



A new approach to quantify the degradation kinetics of linuron with UV, ozonation and UV/O₃ processes

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ABSTRACT

The degradation of linuron, one of phenylurea herbicides, was investigated for its reaction kinetics by different treatment processes including ultraviolet irradiation (UV), ozonation (O₃), and UV/O₃. The decay rate of linuron by UV/O₃ process was found to be around 3.5 times and 2.5 times faster than sole-UV and ozone-alone, respectively. Experimental results also indicate overall rate constants increased exponentially with pH above 9.0 while the increase of rate constants with pH below 9 is insignificant in O₃ system. All dominant parameters involved in the three processes were determined in the assistant of proposed linear models in this study. The approach was found useful in predicting the process performances through the quantification of quantum yield (Φ_{LNR}), k_{OOH} (rate constant for the formation of free radical HOO[•] from ozone decomposition at high pH), rate constant of linuron with ozone ($k_{\text{O}_3\text{LNR}}$), rate constant of linuron with hydroxyl radical ($k_{\text{OH}\cdot\text{LNR}}$), and α (the ratio of the production rate of OH[•] and the decay rate of ozone in UV/O₃ system).

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1. Introduction

The phenylurea herbicides have been widely applied as effective weed killers by inhibiting photosynthesis upon absorption in the roots in the conventional production of corn, cereals, vegetables and fruits since their discovery in 1950 (Sorensen et al., 2005). Generally, these chemicals are characterized as persistent in the environment (half-life in soil was reported to be 38–67 d) (Caux et al., 1998) and thus have been found frequently in surface and ground waters (Garmouma et al., 1997). Linuron (*N*-(3,4-dichlorophenyl)-*N'*-methoxy-*N'*-methylurea) (LNR), one of the most commercialized phenylurea herbicides, was selected as probe compound. LNR was classified by the EPA as a possible human carcinogen; it was incorporated in the Colborn list due to its possible endocrine disrupting effects (Colborn et al., 1993); it was reported to inhibit the activity of 5 α -reductase which is one of the key enzymes of human androgen metabolism (Lo et al., 2007); and it is also highly toxic to non-target aquatic organisms such as fish and shellfish. The LC50 for linuron in trout and bluegill is 16 mg/L, and 40 mg/L in crawfish (EPA, 1984). Some of its naturally decayed intermediates (such as chloroaniline) were also suspected as endocrine disruptors, which encourages the need of developing treatment techniques to eliminate and mineralize these contaminants.

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Ozone process has widely been applied in the treatment of particular organic substances of concern, such as 2,4-dichlorophenoxyacetic acid (Chu and Ching, 2003), trichlorophenol (Graham et al., 2003) and atrazine (Acero et al., 2000). However, the reactions between organic substances and ozone are highly electrophilic and selective (Yao and Haag, 1991), which limit the application of the ozonation as a sole treatment process in meeting drinking water requirements. Therefore, intensive efforts have been put into the research about ozone associated with other oxidation processes, such as O₃/H₂O₂ (Chen et al., 2006), Ultrasound/O₃ (He et al., 2007), UV/O₃ (Lau et al., 2007), ozonation coupled with photocatalysis (Sanchez et al., 1998), and ozonation combined with electrolysis (Kishimoto et al., 2008), in which hydroxyl radical oxidation is believed to play a key role in the mineralization of organic substances due to its non-selective property.

LNR is subjected to growing attentions for investigating its treatability by various techniques, such as biological methods (Dejonghe et al., 2003; Sorensen et al., 2005), O₃/H₂O₂ (Tahmassebi et al., 2002), direct photolysis (Faure and Boule, 1997), photo-Fenton procedure (Katsumata et al., 2005), and photocatalysis (Lopez et al., 2005). However, the study of LNR degradation by UV/O₃ process in aqueous phase is still superficial and the comprehensive investigation on the individual reaction kinetics is very limited. The combined UV/O₃ process has been widely studied (Lau et al., 2007), and its overall oxidation reaction is believed to result from a synergistic effect of several individual reactions, such as direct ozonation, direct photolysis, and indirect radical oxidation. UV

irradiation can lead to ozone being transformed into hydrogen peroxide which can be further photolyzed into OH^\cdot and then initiate a chain of radical reactions (Gurol and Akata, 1996). It is believed that the UV/ O_3 process could provide an effective treatment of LNR and its toxic intermediates present in contaminated waters.

In this study, the degradation and mineralization of LNR was examined by direct photolysis, O_3 , and UV/ O_3 processes in aqueous phase. In addition, the effects of initial pH levels, ozone dose and light intensity on the decay rate of LNR were also investigated. The information was used in subsequent model derivations and rate constants determination for the involved sole-UV, O_3 and UV/ O_3 systems.

2. Methodology

LNR (3-[3,4-(dichlorophenyl)-1-methoxy-1-methylurea]) (99%) and Atrazine (ATZ) were obtained from SUPELCO. 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 room temperature (air-conditioned) at 23 °C in duplicate.

For the tests involving UV photolysis, 600 mL sample was irradiated in a 800 mL (97.8 mm ID \times 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 $\text{L}^{-1} \text{s}^{-1}$.

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 small reduction of dissolved ozone was observed at the beginning of the reaction, which was considered insignificant and could be replenished easily and quickly 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 the OZAT ozone generator (CFS-1A from Ozonia Ltd.). The flow rate of ozone/oxygen mixture into the reactor varied from 1.3 to 2.0 L min^{-1} , which resulted in a 9.96×10^{-6} – 3.09×10^{-5} M ozone concentration in the solution. The concentration of ozone was determined by the Indigo spectrometric method (Chu and Ma, 2000). For the UV/ O_3 experiments, simultaneous UV irradiation was provided during the ozonation period. The remaining ozone in the collected sample was quenched by sodium thiosulfate before quantification of LNR.

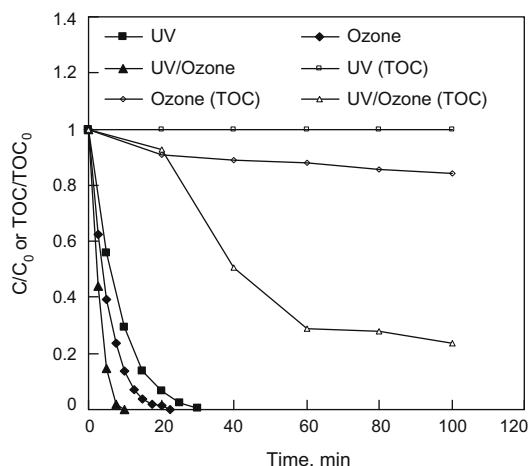


Fig. 1. Comparison of LNR decay (C/C_0) and TOC removal by the different treatment processes at pH 6 ($C_0 = 0.1$ mM).

For UV/ H_2O_2 experiments, a 300 mL quartz beaker with 150 mL solution was centered in the Rayonet™ RPR-200 photoreactor. Typically, LNR and ATZ were spiked first and followed by adding H_2O_2 (while turn on the preheated UV lamps, simultaneously) to initiate the reaction. The concentration of LNR and ATZ were 10 μM while H_2O_2 concentration was 0 and 20 mM. Methanol was used to quench the residual OH^\cdot in the solution, before the quantification of LNR and ATZ.

The amount of LNR and ATZ remaining in the samples was analyzed by HPLC. The system was comprised of a Waters 515 HPLC pump, Waters 2487 Dual λ Absorbance Detector, a Restek pinnacle octylamine (5 μm , 0.46×25 cm) column, and Waters 717plus Autosampler. The maximum adsorption wavelength (λ_{max}) was selected as 246 and 221 nm for LNR and ATZ, respectively. A mixture of 60% acetonitrile and 40% water was used as the mobile phase running at a flow rate of 1 mL/min. Total Organic Carbon was determined by Total Organic Carbon Analyzer (TOC-5000A, Shimadzu).

3. Results and discussion

3.1. Decomposition and mineralization of LNR in UV/ozone system

The degradation and mineralization of 0.1 mM LNR in sole-UV, sole Ozone and combined UV/ozone system was investigated with pH level set at 6.0, ozone concentration and light intensity were fixed at 0.0171 mM and at 6.0×10^{-6} Einstein $\text{L}^{-1} \text{s}^{-1}$, respectively. As indicated in Fig. 1, the decay rate of LNR increases in the order of UV photolysis, ozone and UV/ozone. In addition, LNR (0.1 mM) can be completely removed by the three proposed processes. It takes 35 min to fully decompose 0.1 mM LNR for UV illumination, while 22.5 and 10 min were required for ozonation and UV/ozone, respectively. The photolysis and oxidation of LNR were found to follow pseudo first-order kinetics. As also demonstrated in Fig. 1, no TOC removal was observed in sole-UV process, and TOC removal was insignificant in ozonation process (about 15% mineralization after 100 min). However, nearly 80% mineralization was achieved by using UV/ozone process after 100 min, suggesting the use of UV/ozone is a promising and clean process for the final disposal of LNR.

3.2. Effect of pH level on decay rate of the LNR ozonation

The decay rate of LNR was tested at various pH levels (from 3 to 11) by ozonation process with ozone concentration fixed at

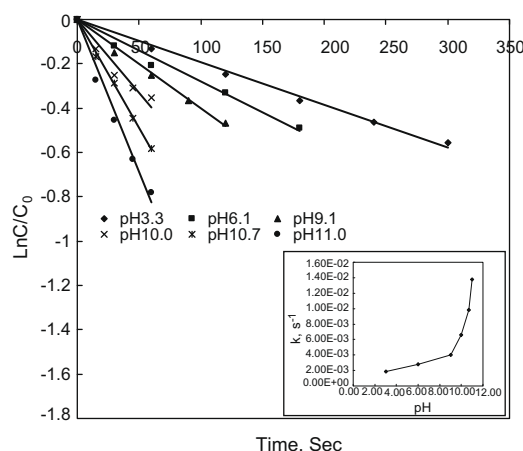


Fig. 2. Pseudo first-order degradation of 0.1 mM LNR in ozone-alone system at various pH levels ($[\text{O}_3] = 1.71 \times 10^{-5}$ M).

0.0171 mM. As indicated in Fig. 2, an increased degradation rate was observed at elevated pH levels. Furthermore, it is interesting to note that the overall rate constants increased linearly at lower pH level (<9), but exponentially at higher pH level (>9) as indicated in the inset of Fig. 2. This can be rationalized by the different oxidation pathways. At lower pH level, the oxidation by ozone molecules is the dominant reaction, while a much faster oxidation by hydroxyl radicals plays a key role under basic conditions (Chu and Ma, 2000).

3.3. Quantum Yield determination in UV system

The photodecay of LNR by sole-UV (at 253.7 nm) was investigated by using four different levels of light intensity at 3.0, 6.0, 9.0 and 12.0×10^{-6} Einstein $L^{-1} s^{-1}$ with other parameters unchanged. The results shown in Fig. 3 suggested that the LNR decay rate constant is linearly increased with the intensity of light. Theoretically, it is possible to determine the quantum yield of LNR decay by simple pseudo first-order kinetics under an optical dilute condition. The decay rate of LNR by sole-UV therefore can be formulated as:

$$-\frac{d[LNR]}{dt} = k_{obs}[LNR] = 2.303\phi_{LNR}\epsilon_{LNR}I_0[LNR] \quad (1)$$

$$k_{obs} = 2.303\phi_{LNR}\epsilon_{LNR}I_0 \quad (2)$$

where ϕ_{LNR} is the quantum yield of LNR decay, k_{obs} is the observed pseudo first-order rate constant (s^{-1}), I_0 is intensity of the incident light at 253.7 nm (Einstein $L^{-1} s^{-1}$), ϵ_{LNR} the molar absorptivity of LNR at 253.7 nm ($13254 M^{-1} cm^{-1}$), and l is the optical path length of the quartz beaker (9.78 cm). The observed rate constant k_{obs} was found to be linearly correlated to initial light intensity as shown in Fig. 3. Therefore, ϕ_{LNR} is calculated to be 0.00122 by the slope of the curve divided by $2.303 \epsilon_{LNR}l$.

3.4. Rate constant determination in ozone system

The degradation of LNR was found to follow a pseudo first-order reaction (Fig. 2) at different pH levels during ozonation. It is well known that the oxidization reaction in ozone system comes from either ozone molecule or hydroxyl free radical with substrates. The decay rate of LNR therefore can be theoretically interpreted by the following equation:

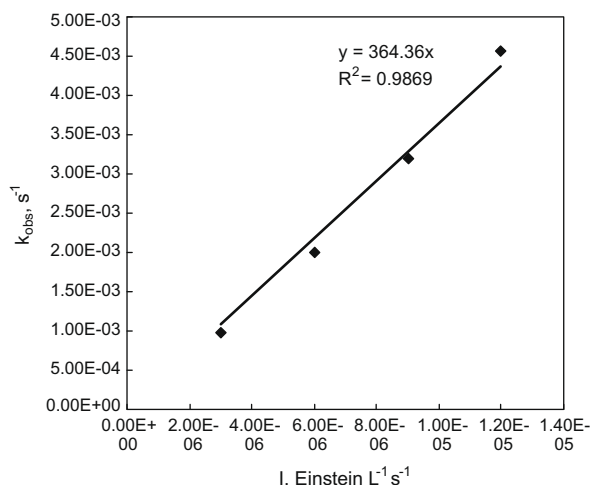


Fig. 3. Pseudo first-order degradation of 0.1 mM LNR in sole-UV system under various light intensity irradiation.

$$-\frac{d[LNR]}{dt} = k_{overall}[LNR] = k_{O_3,LNR}[LNR][O_3] + k_{OH,LNR}[LNR][OH^-] \quad (3)$$

The formation of hydroxyl radicals depends on the pH level of the solution; under a pseudo steady-state condition, the concentration of hydroxyl radicals can be estimated by the following equation (Benitez et al., 1994):

$$[OH^\bullet] = \frac{3k_{OOH}[O_3][OH^-]}{k_{OH,LNR}[LNR]} \quad (4)$$

where k_{OOH} is the rate constant for the formation of free radical HOO^\bullet from ozone decomposition at high pH (Staelin and Hoigne, 1982). By combining Eqs. (3) and (4), the oxidation rate of LNR in ozone system can be derived as following:

$$K_{overall}[LNR] = k_{O_3,LNR}[LNR][O_3] + 3k_{OOH}[O_3][OH^-] \quad (5)$$

in terms of rate constant, Eq. (5) would be:

$$K_{overall} = k_{O_3,LNR}[O_3] + 3k_{OOH}[O_3] \frac{[OH^-]}{[LNR]} \quad (6)$$

In order to determine the k_{O_3} and k_{OOH} , the variations of overall rate constant at different levels of $[O_3]$ and $[OH^-]$ were investigated and

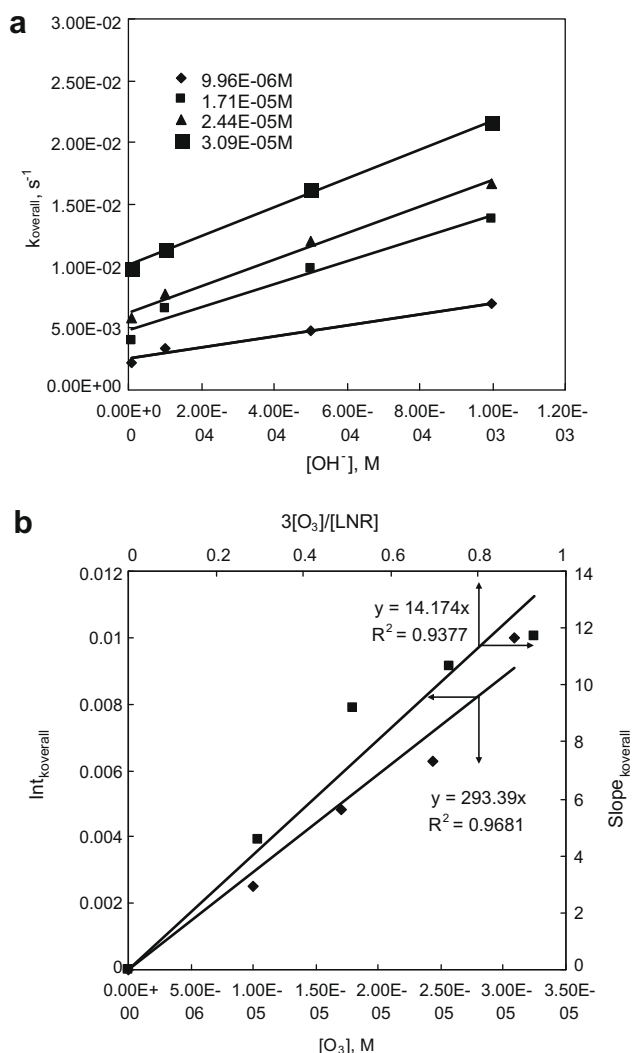


Fig. 4. (a) Variation of decay rate constant of 0.1 mM LNR with various hydroxide ion concentrations at different ozone concentration levels in ozone-alone system. (b) Correlations between $\ln k_{overall}$ and $[O_3]$ or correlations between $\text{slope}_{k_{overall}}$ and $3[O_3]/[LNR]$.

plotted in Fig. 4a. Depending on $[O_3]$, k_{overall} has a good linear correlation with $[OH^-]$ (r^2 ranging between 0.967 and 0.997). According to Eq. (6), the intercepts of these lines would be the $k_{O_3, \text{LNR}} [O_3]$ for the corresponding $[O_3]$, while the slopes stand for the $3k_{\text{OOH}} \frac{[O_3]}{[LNR]}$. Therefore, k_{O_3} can be determined by plotting the intercepts (from Fig. 4a) at different $[O_3]$ as a function of the corresponding ozone concentration as shown in Fig. 4b. Also, k_{OOH} can be calculated by plotting the slopes (from Fig. 4a) at different $[O_3]$ as a function of the term $\frac{3[O_3]}{[LNR]}$ (see Fig. 4b). The correlation lines going through the origin in Fig. 4b result in $k_{O_3, \text{LNR}}$ and k_{OOH} as $293 \text{ M}^{-1} \text{ s}^{-1}$ and $14.2 \text{ M}^{-1} \text{ s}^{-1}$, respectively. The different orders of these two rate constants suggest that the second term of Eq. (5) (i.e. the oxidation due to hydroxyl radical) can be ignored when the hydroxide ion concentration level is much lower than the concentration of the compound. In order to verify the hypothesis that the ozone concentration was close to a constant during the reaction, Hatta number was calculated to compare diffusion time with reaction time based on Eq. (7) (Benitez et al., 1994).

$$Ha = \frac{\sqrt{k_{O_3, \text{LNR}} D_{O_3} C_{\text{LNR}} + 3k_{\text{OOH}} D_{O_3} [OH^-]}}{k_L} \quad (7)$$

where D_{O_3} is the ozone diffusion coefficient in the liquid and k_L is the ozone transfer coefficient to the liquid. D_{O_3} is reported to be $1.76 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ in the water at 20°C (Johnson and Davis, 1996). $k_L a$ was determined to vary from 0.013 to 0.025 s^{-1} according to Huang and Shu (1995). The gas–liquid interfacial area per unit of liquid volume (a) was estimated by Eq. (8) (Lan et al., 2008) and Eq. (9) (Bin et al., 2001).

$$a = \frac{6H_g}{d_{bs}} \quad (8)$$

$$H_g = 5.54U_g^{1.03} \quad (9)$$

where U_g is superficial velocity varied from 2.9×10^{-3} to $4.4 \times 10^{-3} \text{ m s}^{-1}$ in this study. d_{bs} is the Sauter bubble diameter calculated from the correlation of Bouaifi and Roustan (1998). As a result, Hatta number was estimated to be ranged from 0.0046 to 0.0217 which is below 0.03, indicating the kinetic regime is very slow.

To determine the $k_{\text{OH}, \text{LNR}}$, an independent UV/ H_2O_2 experiment using ATZ as a reference compound was conducted, where the LNR decay due to sole-UV has been deducted from the reaction data. In theory, $k_{\text{OH}, \text{LNR}}$ can be determined to be $2.74 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ($k_{\text{OH}, \text{ATZ}}$ was reported to be $2.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Acero et al., 2000) by using Eq. (10) under the same reaction conditions in oxidizing the model compound ATZ:

$$\ln \frac{[LNR]_0}{[LNR]_t} = \frac{k_{\text{OH}, \text{LNR}}}{k_{\text{OH}, \text{ATZ}}} \ln \frac{[ATZ]_0}{[ATZ]_t} \quad (10)$$

3.5. Derivation of rate models and rate constant determination in UV/ O_3 system

The decomposition of LNR in UV/ O_3 system is an extremely complicated process since many individual reactions, such as direct photolysis, direct (molecular) ozonation, and various free radical oxidation are believed to be involved in this system. According to Gurol and Akata, the principal reactions expected in UV/ O_3 aqueous system are summarized in Table 1 (Gurol and Akata, 1996).

From the table, the inclusion of all sub-reactions to develop kinetic model in this system will be difficult and the result is likely impracticable due to the involvement of too many parameters. Therefore, a different approach using ozone molecule oxidation, hydroxyl radical oxidation, and UV-induced degradation to describe the overall process were proposed. The decay of LNR in UV/ O_3 system therefore can be described as below:

$$\begin{aligned} -\frac{d[LNR]}{dt} &= k_{\text{overall}}[LNR] \\ &= k_{O_3, \text{LNR}}[LNR][O_3] + k_{\text{OH}, \text{LNR}}[LNR][OH^-] \\ &\quad + 2.303\phi_{\text{LNR}}\epsilon_{\text{LNR}}I[LNR] \end{aligned} \quad (29)$$

The $[OH^-]$ of the second term in Eq. (29) theoretically may come from the hydroxide ion initiated decomposition of ozone and the photolysis of ozone by UV. Under acidic condition, however, the contribution of the hydroxide ion initiated decomposition of ozone to the production of OH^\cdot is insignificant at low pH levels as discussed previously. The photolysis of ozone can be assumed as the only source of OH^\cdot in UV/ O_3 system.

Table 1

Summary of the principal reactions expected in UV/ O_3 aqueous system.

Reaction	Rate constant ($\text{M}^{-1} \text{s}^{-1}$) and equilibrium constant (pK_a)	Equations
$O_3 + h\nu \rightarrow H_2O_2$		11
$H_2O_2 + h\nu \rightarrow 2OH^\cdot$		12
$H_2O_2 \leftrightarrow HO_2^- + H^+$	$\text{pK}_{a,10} = 11.8$	13
$HO_2^- + O_3 \rightarrow O_3^- + HO_2^\cdot$	$k_{11} = 2.8 \times 10^6$	14
$HO_2^\cdot \leftrightarrow H^+ + O_2^-$	$\text{pK}_{a,12} = 4.8$	15
$O_2^- + O_3 \rightarrow O_3^- + O_2$	$k_{13} = 1.6 \times 10^9$	16
$O_3^- + H^+ \rightarrow OH^\cdot + O_2$	$k_{14} = 5.2 \times 10^{10}$	17
$OH^\cdot + H_2O_2 \rightarrow HO_2^\cdot + H_2O$	$k_{15} = 2.7 \times 10^7$	18
$OH^\cdot + HO_2^- \rightarrow HO_2^\cdot + OH^-$	$k_{16} = 7.5 \times 10^9$	19
$OH^\cdot + O_3 \rightarrow HO_2^\cdot + O_2$	$k_{17} = 3.0 \times 10^9$	20
$2OH^\cdot \rightarrow H_2O_2$	$k_{18} = 5.5 \times 10^9$	21
$2HO_2^\cdot \rightarrow H_2O_2 + O_2$	$k_{19} = 7.6 \times 10^5$	22
$HO_2^\cdot + O_2^- + H_2O \rightarrow H_2O_2 + O_2 + OH^-$	$k_{20} = 8.9 \times 10^7$	23
$O_3 + OH^- \rightarrow HO_2^- + O_2$	$k_{21} = 14.2$	24
$O_3 + LNR \rightarrow \text{products}$	$k_{O_3, \text{LNR}} = 293$	25
$LNR + uv \rightarrow \text{products}$		26
$OH^\cdot + LNR \rightarrow \text{products}$	$k_{\text{OH}, \text{LNR}} = 2.74 \times 10^9$	27
Other radicals + LNR \rightarrow products		28

Since OH[•] is so reactive that it does not accumulate to an appreciable level in the solution, a steady-state approximation can be made (from the equations listed in Table 1):

$$\begin{aligned} \frac{d[\text{OH}^\bullet]}{dt} = & 2 \frac{d[\text{H}_2\text{O}_2]}{dt} + k_{14}[\text{O}_3^\bullet][\text{H}^+] - k_{15}[\text{OH}^\bullet][\text{H}_2\text{O}_2] \\ & - k_{16}[\text{OH}^\bullet][\text{HO}_2^\bullet] - k_{17}[\text{OH}^\bullet][\text{O}_3] - k_{18}[\text{OH}^\bullet]^2 \\ & - k_{\text{OH,LNR}}[\text{OH}^\bullet][\text{LNR}] = 0 \end{aligned} \quad (30)$$

$$\begin{aligned} \text{or } 2 \frac{d[\text{H}_2\text{O}_2]}{dt} + k_{14}[\text{O}_3^\bullet][\text{H}^+] = & k_{15}[\text{OH}^\bullet][\text{H}_2\text{O}_2] + k_{16}[\text{OH}^\bullet][\text{HO}_2^\bullet] \\ & + k_{17}[\text{OH}^\bullet][\text{O}_3] + k_{\text{OH,LNR}}[\text{OH}^\bullet][\text{LNR}] \end{aligned} \quad (31)$$

Under acidic conditions (the reaction condition of this test), HO₂[•] concentration would be at extremely low level (judging from the pK_a of 11.8 as shown in Eq. (13)), which means O₃[•] as a source of OH[•] is negligible (from Eqs. (14) to (17)) comparing to H₂O₂ (Eq. (12)). In addition, the contribution of Eq. (16) to OH[•] consumption can also be ignored. Furthermore, the termination of OH[•] through radical–radical termination reactions as presented by Eqs. (21)–(23) is insignificant and can be neglected due to very low OH[•] radical concentrations (Gurol and Akata, 1996). According to Table 1, k₁₅ is much smaller than k₁₇ and k_{OH,LNR} (more than 100 times), while [O₃] (a continuous input) is much higher than [H₂O₂], Eq. (18) can therefore be ignored. Thus, Eq. (31) can safely be simplified to:

$$2 \frac{d[\text{H}_2\text{O}_2]}{dt} = k_{17}[\text{OH}^\bullet][\text{O}_3] + k_{\text{OH,LNR}}[\text{OH}^\bullet][\text{LNR}] \quad (32)$$

In Eq. (32), [OH[•]] still cannot be calculated since the variation of [H₂O₂] is difficult to be determined. However, if Eqs (11) and (12) are merged together, the left-hand side of Eq. (32) can be redefined as $-\alpha \frac{d[\text{O}_3]}{dt}$ (α is defined as the ratio of the production rate of OH[•] and/or the decay rate of ozone) since the rate of Eq. (11) is likely much faster than that of Eq. (12). Then Eq. (32) becomes:

$$\begin{aligned} -\alpha \frac{d[\text{O}_3]}{dt} = & 2.303\alpha\phi_{\text{O}_3}I\varepsilon_{\text{O}_3}l \\ = & k_{17}[\text{OH}^\bullet][\text{O}_3] + k_{\text{OH,LNR}}[\text{OH}^\bullet][\text{LNR}] \end{aligned} \quad (33)$$

where ϕ_{O_3} is the quantum yield of ozone decay, l is the optical light path (i.e. the diameter) of the quartz beaker and ε_{O_3} is the molar absorptivity of ozone (3600 L mol^{−1} cm^{−1}) (Bahnmann and Hart, 1982) at 253.7 nm.

or

$$[\text{OH}^\bullet] = 2.303 \frac{\alpha\phi_{\text{O}_3}I\varepsilon_{\text{O}_3}l}{k_{17}[\text{O}_3] + k_{\text{OH,LNR}}[\text{LNR}]} \quad (34)$$

The decay rate of LNR can therefore be defined in Eq. (35) by incorporating Eqs. (29) and (34):

$$\begin{aligned} k_{\text{overall}} = & k_{\text{O}_3}[\text{O}_3] \\ & + 2.303I \left\{ k_{\text{OH,LNR}} \frac{\alpha\phi_{\text{O}_3}\varepsilon_{\text{O}_3}l}{k_{17}[\text{O}_3] + k_{\text{OH,LNR}}[\text{LNR}]} + \phi_{\text{LNR}}\varepsilon_{\text{LNR}}l \right\} \end{aligned} \quad (35)$$

It should be noted that many chemicals in the solution are capable of absorbing UV light at 253.7 nm, which may result in an effect of light attenuation. This is especially noticeable when their concentration or the associated molar absorptivity is high. Since this study focused on the initial rate, the contribution to light attenuation from intermediates can be negligible, which makes LNR and ozone the major components contributing to the attenuation effect. The attenuated light intensity can be quantified by the following equation in a cylindrical reactor (Chu et al., 2005):

$$I = \frac{I_0}{-2.303A} [e^{-2.303A} - 1] \quad (36)$$

where $A = \sum_{i=1}^n \varepsilon_i C_i l = \varepsilon_{\text{O}_3} C_{\text{O}_3} l + \varepsilon_{\text{LNR}} C_{\text{LNR}} l$. Due to high molar absorptivity of ozone and LNR (as indicated before), the term $e^{-2.303A}$ approaches zero, then Eq. (36) can be further simplified to:

$$I = \frac{I_0}{2.303A} \quad (37)$$

By substituting Eq. (37) into Eq. (35), Eq. (35) becomes:

$$\begin{aligned} k_{\text{overall}} = & k_{\text{O}_3,\text{LNR}}[\text{O}_3] \\ & + \frac{I_0}{A} \left\{ k_{\text{OH,LNR}} \frac{\alpha\phi_{\text{O}_3}\varepsilon_{\text{O}_3}l}{k_{17}[\text{O}_3] + k_{\text{OH,LNR}}[\text{LNR}]} + \phi_{\text{LNR}}\varepsilon_{\text{LNR}}l \right\} \end{aligned} \quad (38)$$

The tested results of k_{overall} under different light intensity were correlated to $\frac{I_0}{A}$ as shown in Fig. 5, where a linear curve was observed as predicted in Eq. (38). The slope of the linear curve would be the complex term inside the bracket of Eq. (38), and the intercept revealed the $k_{\text{O}_3,\text{LNR}}[\text{O}_3]$. Because ϕ_{O_3} was reported to be 0.48 and the other parameters are all known, the α is determined to be 6.92×10^{-5} .

A high $k_{\text{O}_3,\text{LNR}}$ value (293 M^{−1} s^{−1}) and low k_{OOH} (14.2 M^{−1} s^{−1}) justifies the observation that OH[•] plays a much more important role at pH levels above 9 than pH levels below 9. It has been reported that $k_{\text{O}_3,\text{LNR}}$ is 1.9 M^{−1} s^{−1} (Benitez et al., 2007) or 3.1 M^{−1} s^{−1} at pH 2.0 (DeLaat et al., 1996), which is lower than the value obtained in this study. This can be rationalized by the pK_a value of LNR and the highly electrophilic property of ozone. The pK_a of phenylurea was reported to vary in the range from 4.3 to 5.5 (Lopez et al., 2005), as a result, LNR would be charged positively at pH 2 while charged negatively at pH 9–11 in this study. The negatively-charged compounds show higher reactivity toward ozone than positively-charged one (Hoigne and Bader, 1983), leading to a higher $k_{\text{O}_3,\text{LNR}}$ value under basic conditions. The k_{OOH} is lower than the value (48 ± 12 M^{−1} s^{−1}) reported previously (Forni et al., 1982). It is probably because the value reported by Forni was determined at pH levels of 11.2–12.3 while pH level in this study varied from 9 to 11. The $k_{\text{OH,LNR}}$ was determined to be 2.74×10^9 M^{−1} s^{−1} which is about the same order of the value $(4.2 \pm 0.4) \times 10^9$ M^{−1} s^{−1} with 248 nm UV irradiation reported by Lopez et al. (2005).

The observed LNR decay rate and predicted overall decay rate by the proposed model under various conditions were compared and shown in Table 2, where the error ranges from 2.2% to 11.5%,

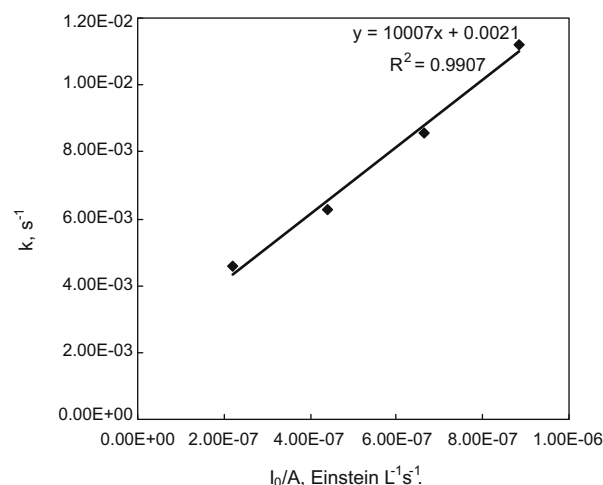


Fig. 5. Variation of decay rate constant of 0.1 mM LNR under different light intensity irradiation in UV/O₃ system (pH₀ = 4.03, [O₃] = 1.71 × 10^{−5} M).

Table 2

Comparison between the predicted k_{overall} from the proposed model and the observed k_{overall} .

Reaction conditions	Predicted k_{overall} based on the proposed model (s^{-1})	Observed k_{overall} in this study (s^{-1})
Sole-UV system		
$I_0 = 9.0 \times 10^{-6} \text{ Einstein L}^{-1} \text{s}^{-1}$ [LNR] = $1.0 \times 10^{-4} \text{ M}$	3.27×10^{-3}	3.20×10^{-3}
Ozone system		
$[\text{O}_3] = 1.71 \times 10^{-5} \text{ M}$ pH 11.0 [LNR] = $1.0 \times 10^{-4} \text{ M}$	1.23×10^{-2}	1.38×10^{-2}
Ozone system		
$[\text{O}_3] = 9.96 \times 10^{-6} \text{ M}$ pH 11.0 [LNR] = $1.0 \times 10^{-4} \text{ M}$	7.16×10^{-3}	7.00×10^{-3}
UV/ozone system		
$[\text{O}_3] = 3.09 \times 10^{-5} \text{ M}$ $I_0 = 6.0 \times 10^{-6} \text{ Einstein L}^{-1} \text{s}^{-1}$ pH 6.0 [LNR] = $1.0 \times 10^{-4} \text{ M}$	1.304×10^{-2}	1.154×10^{-2}

indicating the proposed models offer an accurate way to predict the LNR decay in the UV, O_3 and UV/ O_3 under varied conditions.

4. Conclusions

The degradation for LNR by UV, O_3 , and UV/ O_3 processes has been investigated. The decay rate of linuron by UV/ O_3 process was found to be around 3.5 times and 2.5 times faster than sole-UV and ozone-alone, respectively. No TOC removal was observed in sole-UV process, and TOC removal was insignificant in ozonation process (about 15% mineralization after 100 min). However, nearly 80% mineralization was achieved by using UV/ozone process after 100 min. The overall rate constants increase exponentially with pH above 9.0 while the increase of rate constants with pH below 9 is insignificant in O_3 system. All predominating parameters involved in the three processes were determined in the assistant of proposed linear models. The proposed approach could furnish a useful method to explore the major kinetic constants, while minimizing the requirement in defining the minor rate constants. This is helpful in real applications for determining a quick but accurate prediction in system design.

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