and 3	10.61, 12.62	200	199, 142		✓	✓	✓
4	11.61	186	185, 165, 141, 119		✓		✓
5	13.26	214	213				✓
6 and 7	14.11 and 15.40	230	229, 37, 119, 109		✓	✓	✓
8	14.90	250	249, 219, 202, 176, 137, 119, 109				✓
9	15.44, 15.56	220	219, 203, 176, 137, 119, 109				✓
10	15.68	234	233, 203, 160, 137, 119, 109		✓	✓	✓

Table 1(Continued)

Compound	Retention time	Molecular weight	Molecular ion and main fragments	Structural formula	Detected in		
					UV	O ₃	UV/O ₃
11	16.31	204	203, 160, 137,119,109		✓	✓	✓
12	16.93	234	233, 202,176, 137,119,109		✓	✓	✓
13	17.46	218	217, 160, 137,119,109		✓	✓	✓
14	18.74	248	247, 202, 204		✓		✓
15	18.93	232	231,202,188 160, 137,119,109		✓	✓	✓
16 and 17	19.30, 19.72	264	263, 233, 217, 202,188,156,119, 109	or 		✓	✓

Riedel-dehaën. All chemicals are analytic purity and all solvents are HPLC grade and used without further purification. For pH adjustment, 0.1 M sulfuric acid and 0.1 M sodium hydroxide were used. All experiments were carried out at air-conditioned room temperature at 23 °C in duplicate and the error is within 5%.

For the tests involving UV photolysis, 600 mL sample was irradiated in a 800-mL (97.8 mm ID × 125 mm H) quartz beaker with magnetic stirring. The beaker was placed in the center of a Rayonet™ RPR-200 photoreactor, which was equipped with phosphor-coated low-pressure mercury lamps, emitting 253.7 nm monochromatic UV at a light intensity of 1.5×10^{-6} Einstein L⁻¹ s⁻¹.

For the tests involving ozonation, 400 mL of deionized water was pre-ozonated for 15 min (to produce a saturated ozone solution), after adding 200 mL of LNR stock solution into the pre-ozonated solution, a reduction of dissolved ozone was observed at the beginning of the reaction, which could be replenished within 1 min by continuous feeding of ozone gas into the reactor through a glass sparger (pore size ranges from 16 to 40 μm) located just above the bottom of the reactor. Ozone gas was produced by OZAT

ozone generator (CFS-1A from Ozonia, Ltd.) with oxygen feedgas at 3.5 m³_{STP}/h, the pressure set at 0.9 bar and 5% power, which produced 0.0245 mM saturated ozone solution. The concentration of ozone was determined by the Indigo spectrometric method [13]. Ozone was continually fed into the reactor during the reaction. For the UV/O₃ experiments, simultaneous UV irradiation was provided during the ozonation period. The remaining ozone in the collected sample was quenched by sodium thiosulfate before the quantification of LNR. For those intermediate compounds, of which standards are not available commercially were quantified in terms of ion intensity relative to the initial LNR concentration for comparison.

A Thermo Quest Finnigan LCQ Duo Mass Spectrometer system was used to identify the reaction intermediates, which consisted of a PDA-UV detector, and an electrospray ionization with a quadrupole ion-trap mass spectrometer operating at a negative mode. The mobile phase was a mixture of (A) 5 mM ammonia acetate (pH 4.6) and (B) acetonitrile (100%). The composition of the mobile phase was changed according to the following gradient: 95% of A was kept during the first 2 min. From 2 to 26 min, B was steadily increased from 5% to 95%. From 26 to 27 min, B was kept

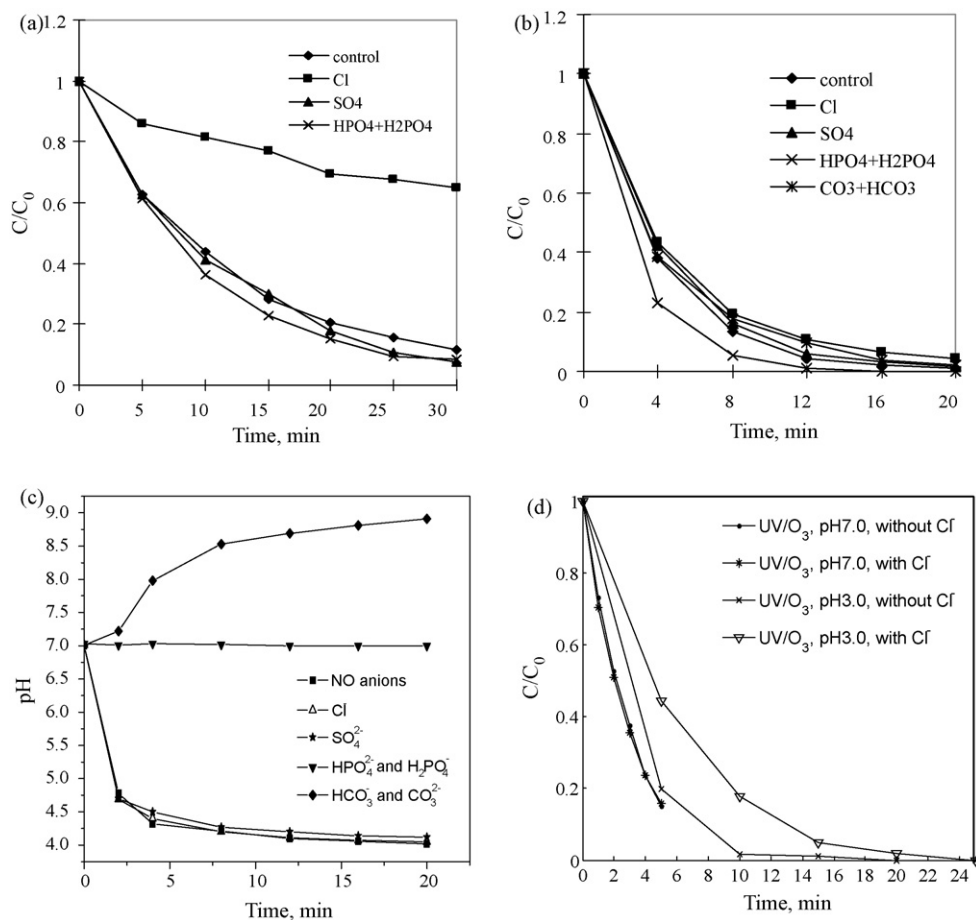


Fig. 1. (a) The effect of varied anions on the performance of ozonation at pH 3. (b) The effect of varied anions on the performance of ozonation at pH 7. (c) The variation of pH during the ozonation of LNR with the presence of various anions. (d) The effect of chloride ion on the performance of UV/O₃. (Notes: [LNR]₀ = 0.1 mM, [anions] = 0.01 M, [I₀] = 6.0 × 10⁻⁶ Einstein L⁻¹ s⁻¹).

at 95%. Finally, the mobile phase turned to the initial composition until the end of the run.

The generation of chloride, nitrite and nitrate ions were monitored by the ion chromatography (Dionex Series 4500i) composed of an anion column (Dionex IonPac[®] AS14 (4 mm × 250 mm)), Dionex CD25 Conductivity Detector and Dionex AS 40 Automated sampler. A mixture of 1 mM of NaHCO₃ and 3.5 mM of Na₂CO₃ was used as the mobile phase eluting at 1 mL min⁻¹. For the quantification of the ammonium ion produced during the reaction, Dionex IonPac[®] CS12 (4 mm × 250 mm) was used as a cation column and 0.022 M MSA (methane sulfonic acid) was used as the mobile phase eluting at 1 mL min⁻¹. The total organic carbon (TOC) was analyzed by a Shimadzu TOC-5000A analyzer equipped with an ASI-5000A autosampler to determine the mineralization of the organic pollutants during the processes.

3. Results and discussion

3.1. The effect of varied anions on the LNR decay in sole-ozone system

The effect of various cations such as Mn²⁺, Fe²⁺, Co²⁺, Zn²⁺, Cu²⁺ and Ti²⁺ on the performance of ozonation process has been well documented [14–17]. The information about whether or not the anions may influence the functioning of sole-ozonation process still remains very limited.

In this section, the effect of various anions on the LNR decay was investigated at pHs 3 and 7 in a sole-ozonation system. As

indicated in Fig. 2, the existence of 0.01 M chloride leads to the significant retardation of LNR decay at pH 3, while chloride does not show considerable influence on the degradation of LNR at pH 7. It was reported that chloride could react with ozone under acidic conditions as shown in Eqs. (1) and (2) [18]:



The first reaction is the rate-determining step while the second one is reversible and relatively faster. At pH 3, high proton concentration favors the second reaction proceeding towards right side, which may accelerate the first reaction. Therefore, at pH 3, chloride ions can effectively compete for O₃ with LNR to produce Cl₂ which is a much weaker oxidant than ozone. On the other hand, at pH 7, lower proton concentration deactivates the above reactions, restricts the reaction between ozone and chloride, and minimizes the competition between chloride and LNR for O₃. In addition, a little retardation in the LNR decay rate was observed after 4 min reaction at pH 7. This is possibly due to the decrease of pH during the reaction as shown in Fig. 2c.

It is also interesting to note that the LNR decay rate can be accelerated with the existence of HPO₄²⁻ and H₂PO₄⁻ at pH 7 while such an effect is not significant at pH 3, in which the solution pH remains unchanged during the reaction for every scenario (data not shown). At pH 7, however, the buffer capacity of HPO₄²⁻ and H₂PO₄⁻ made the pH of the solution very stable throughout the reaction, while the pH level decreased from 7 to 4.78 during the first 2 min reaction in the other cases (including control) as indicated in Fig. 2c. The

higher pH level may result in a faster decay of LNR in the reaction with the existence of HPO_4^{2-} and H_2PO_4^- , as discussed previously.

When 0.01 M Na_2CO_3 was added into the solution at pH 7, another interesting point is the increase of pH level during the reaction, where no improvement of LNR decay rate was observed even though the higher pH should theoretically improve the LNR decay. This is because carbonate ions can quench the hydroxyl radicals in the solution and generate hydroxide ions as described in Eq. (3):



Since carbonate and bicarbonate can compete for hydroxyl radicals with LNR, which can hinder the beneficial effect resulting from the increment of pH level, these two effects counteract each other and this rationalizes no appreciable influence of bicarbonate and carbonate ions on the LNR degradation rate.

Since the existence of chloride ion exerted a significant influence on the LNR degradation by ozonation at pH 3.0, it may be interesting to investigate the effect of chloride on the performance of UV/O₃ system (see Fig. 1d). Results observed in UV/O₃ system are quite similar to that in sole-ozone system. At pH 3.0, the existence of chloride ion noticeably inhibited LNR degradation while such effect was not observed at pH 7.0.

3.2. Reaction mechanism of LNR

In order to have a better understanding about the LNR degradation by UV, ozone and UV/ozone processes, the intermediates were identified and the evolution of major intermediates was investigated in each process. Seventeen intermediates were identified and summarized in Table 1.

3.2.1. UV photolysis

The direct photolysis of LNR and evolution profiles of intermediates by UV at 254 nm is shown in Fig. 2a. The LC-MS analysis revealed that twelve intermediates were produced during the reaction. The “demethoxylation” pathway is believed to be one of the major reaction pathways since the compound 13 (N-(3,4-dichlorophenyl)-N'-methylurea, DCPMU) is the dominant intermediate during photolysis of LNR as indicated in Fig. 2a. Similar observation has been reported earlier [9]. The formation of intermolecular hydrogen bond between one hydrogen atom of N-methoxyl and the oxygen of neighboring C=O bond and subsequent generation of formaldehyde were proposed to be the mechanism of this demethoxylation pathway. Faure and Boule reported four intermediates (compounds 6, 7, 11 (1-(3,4-dichlorophenyl)urea, DCPU) and 13 (DCPMU)) in the photolysis of LNR by UV at 254 nm [9] while eight new intermediates (compounds 2, 3, 4, 5, 10, 12, 14 and 15) were detected in this study. Photohydrolysis–dechlorination is believed to be another major reaction mechanism during the photolysis of LNR by UV at 254 nm, judging from the yields of the products from photohydrolysis–dechlorination and chloride ions during the reaction (see Fig. 2c). There are two pairs of isomers (6/7 and 2/3) which are the products of photohydrolysis–dechlorination among these intermediates. Compounds 6 and 7 are believed to come from the hydroxylation on the ring with simultaneous dechlorination of LNR. Compounds 2 and 3 originate from the photohydrolysis–dechlorination of compound 13 (DCPMU), and the photohydrolysis–dechlorination of compound 11 (DCPU) produces compound 4, which have been corroborated by two individual tests using compound 13 (DCPMU) and 11 (DCPU) as initial probe compounds by UV process at 254 nm. In addition, compound 12 was detected in the degradation of LNR and compound 13 (DCPMU) by UV irradiation at 254 nm, indicating this product is from the hydroxylation of benzene ring of DCPMU. The hydroxylation of benzene ring has been reported

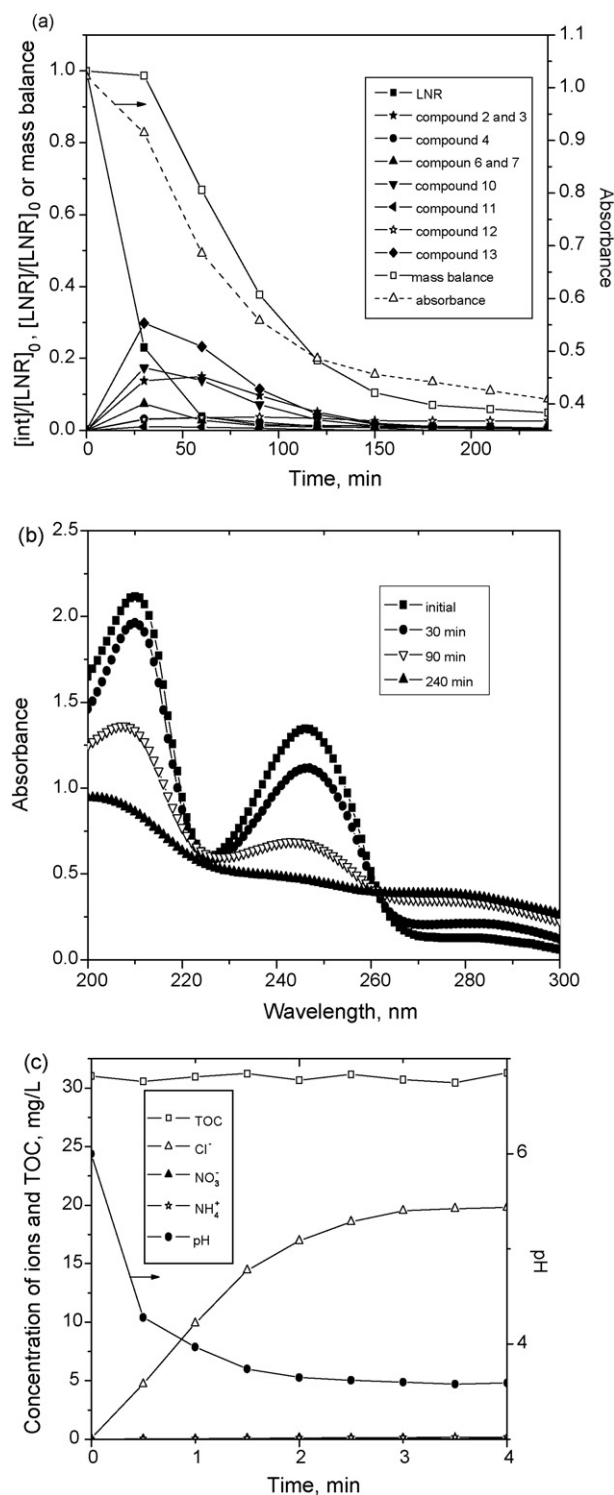
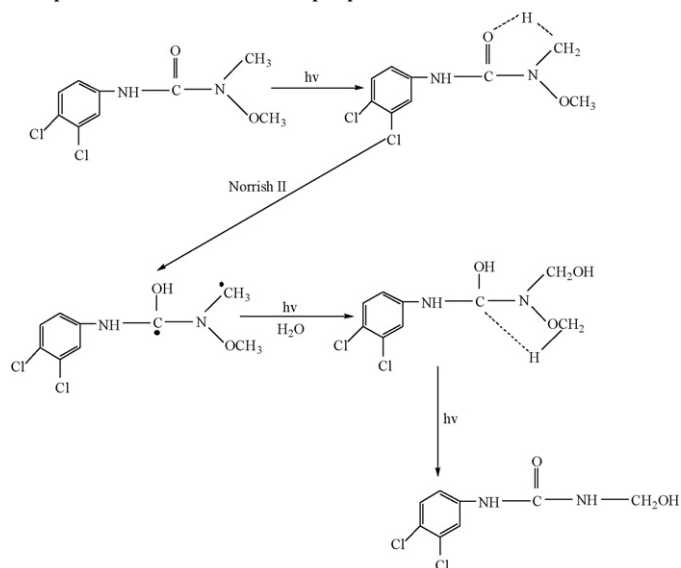


Fig. 2. (a) The evolution profiles of LNR and intermediates in the photolysis of LNR at 254 nm. (b) UV absorption spectrum of the solution at different time intervals. (c) The evolution profiles of TOC, pH, Cl^- , NO_3^- , and NH_4^+ concentration. (Notes: $[\text{LNR}]_0 = 0.285 \text{ mM}$, $\text{pH}_0 = 6.0$, $[\text{I}_0] = 9.0 \times 10^{-6} \text{ Einstein L}^{-1} \text{ s}^{-1}$).

by other researchers [19,20]. Jin et al. proposed two possible mechanisms (one is the presence of oxygen leading to the production of $\text{O}_2^{\bullet-}$ and HO_2^\bullet , and the other is that the benzene ring of the parent compound is hydroxylated via endoperoxide without involving free radicals). Oxygen was believed to be involved in both mechanisms, and it was suggested that the presence of oxygen could significantly increase the decay rate of

tyrosine [20]. This, however, is not observed in this study. In a separate test that the LNR solution was deoxygenated by argon before and during the irradiation by UV at 254 nm, the same twelve intermediates were identified and no reduction in LNR decay rate was observed in the absence of oxygen (data are not shown).

A different mechanism—direct hydrolysis of benzene ring of DCPMU, not involving oxygen, thus, is proposed and may rationalize the generation of compound 12. Compound 10 also escaped from the identification in earlier studies. It was convenient to assume that compounds 10 and 11 (DCPU) originate from *N*-oxidation and subsequent demethylation of DCPMU, respectively as observed in the work of Jirkovsky et al. [21]. However, it is interesting to find that compounds 10 and DCPU were not detected in the photolysis of DCPMU, indicating DCPMU is not the source of compound 10. Compounds 10 and 11 were detected in the photolytic degradation of LNR without the existence of oxygen, suggesting that oxygen was not involved in the production of these two compounds, either. The possible mechanism for the generation of compound 10, therefore, was proposed as below:



DCPU is believed to result from compound 10 since the photolysis of DCPMU does not generate DCPU. Therefore, the decay pathway of LNR by UV process was proposed (Fig. 3) based on the evolution profile analysis of intermediates during the photolysis of LNR and the information resulted from the photolysis of intermediates, DCPMU and DCPU, as the initial compounds. The percentages in Fig. 3 stand for the fraction of LNR transformed to a particular intermediate during the initial phase (30 min). Fig. 3 also reveals that demethoxylation is the predominant decay mechanism of LNR by UV process at 254 nm since 63.1% ($([\text{DCPMU}] + [\text{compounds 2 and 3}] + [\text{compound 12}]) / [\text{LNR}]_{\text{removed}}$) of LNR was eliminated via this pathway. Furthermore, the individual test using DCPMU as the initial compound reveals that photohydrolysis–dechlorination is the dominating mechanism in terms of the photolysis of DCPMU (96.9% of DCPMU was removed via this pathway).

As also indicated in Fig. 2a, all intermediates would be encountered when 90% LNR was removed by UV photolysis and compound 2, 3, 6, 7, 10, 12 and 13 would still exist in the reaction solution when 99% LNR decomposition was achieved. Fig. 2b shows UV spectrum of the reaction solution at different time intervals. It is well known that a benzene ring has two absorption bands (one occurs near 205 nm, and another one appears near 250 nm). As indicated in Fig. 2b, both absorption bands are vanishing during the photolysis reaction. Judging from the mass balance of benzene ring and the decreased absorbance of the solution at 254 nm (see

Fig. 2a and b), it is believed that ring-opening occurs during the photolytic decomposition of LNR. Unfortunately, mineralization of LNR was not observed in this process due to the lack of oxidants as demonstrated in the TOC curve (Fig. 2c). Fig. 2c also reveals that photohydrolysis–dechlorination led to considerable decrease of pH level from 6.0 to 3.59. It was observed that around 98% of chlorine on the benzene ring was released and trace amount of NH_4^+ and NO_3^- was detected, indicating de-nitrogenation could be achieved in the photolytic degradation of LNR by UV at 254 nm.

3.2.2. Ozonation

Benzene ring is susceptible to electrophilic attack (by electrophilic agents) due to its exposed π electrons. However, substituted groups on the benzene ring are believed to exert a significant influence on the reactivity of electrophilic reaction. LNR is tri-substituted by two chlorines and a side chain ($\text{NHCHON}(\text{OCH}_3)(\text{CH}_3)$). Bi-substitution by chlorine may result in decrease on the electron density of benzene ring due to electron-withdrawing ability of chlorine while the side chain can be a moderately activating substituent because the unshared electron pair on the nitrogen atom adjacent to the benzene ring may make a contribution to the electron density on the benzene ring through resonance [22]. Ozone is a highly electrophilic agent. The degradation of LNR by ozonation, therefore, becomes very complicated.

Ten intermediates were identified and summarized in Table 1 in this study. The evolution profiles of LNR and five major intermediates (compounds 6/7, 10, 11, and 13) were demonstrated in Fig. 4a. It is interesting to note that the profile of mass balance (of benzene ring) is quite similar to that of LNR, indicating the intermediates only account for a small portion to the total mass. This may suggest all the intermediates are susceptible to ozonation process. In addition, six minor intermediates (compounds 2/3, 12, 15, 16 and 17) were detected at trace levels in this system. Isomer compound 6/7 is believed to come from the dechlorination–hydroxylation of LNR while compounds 16 and 17 may originate from the *N*-terminus oxidation of LNR. Demethoxylation of LNR leads to the generation of compound 13 (DCPMU). The remaining intermediates (compounds 2/3, 10, 11, 12 and 15) are believed to come from DCPMU, which was confirmed by an independent test using DCPMU as initial probe compound in this process. Compounds 2 and 3 are from dechlorination–hydroxylation of DCPMU. *N*-terminus oxidation of DCPMU produces compounds 10 and 15. Compound 11 (DCPU) is believed to result from the demethylation of DCPMU, while hydroxylation of the benzene ring of DCPMU gives rise to the production of compound 12. A decay pathway of LNR by ozonation, thus, was proposed accordingly (see Fig. 6).

Judging from the low yield of isomer compound 6/7, the dechlorination is likely to be a minor mechanism of LNR decay by ozonation while *N*-terminus oxidation should be the major mechanism. However, more than 50% of total chlorine was released to the solution after 20 min of reaction as shown in Fig. 4b, which contradicts to the previous assumption. One possible explanation is that dechlorination–hydroxylation intermediates may not accumulate to an appreciable level due to fast decays. With the chlorine on the benzene ring being substituted by hydroxyl, the electron-donating resonance effect of hydroxyl group favors the enhancement of the electron density of benzene ring and the susceptibility of these dechlorination–hydroxylation intermediates to ozonation. Fig. 4a also shows compounds 6, 7 and 10 were encountered in this system when 90% LNR was removed by ozonation while no intermediates existed in the reaction solution when 99% LNR degradation was achieved.

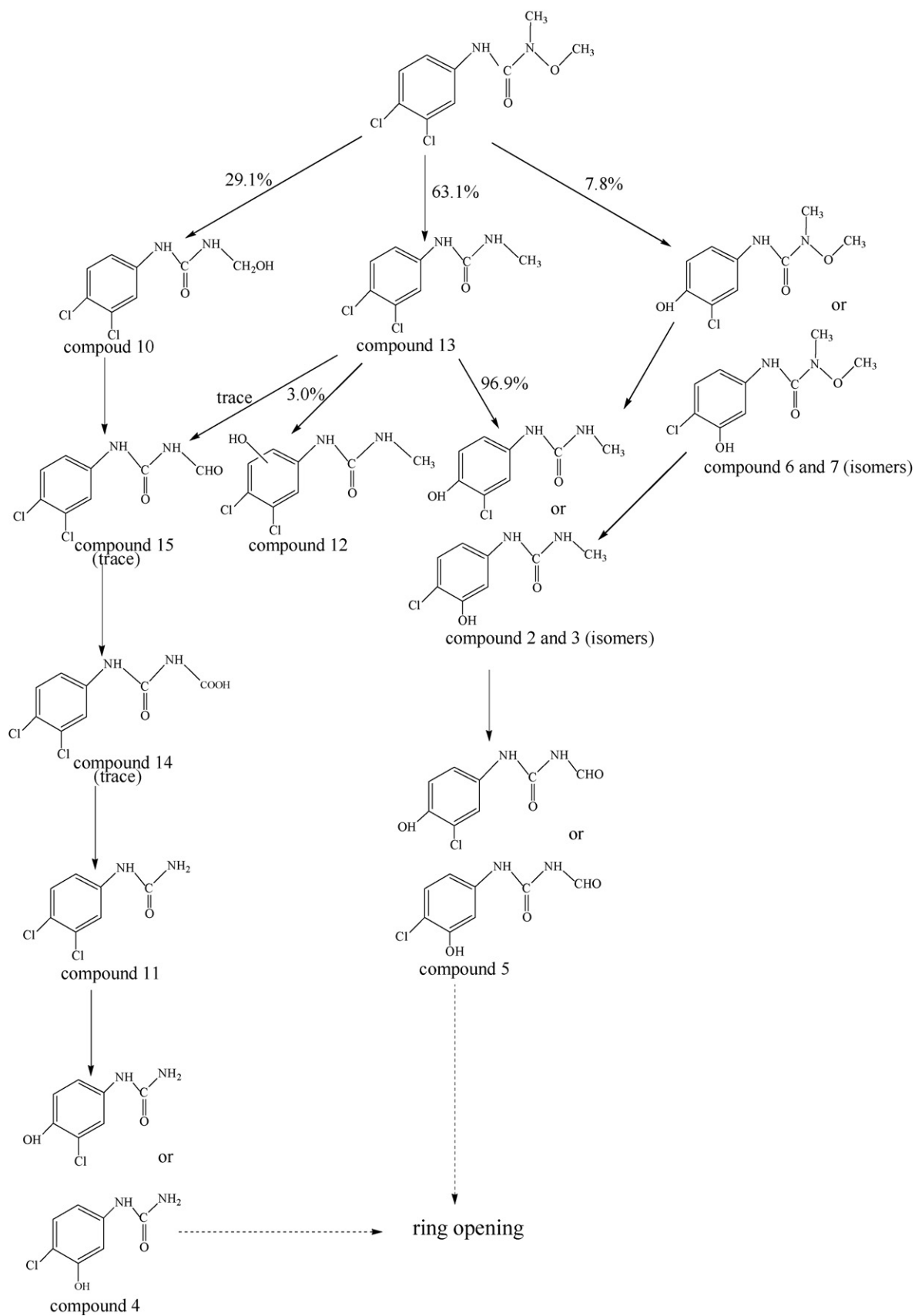


Fig. 3. The decay pathways of LNR under the irradiation by UV at 254 nm.

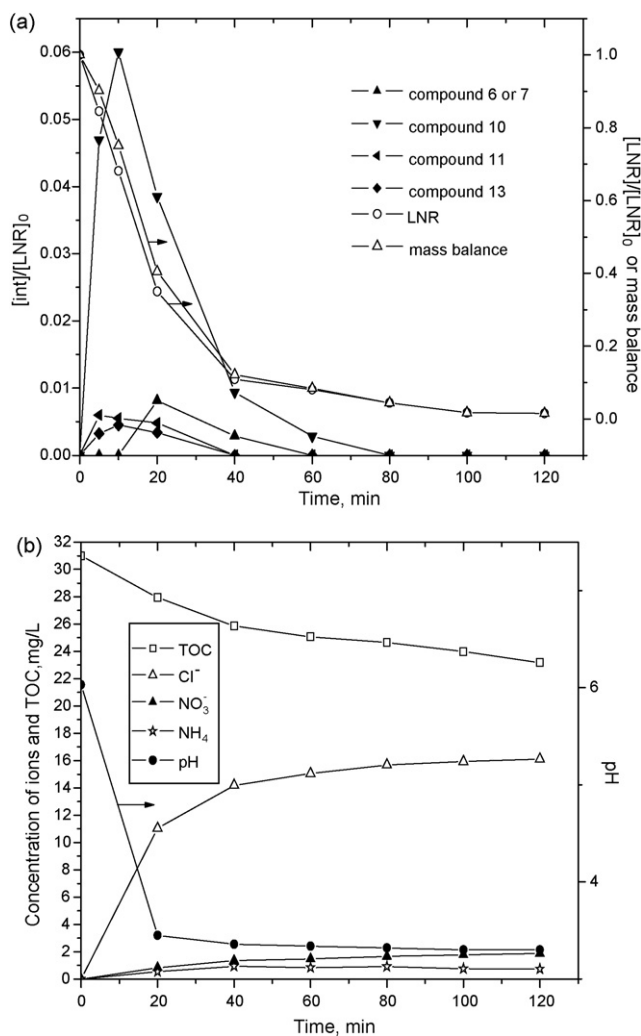


Fig. 4. (a) The evolution profiles of LNR and intermediates for the degradation of LNR by ozonation. (b) The evolution profiles of TOC, pH, Cl^- , NO_3^- , and NH_4^+ for the degradation of LNR by ozonation. (Notes: $[LNR]_0 = 0.285$ mM, $pH_0 = 6.0$).

Although mass balance of benzene ring nearly approaches zero, the TOC removal levels off at around 25% after 120 min (see Fig. 4b). This may be due to the high selectivity of ozone leading to its incapability to degrade some low molecular organic compounds resulting from the cleavage of benzene ring. As shown in Fig. 4b, the pH decreases significantly during the initial 20 min of the reaction due to the release of chloride and probably the generation of aliphatic acid. Fig. 4b also reveals that 13% of nitrogen was released to the solution as nitrate and ammonia ions after 120 min.

3.2.3. UV/O₃ process

It is generally agreed that several individual reactions such as direct (molecular) ozonation, direct photolysis, and radical oxidation (mainly hydroxyl radical) are involved in the degradation of organic compounds by UV/O₃ process. Therefore, more intermediates (seventeen) were detected in this system than sole-ozone and sole-UV (See Table 1). The evolution profiles of LNR and major products were shown in Fig. 5a. The decay pathway of LNR by UV/O₃ was proposed and illustrated in Fig. 6, where the degradation pathways by UV/O₃ are quite similar to that of ozonation. However, the yield of major intermediates is much higher in UV/O₃ system than that of major products in sole-ozone system as indicated in Fig. 5a. This is likely because these intermediates originate from more decay

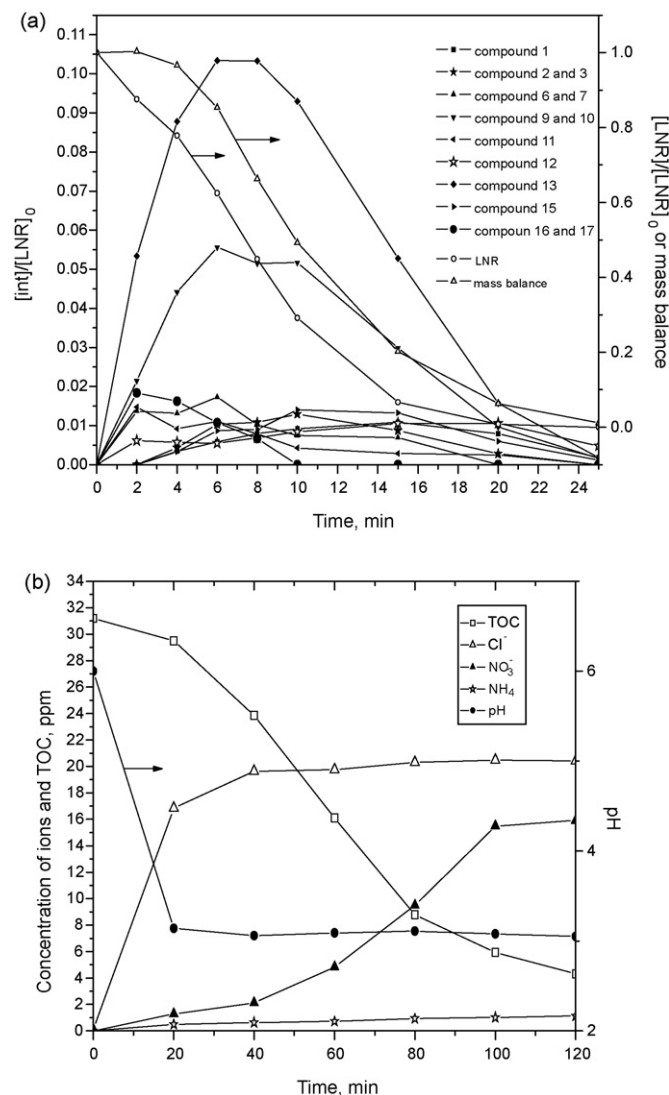


Fig. 5. (a) The evolution profiles of LNR and intermediates for the degradation of LNR by UV/O₃. (b) The evolution profiles of TOC, pH, Cl^- , NO_3^- , and NH_4^+ for the degradation of LNR by UV/O₃. (Notes: $[LNR]_0 = 0.285$ mM, $[I_0] = 9.0 \times 10^{-6}$ Einstein $L^{-1} s^{-1}$, $pH_0 = 6.0$).

mechanisms in parallel including photolysis, radical oxidation and oxidation offered by ozone molecule. At the initial stage of reaction, photolysis may play a major role in the degradation of LNR since both UV/O₃ and UV processes produce the same dominating intermediates (the yield of compound 13 is the highest and followed by compound 10) (see Figs. 2a and 5a). This phenomenon can be rationalized as follows.

Ozone can be rapidly photolyzed into hydrogen peroxide under UV irradiation at the wavelength of 254 nm due to its high molar absorptivity ($3600 M^{-1} cm^{-1}$) and quantum yields (0.48) [23].

The low molar absorptivity of H_2O_2 ($19.6 M^{-1} cm^{-1}$) [23] may make H_2O_2 incapable of competing with LNR (the molar absorptivity of LNR is $13254 M^{-1} cm^{-1}$) [8] for photons to produce hydroxyl radical.

As also illustrated in Fig. 5a, all other intermediates still remained in the reaction solution except compounds 16 and 17 when 90% LNR degradation was achieved while compounds 1, 2 or 3, 10, 11, 12, 13 and 15 were encountered after 99% LNR was removed in UV/O₃ system.

The evolution of TOC, pH and varied ion products in UV/O₃ process was also investigated and summarized in Fig. 5b. As demon-

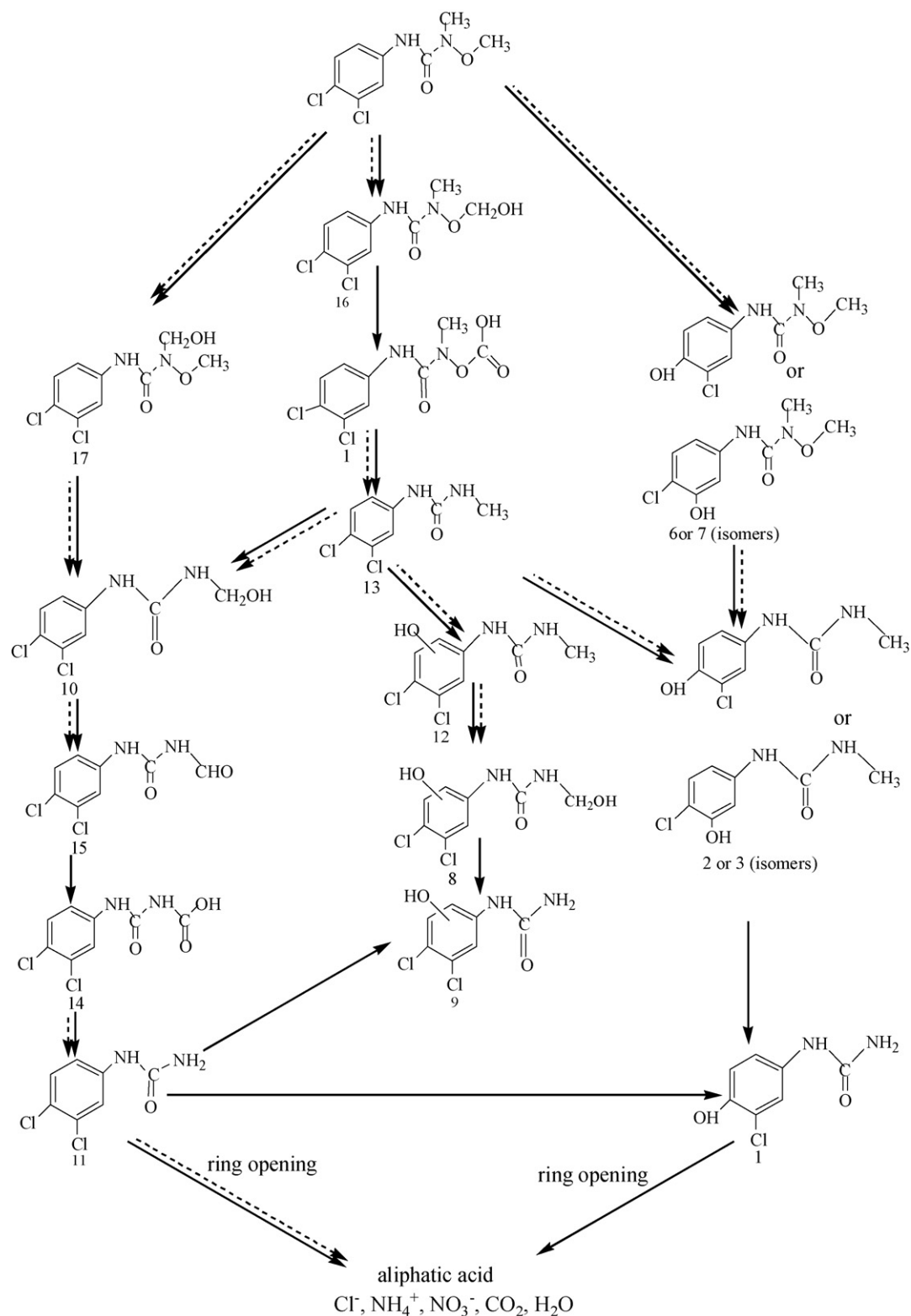


Fig. 6. The degradation pathways of LNR by ozonation and UV/O₃ processes. (Notes: Solid arrows indicate UV/O₃ process while dashed arrows indicate ozonation).

strated in Fig. 5, the UV/O₃ process has shown several advantages over sole-UV and ozonation including: (1) more than 86% mineralization; (2) faster degradation of LNR (complete decomposition of LNR was observed after 25 min); (3) greater and faster removal

in terms of mass balance; and (4) greater and faster dechlorination and de-nitrogenation (a complete release of chlorine was achieved after 80 min and around 56% of nitrogen was released as ammonia and nitrate ions after 120 min).

4. Conclusions

The degradation of LNR by UV, O₃ and UV/O₃ processes was examined. The effect of various anions on the performance of ozonation was also investigated. Chloride ion was observed to significantly retard the degradation of LNR at pH 3 while it exerted no effect on the performance of ozonation at pH 7. The presence of phosphate ion leads to the increase of LNR decay rate at pH 7 due to its buffer capacity to maintain a stable pH, and has no influence on the LNR decay rate. In addition, the reaction mechanisms were proposed via identification of intermediates and evolution profile analysis of intermediates in UV, O₃ and UV/O₃ processes. Among these three treatment processes, UV/O₃ process has exhibited the best overall performance. It demonstrated significant advantages not only in the decay rate of LNR but also in achieving 86% mineralization at the end of the process (120 min).

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