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Enhanced oxidation of urea by pH swing during chlorination: pH-Dependent reaction mechanism

pH 스윙을 이용한 수중 요소의 향상된 염소산화: pH 에 따른 반응 메커니즘

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Abstract

Enhanced oxidation of urea by pH swing during chlorination: pH-Dependent reaction mechanism

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Urea reacts with chlorine to form chlorinated urea (chlorourea), and fully chlorinated urea is degraded by hydrolysis. The degradation of urea during chlorination was greatly enhanced by the pH swing, in which urea reacted with chlorine at pH 3 for 30 minutes (first step) and pH was elevated to pH 7 and reacted for 120 minutes (second step). 20% and 16% of urea were degraded at pH 3 and pH 7, respectively, but 92% was degraded by the pH swing method. Moreover, the degradation efficiency of urea by the pH swing increased as the chlorine dose increased. The degradation rate of urea by pH swing increased with increasing pH from 3 to 10, and the speciation changes of the chloroureas were suggested as the reason for this enhancement. The increase in deprotonated monochlorourea ($\mathrm{p}K_a = 9.7 \pm 1.1$) and dichlorourea ($\mathrm{p}K_a = 5.1 \pm 1.4$) with increasing pH accelerated the chlorination. The deprotonation of dichlorourea accelerated the degradation rate in

the pH 3-7.5 region, and the deprotonation of both monochlorourea and dichlorourea greatly enhanced the degradation rate in the pH 7.5-10 region. Lower concentrations of products were measured in the open system than in the closed system because chloramines are volatile. Moreover, the chloramines were oxidized to form NO_3^- and gaseous nitrogen compounds were produced as pH increased.

Keywords: Urea, Oxidation, Chlorination, pH Swing, pH-Dependent mechanism, Deprotonation

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Chapter 1. Introduction

Urea is utilized in extensive fields such as a nitrogen fertilizer,[1, 2] pharmaceuticals for dry skin,[3] and pesticides ingredient.[4] These applications induce the increase of urea concentrations in industrial wastewater. Furthermore, urea is excreted by human in urine and sweat and is dispersed to the environment through domestic wastewater.[2, 5] Since spontaneous hydrolysis of urea is a slow reaction,[6] the release of urea would advance eutrophication in water, which leads to harmful algal blooms.[2, 7, 8] Moreover, the presence of urea is the critical cause of TOC in ultrapure water, which impacts adversely on the quality of semiconductors.[9]

Several techniques to degrade urea in water by chemical oxidants have been introduced from previous investigations (Table 1). UV and VUV coupled with hydrogen peroxide (UV/H_2O_2, VUV/H_2O_2) which produce hydroxyl radicals have been suggested to remove urea.[10] However, these systems require a high dose of oxidant since urea has a low molecular weight and low reaction rate with hydroxyl radical ($7.9 \times 10^5\ \mathrm{M^{-1}s^{-1}}$).[11] UV and VUV coupled with persulfate (UV/$K_2S_2O_8$, UV/$Na_2S_2O_8$, VUV/$K_2S_2O_8$) have been reported that they produce sulfate radicals, which are more efficient to degrade urea than hydroxyl radicals.[9, 10] These systems could decompose urea with lower oxidant concentration and reaction time than UV/H_2O_2 and VUV/H_2O_2. However, they require high electrical energy per order (E_{EO}) (36.1 kWh/m^3 for UV/$K_2S_2O_8$ and 12.0 kWh/m^3 for VUV/$K_2S_2O_8$),[10] so they are not suitable for practical applications.[12]

Table 1. Previous studies on the degradation of urea by chemical oxidants.

Method		$[Urea]_0$ (μM)	$[Oxidant]_0$ (μM)	Removal efficiency (%)	Reaction time (h)	Reference
Hydrogen peroxide	UV/H_2O_2	83	1000	12.8	3	10
	VUV/H_2O_2	83	1000	51.2	3	10
Persulfate	UV/$K_2S_2O_8$	83	100	67.8	1	10
	UV/$Na_2S_2O_8$	1.65	20	90	-	9
	VUV/$K_2S_2O_8$	83	100	95.8	1	10
Chlorine	Pre-chlorination and UV	3000 ([*N*-chlorourea] = 186 μM)	178	5.6 for urea (90.5% for *N*-chlorourea)	1.5	13
	Chlorine	50	290	100	144	14

Chlorine has the advantage of low cost and convenience for application, so it is generally used in water treatment plants for the disinfection of microorganisms.[13] The reaction kinetics and the mechanism of chlorination of urea have been studied by only a few research groups.[14, 15] In respect of kinetics, 144 hours was needed to completely degrade urea by a chlorine/urea molar ratio of 6 mol/mol,[14] showing the low reactivity of urea with chlorine. Since the carbonyl group of urea is the electron-withdrawing group, it decreases the reactivity with chlorine.[16]

The mechanism of chlorination of urea has been suggested by Blatchley and Cheng (Reactions (1)-(5)).[15]

$$\mathrm{CO(NH_2)_2 + Cl_2 \rightarrow H_2NCONHCl + HCl} \quad (1)$$

$$\mathrm{H_2NCONHCl + HOCl \rightarrow CO(NHCl)_2 + H_2O} \quad (2)$$

$$\mathrm{CO(NHCl)_2 + HOCl \rightarrow Cl_2NCONHCl + H_2O} \quad (3)$$

$$\mathrm{Cl_2NCONHCl + HOCl \rightarrow CO(NCl_2)_2 + H_2O} \quad (4)$$

$$\mathrm{CO(NCl_2)_2 + HOCl \rightarrow HCl + CO_2 + NCl_3 + NCl} \quad (5)$$

They proposed that the Cl atom of chlorine could replace the H atom of urea by an electrophilic substitution reaction, and four Cl atoms could be substituted theoretically; forming mono-, di-, tri-, and tetrachlorourea. They also suggested that C-N bond cleavage of urea only occurs after tetrachlorourea formation. This study has mainly focused on the first chlorination of urea, which is the reaction to produce monochlorourea. It has been reported that the first chlorination rate of urea increases as pH decreases, because the stronger electrophile, Cl_2, increases as pH decreases.

They also examined the concentration change of monochlorourea under excess urea relative to chlorine concentration at pH 3 and 7.5.[15] At pH 3, chlorine was rapidly consumed as monochlorourea was produced, and the monochlorourea concentration maintained constant in the absence of chlorine. However, the formation of monochlorourea and consumption of chlorine were slower at pH 7.5 than at pH 3. Furthermore, the disappearance of monochlorourea in the presence of free chlorine was observed at pH 7.5, meaning that monochlorourea reacts with chlorine to form highly chlorinated urea at this pH condition. However, the previous study did not use these results to accelerate the chlorination of urea. In this study, the pH swing method was introduced to enhance the degradation rate of urea by chlorine by combining the information from the previous investigation. The pH swing method is divided into two steps; the first step is adjusting pH to pH 3 to promote the first chlorination of urea; the second step is increasing pH to pH 7 to accelerate the subsequent chlorination.

The objectives of this study were (i) to develop the enhanced chlorine oxidation system for urea degradation and (ii) to elucidate the overall chlorination mechanism of urea depending on pH. The degradation of urea by chlorination and consumption of chlorine were examined under three different conditions (i.e., pH 3, pH 7, and the pH swing from 3 to 7) and different chlorine doses. The pseudo-first-order rate constant for the urea degradation by chlorine using the pH swing method was calculated by varying the pH in the second step. The intermediates of reaction were analyzed by mass spectrometry, and the pK_a values of the intermediates were calculated. In addition, the products formed by the chlorination of urea were analyzed by ion chromatography.

Chapter 2. Materials and methods

2.1 Materials

All chemicals were of reagent grade and used as received without further purification. Urea (CH_4N_2O, 98%), sodium hypochlorite solution (NaOCl, 10-15%), N, N-diethyl-p-phenylenediamine sulfate salt (DPD, ≥ 99%), sulfuric acid (H_2SO_4, 95-98%), iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 97%), potassium iodide (KI, ≥ 99%) were purchased from Sigma-Aldrich. Diacetyl monoxime ($C_4H_7NO_2$, 99%) was purchased from Daejung. Thiosemicarbazide (CH_5N_3S, 98%) was purchased from Alfa Aesar. All solutions were prepared using deionized (DI) water (> 18.2 MΩ·cm) produced by a water purification system (Milli-Q Integral 5, Millipore).

2.2 Experimental procedure

The experiments to determine the degradation rate of urea by chlorine were conducted using 100 mL solutions containing urea (100 μM). The pH of the solution was adjusted to the desired value using 1 M $HClO_4$ or 1 M NaOH. An aliquot of sodium hypochlorite solution was added to the reaction solution to initiate the reaction ($[NaOCl]_0$ = 400 μM or 800 μM). For the experiment sets using the pH swing method, the pH of the solution was adjusted to pH 3 for the first 30 minutes and increased to the desired value by 0.5 M phosphate buffer and 1 M NaOH. Samples (1 mL and 0.25 mL) were withdrawn at predetermined time intervals and

immediately diluted with DI water for the analysis of urea and free chlorine. All experiments were conducted at least in duplicate, and the average values with standard deviations were presented.

The experiments to quantify NH_4^+ and NO_3^- were conducted using 40 mL solutions in bottles with two conditions. Bottles with the caps closed were required for the closed system experiments, and bottles open to the atmosphere were required for the open system experiments. The pH of the solution was adjusted to the desired value using 1 M $HClO_4$ or 1 M NaOH. An aliquot of sodium hypochlorite solution was added to the reaction solution to initiate the reaction ($[NaOCl]_0$ = 400 μM). The number of experimental sets corresponding to the number of sampling times was conducted simultaneously, and 1 mL of sample was withdrawn in each set. 20 μL of sodium thiosulfate solution (20 mM) was immediately added to the samples to quench the residual chlorine.

The experiments to analyze total nitrogen were performed with 400 mL solutions containing urea (100 μM). The pH of the solution was adjusted to the desired value using 1 M $HClO_4$ or 1 M NaOH. An aliquot of sodium hypochlorite solution was added to the reaction solution to initiate the reaction ($[NaOCl]_0$ = 400 μM). Samples (30 mL) were withdrawn at predetermined time intervals and 0.12 mL of sodium thiosulfate solution (100 mM) was immediately added to quench the residual chlorine.

2.3 Analytical Methods

The concentration of urea was determined by measuring the absorbance of the color complex formed by the diacetyl monoxime method (the absorbance decrease at 515 nm) using UV/Vis spectrophotometry (LAMBDA 465, PerkinElmer).[17] The concentration of urea measured by the diacetyl monoxime method included the concentration of chloroureas, because the diacetyl monoxime method cannot distinguish urea and chloroureas. Therefore, the measured urea was expressed as (chloro-)ureas in this study.

The concentration of free chlorine was determined using the DPD colorimetric method. For the DPD colorimetric method, 125 μL of phosphate-buffered solution (0.5 M, pH 6) and 125 μL of DPD solution (1% w/v, dissolved in 0.1 N H_2SO_4 solution) were added to 2.5 mL of sample, and the absorbance was measured at 515 nm by UV/Vis spectrophotometry (LAMBDA 465, PerkinElmer).

The concentrations of NH_4^+ and NO_3^- were analyzed by ion chromatography (DIONEX Aquion, Thermo Fisher Scientific). 30 mM methanesulfonic acid was used as the eluent at the flow rate of 1 mL/min, and Dionex IonPac CS16 column (Thermo Fisher Scientific.) was used for the analysis of NH_4^+. The mixture of 4.5 mM Na_2CO_3 and 1.4 mM $NaHCO_3$ was used as the eluent at the flow rate of 1.2 mL/min, and Dionex IonPac AS22 column (Thermo Fisher Scientific.) was used for the analysis of NO_3^-. NH_4^+ was measured after adding sodium thiosulfate as a chlorine quenching reagent to the sample. Sodium thiosulfate is a powerful reducing agent that can reduce chloramines in water to NH_4^+.[18] Therefore, the measured NH_4^+

by ion chromatography contained the concentrations of chloramines, and the measured NH_4^+ was expressed as NH_4^+ + chloramines in this study.

The intermediates of chlorination (chloroureas) were analyzed by a mass spectrometer (Finnigan TSQ Quantum Discovery MAX, Thermo Fisher Scientific). The mass spectrometer was operated in the electrospray ionization with positive mode under the following conditions: spray voltage + 5000 V; sheath gas pressure 8 units; ion sweep gas pressure 15.0 units; aux gas pressure 0 units; capillary temperature 320 ℃. The mass spectra were obtained in full scan mode from 20 to 300 m/z. The concentration of total nitrogen was determined by a TOC/TN analyzer (TOC-VCPH, Shimadzu).

Chapter 3. Results and discussion

3.1 Degradation of urea by chlorine using pH swing

The degradation of (chloro-)ureas by chlorination were examined under three different conditions (i.e., pH 3, pH 7, and the pH swing from 3 to 7) (Figure 1a). The (chloro-)ureas were degraded by 21% and 17% for 150 min at pH 3 and pH 7, respectively. Whereas, (chloro-)ureas were degraded by 92% using the pH swing method, which reacted with chlorine for 30 minutes at pH 3 and then reacted at pH 7 for 120 minutes. In the pH swing method, the acid pretreatment process at pH 3 for 30 minutes was defined as the first step, and the process of increasing the pH to 7 and reacting for 120 minutes was defined as the second step.

Furthermore, the consumption of chlorine during the chlorination at different pH conditions were investigated (Figure 1b). 64% of chlorine was consumed during the chlorination of urea at pH 3 for 150 minutes. Most of the chlorine was rapidly consumed within 30 minutes of the chlorination at pH 3. 24% of chlorine was gradually consumed during the chlorination of urea at pH 7. Chlorine was completely consumed for 150 minutes using the pH swing method. The chlorine consumption result at pH 3 indicates that the first chlorination of urea to from monochlorourea is rapid and the subsequent reactions to degrade urea are rate-determining at acidic pH. The chlorine consumption rate was slower at pH 7 than at pH 3, which coincides with the previous research that Cl_2 is more favorable to initiating the chlorination of urea than HOCl ($k_{Cl_2} = 2.35 \times 10^4\ \mathrm{M^{-1}s^{-1}}$ and $k_{\mathrm{HOCl}} = 0.075\ \mathrm{M^{-1}s^{-1}}$).[15, 16]

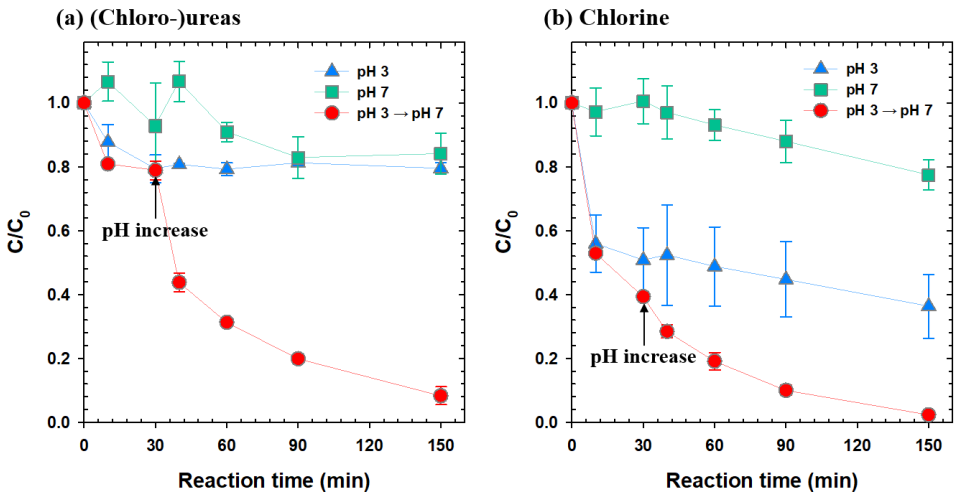

Figure 1. (a) Degradation of (chloro-)ureas and (b) consumption of chlorine during chlorination under different pH conditions; The black arrow indicates the point when pH was elevated from 3 to 7 ($[Urea]_0$ = 100 μM; $[Chlorine]_0$ = 400 μM; pH 3 for first 30 min and pH was elevated to 7 for pH swing condition).

The intermediates of the chlorination under different pH conditions were identified by a mass spectrometer to interpret why the degradation rate of (chloro-)ureas varied with pH. The peaks of urea, monochlorourea, and dichlorourea were observed under pH 3, and the peak intensity of monochlorourea was the highest (Figure 2a). Only the peak of urea was observed under pH 7 (Figure 2b). The peaks of urea and monochlorourea were observed under the pH swing condition, but the peak intensity of monochlorourea was lower than that under pH 3(Figure 2c).

The highest peak intensity of monochlorourea under pH 3 indicates that monochlorourea dominantly exists under pH 3, and the subsequent reaction to form dichlorourea occurs slowly even in the presence of free chlorine. The peak of chloroureas was not observed under pH 7, meaning that the chlorination initiates slowly at pH 7. The relatively low peak intensity of monochlorourea under pH swing condition than under pH 3 demonstrates that monochlorourea reacts relatively fast with chlorine at neutral pH than at acidic pH.

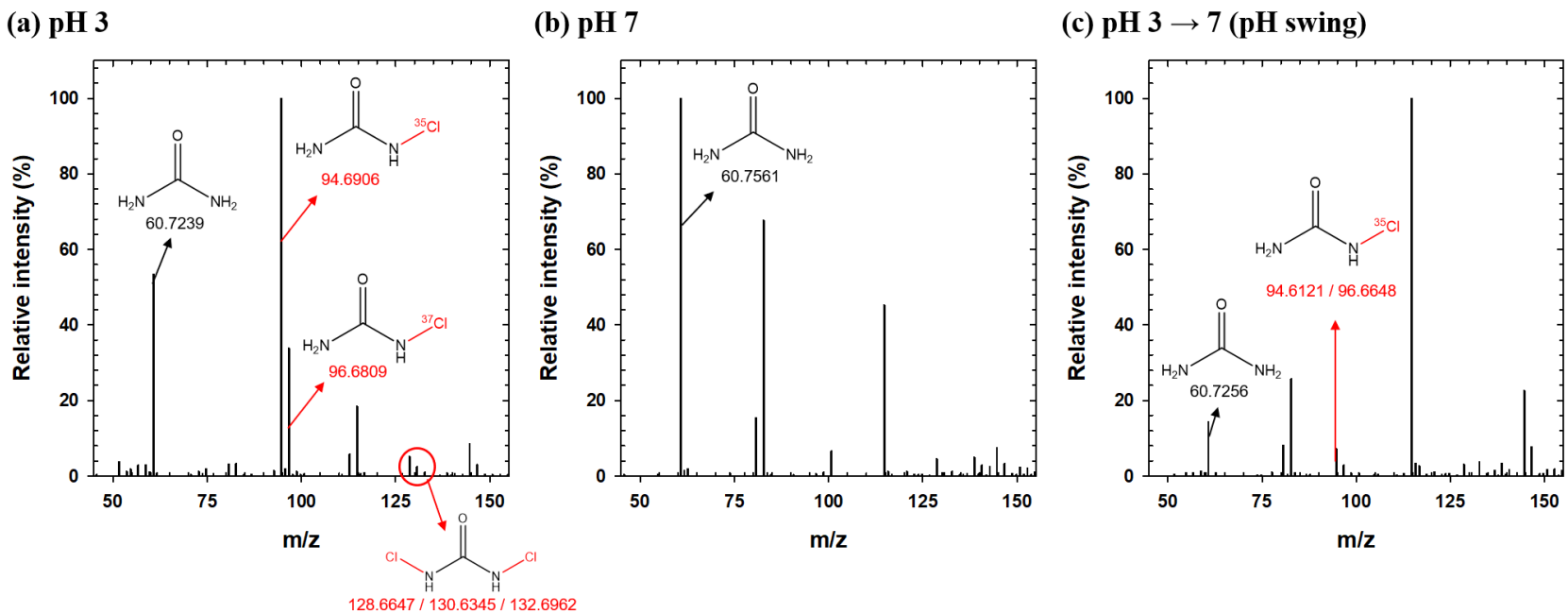

Figure 2. ESI-MS spectra of chlorinated products of urea after 90 minutes of reaction under (a) pH 3, (b) pH 7, and (c) the pH swing condition (positive full scan mode; $[\text{Urea}]_0$ = 100 μM; $[\text{Chlorine}]_0$ = 400 μM; pH 3 for first 30 min and pH was elevated to 7 for (c)).

The acid pretreatment time for the pH swing method was regulated to 30 minutes, but it is necessary to check whether this time is sufficient. The purpose of the acid pretreatment was to promote the first chlorination of urea to from monochlorourea, so the decrease in urea concentration by the first chlorination was calculated by Mathematica (Table 2 and Figure 3). The calculated result shows that 99% of urea was used to produce monochlorourea for 30 minutes at pH 3, meaning that 30 minutes of reaction time is sufficient. Moreover, the result shows that 83% of urea was used for 10 minutes, indicating the possibility of reducing the reaction time from 30 minutes to 10 minutes. Therefore, the degradation experiment using the pH swing method with the acid pretreatment time of 10 minutes was conducted (Figure 4). The (chloro-)ureas were degraded by 88% under this condition, meaning that 10 minutes of pretreatment time is enough to degrade urea.

Table 2. Reactions used for the calculation by Mathematica.

Reaction	**Rate constant (*k*)**	**Reference**
$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$	$22.3\ s^{-1}$	19
$HOCl + H^+ + Cl^- \rightarrow Cl_2 + H_2O$	$2.14 \times 10^4\ M^{-2}s^{-1}$	19
$CO(NH_2)_2 + Cl_2 \rightarrow H_2NCONHCl + HCl$	$2.35 \times 10^4\ M^{-1}s^{-1}$	15
$CO(NH_2)_2 + HOCl \rightarrow H_2NCONHCl + H_2O$	$0.075\ M^{-1}s^{-1}$	16

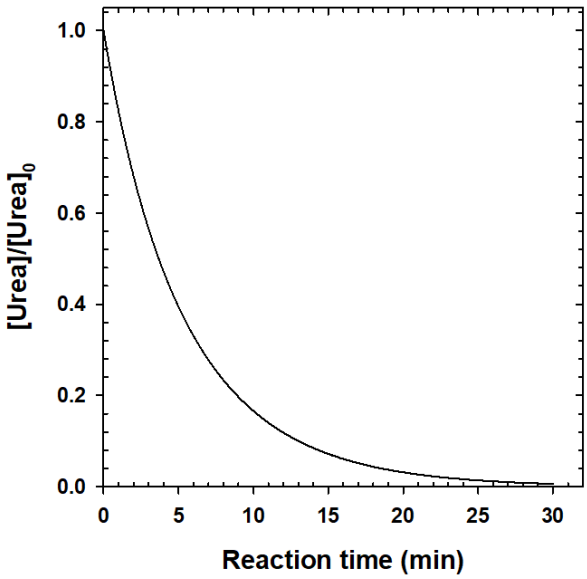

Figure 3. Time-concentration profile of urea during the first chlorination calculated by Mathematica ($[Urea]_0 = 100$ μM; $[Chlorine]_0 = 400$ μM; pH 3).

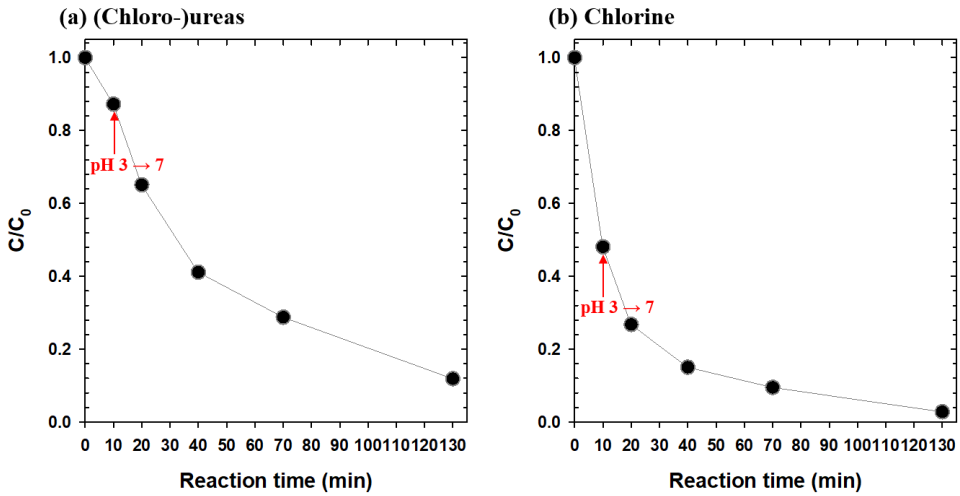

Figure 4. (a) Degradation of (chloro-)ureas and (b) consumption of chlorine during chlorination by pH swing; The red arrow indicates the point when pH was elevated from 3 to 7 ($[Urea]_0 = 100$ μM; $[Chlorine]_0 = 400$ μM; pH 3 for first 10 minutes and pH was elevated to 7; reaction time = 130 min).

The pH swing method was applied when the initial concentration of urea was lower. The acid pretreatment time for the pH swing method was increased from 30 minutes to 120 minutes because the initial concentration of urea was low. The chlorine/urea molar concentration ratio was also increased from 4 mol/mol to 10 mol/mol because of the same reason. The (chloro-)ureas were degraded by 87% using the pH swing method, while the degradation of (chloro-)ureas at pH 3 and pH 7 was negligible (4% and 11%, respectively) (Figure 5a). 90% of chlorine was consumed during the chlorination by the pH swing method, but the chlorine consumption at pH 3 and pH 7 was 47% and 41%, respectively. (Figure 5b). These results illustrate that pH swing method could accelerate the degradation of urea by chlorine even at low initial concentration of urea.

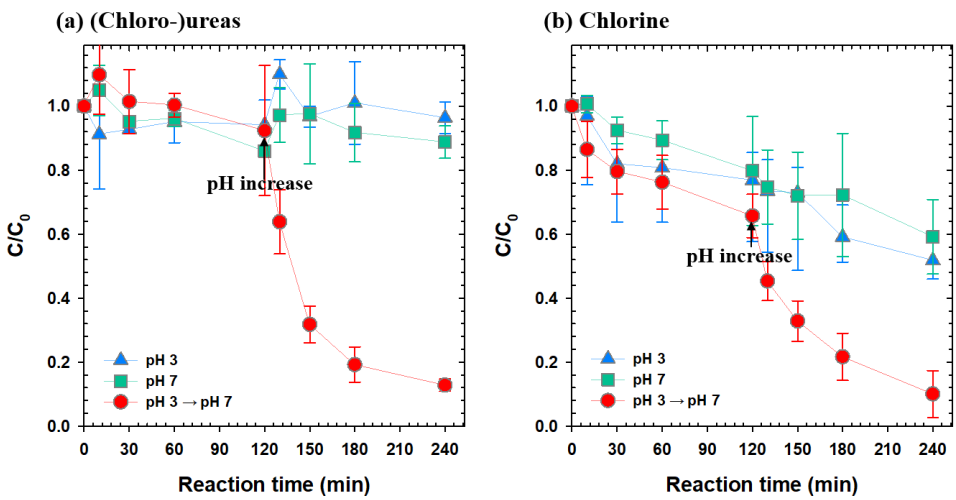

Figure 5. (a) Degradation of (chloro-)ureas and (b) consumption of chlorine during chlorination under different pH conditions; The black arrow indicates the point when pH was elevated from 3 to 7 ($[Urea]_0$ = 3.3 μM; $[Chlorine]_0$ = 33 μM; pH 3 for first 120 min and pH was elevated to 7 for pH swing condition).

3.2 Effect of chlorine dose on urea degradation

The effect of chlorine dose on urea degradation by pH swing was examined. The degradation rate of (chloro-)ureas by pH swing at the chlorine dose of 100 μM was negligible, and the degradation rate of (chloro-)ureas by pH swing increased as the chlorine dose increased (Figure 6a). However, the final degradation efficiency of (chloro-)ureas was similar when the chlorine dose was more than 400 μM, indicating that 400 μM of chlorine is enough to degrade urea by pH swing. The chlorine consumption rate during the chlorination by pH swing decreased as the chlorine dose increased (Figure 6b). Moreover, the proportion of chlorine that remained after the acid pretreatment increased as the chlorine dose increased. The degradation of (chloro-)ureas by pH swing at the chlorine dose of 100 μM was insignificant because more than 90% of chlorine was consumed at the acid pretreatment. Therefore, the increase of the (chloro-)ureas degradation could be explained by the increase of the remaining chlorine after the acid pretreatment.

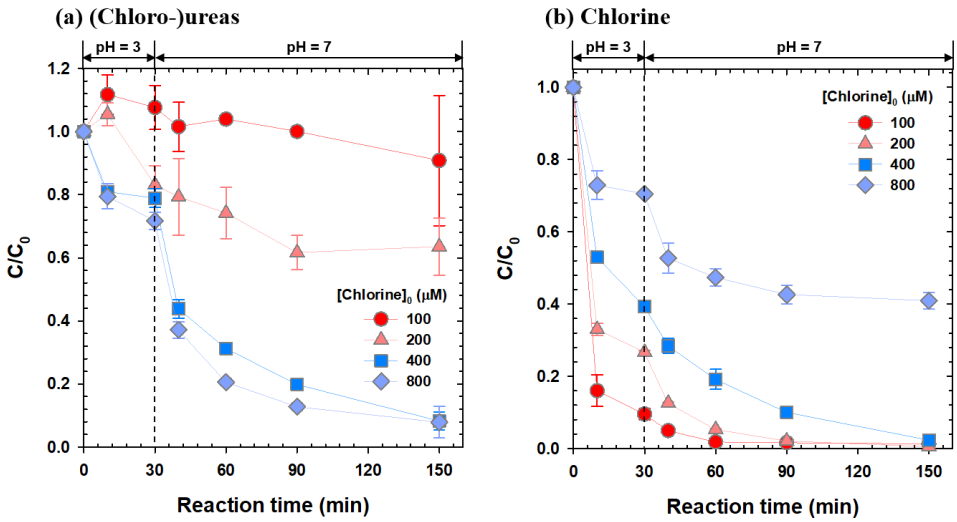

Figure 6. (a) Degradation of (chloro-)ureas and (b) consumption of chlorine during chlorination using pH swing method at different chlorine doses; The black dashed line indicates the point when pH was elevated from 3 to 7 ($[Urea]_0$ = 100 μM; $[Chlorine]_0$ = 100~800 μM; pH 3 for first 30 min and pH elevated to 7).

In addition, the effect of chlorine dose on urea degradation at pH 3 was investigated. The degradation rate of (chloro-)ureas slightly increased as the chlorine dose increased (Figure 7a). The (chloro-)ureas were degraded by only 23% for 150 minutes even at the chlorine dose of 800 μM. The chlorine was consumed rapidly for 30 minutes and a small amount of chlorine was utilized after 30 minutes when the chlorine dose was below 800 μM (Figure 7b). These results show that only the first chlorination of urea is rapid at acidic condition.

The effect of chlorine dose on urea degradation at pH 7 was also investigated. The degradation rate of (chloro-)ureas increased as the chlorine dose increased (Figure 8a). However, the chlorine consumption rate hardly changed with the increase in the chlorine dose (Figure 8b). This result means that the amount of chlorine consumed increased as the chlorine dose increased. Therefore, the increase of chlorine dose at neutral pH condition could accelerate the chlorination of urea.

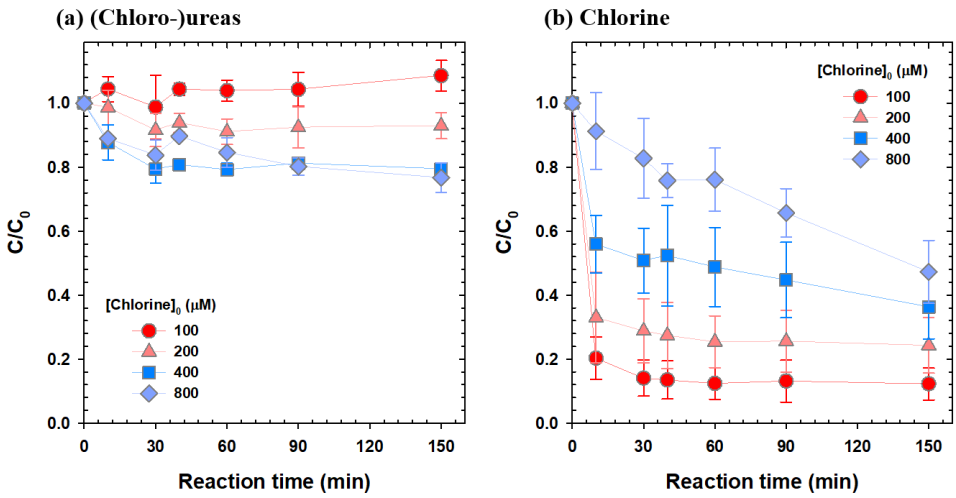

Figure 7. (a) Degradation of (chloro-)ureas and (b) consumption of chlorine during chlorination at different chlorine doses under pH 3 conditions ($[Urea]_0$ = 100 μM; $[Chlorine]_0$ = 100~800 μM; pH 3).

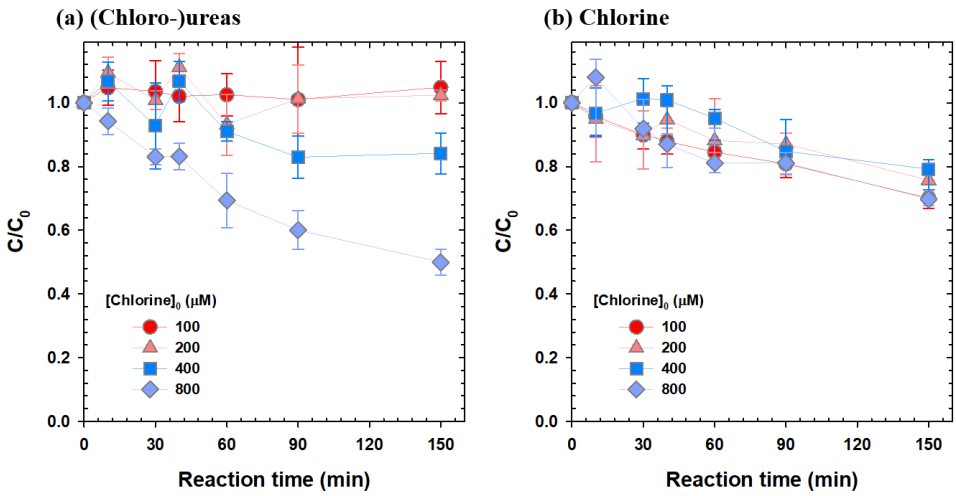

Figure 8. (a) Degradation of (chloro-)ureas and (b) consumption of chlorine during chlorination at different chlorine doses under pH 7 conditions ($[Urea]_0$ = 100 μM; $[Chlorine]_0$ = 100~800 μM; pH 7).

3.3 Effect of pH on urea degradation using pH swing

The degradation of (chloro-)ureas by pH swing under different increased pH values of the second step (pH 3-10) were examined (Figure 9a). The degradation of (chloro-)ureas increased as the pH of the second step increased. The pseudo-first-order rate constants (k) were calculated by plotting ln([(chloro-)ureas]$_0$/[(chloro-)ureas]) versus reaction time of the second step. [(Chloro-)ureas]$_0$ values were set as the concentration at the time when the second step of the pH swing began. The data points before the degradation efficiency of 80% were used for the pseudo-first-order fitting.[20]

The calculated pseudo-first-order rate constants of the degradation of (chloro-)ureas were shown in Figure 9b. The increase in the degradation rate could be divided into two regions; pH 3-7.5 region where the reaction rate increased gradually; pH 7.5-10 region where the reaction rate increased drastically.

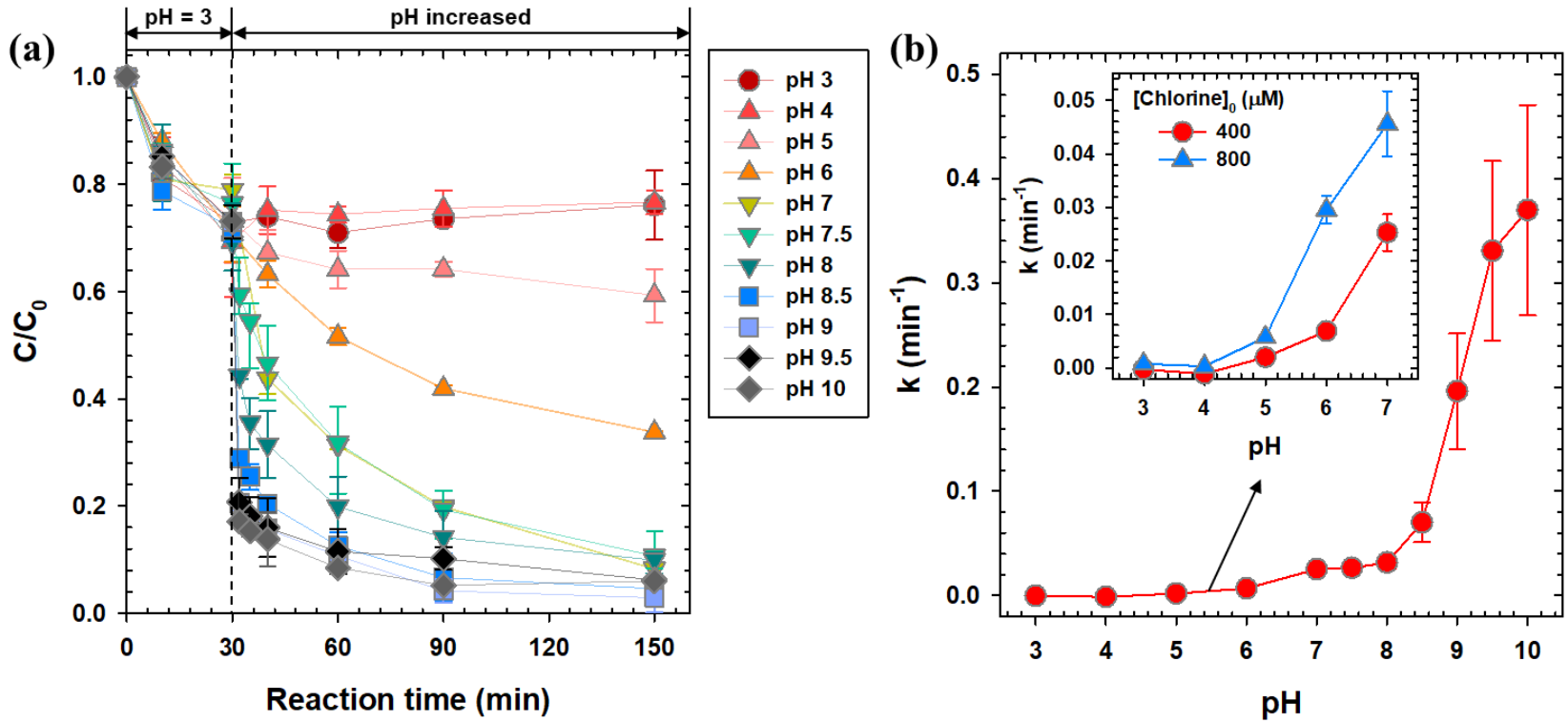

Figure 9. (a) Degradation of (chloro-)ureas during chlorination using pH swing method at different increased pH values; The black dashed line indicates the point when pH was elevated from 3. (b) (Chloro-)ureas degradation rate constants by pH swing method as functions of increased pH values. Inset: (chloro-)ureas degradation rate constants by pH swing method at different chlorine doses as functions of increased pH values ($[Urea]_0$ = 100 μM; $[Chlorine]_0$ = 400 μM; pH_i = 3.0; reaction time for pH 3 pretreatment = 30 min).

The reasonable factor that affects the degradation rate of (chloro-)ureas is the change in speciation of the chlorine and chlorourea by pH. The speciation of chlorine by pH is well known from the literature (Reactions (6)-(7)).[19, 21, 22]

$$\mathrm{HOCl} \rightleftarrows \mathrm{ClO^-} + \mathrm{H^+} \qquad \mathrm{p}K_a = 7.54 \tag{6}$$

$$\mathrm{Cl_2} + \mathrm{H_2O} \rightleftarrows \mathrm{HOCl} + \mathrm{H^+} + \mathrm{Cl^-} \qquad K = 1.04 \times 10^{-3}\ \mathrm{M}^2 \quad (\mu = 0.5\ \mathrm{M}) \tag{7}$$

The order of the reactivity of chlorine species is Cl_2 > HOCl > OCl^- to most organic compounds, because the electrophilicity increases in the same direction.[15, 16, 23-28] Moreover, urea decomposition did not proceed when most free chlorine presented as HOCl at pH 3. Therefore, the speciation of chlorourea could be the significant factor that affects the urea degradation rate.

The deprotonation of chloroureas could promote the chlorination of urea because chlorination is an electrophilic reaction in which Cl^+ of free chlorine transfers to the nitrogen atom of urea.[29, 30] The nitrogen atom of deprotonated chloroureas would have higher electron density than the nitrogen atom of chloroureas. Therefore, the nitrogen atom of deprotonated chloroureas could more readily donate electrons, accelerating the subsequent chlorination. Mono-, di-, tri-, tetrachlorourea could be produced by chlorination of urea.[15] $\mathrm{p}K_a$ of the chloroureas were predicted by the ACD/Percepta 2021.2.0 software (Advanced Chemistry Development Inc.), and the calculated values were summarized in Table 3. In particular, the $\mathrm{p}K_a$ of monochlorourea (9.7 ± 1.1) and dichlorourea (5.1 ± 1.4) could explain the increase in degradation rate.

Table 3. Predicted pK_a values for urea and chloroureas.

Compound	**Calculated pK_a**
Urea	14.3 ± 0.4
Monochlorourea	9.7 ± 1.1
Dichlorourea	5.1 ± 1.4
Trichlorourea	0.5 ± 1.8

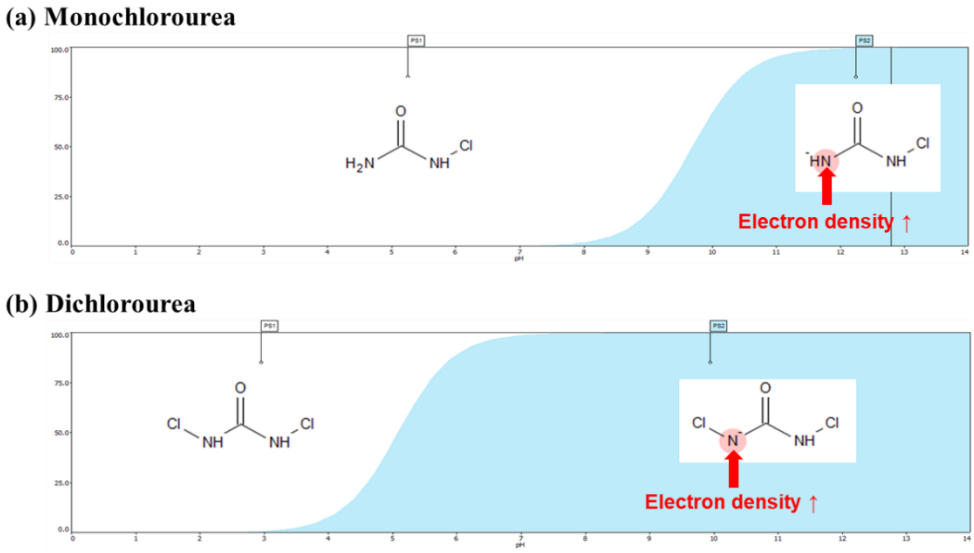

Figure 10. Deprotonated state ratio of (a) monochlorourea and (b) dichlorourea as a function of pH calculated by ACD/Percepta 2021.2.0 software (Advanced Chemistry Development Inc.).

According to the calculated results, the deprotonated state of monochlorourea and dichlorourea exist from pH 7.4 and 3, respectively (Figure 10). Therefore, the deprotonation of dichlorourea would promote the chlorination of urea in the pH 3-7.5 region. The proportion of deprotonated dichlorourea raises as pH increases in the pH 3-7.5 region because the $\mathrm{p}K_a$ of dichlorourea is 5.1 ± 1.4 (Reaction (8)). The formation of trichlorourea is accelerated by the chlorination of deprotonated dichlorourea since the nitrogen atom of the deprotonated dichlorourea becomes more electron-rich (Reaction (9)).

$$\mathrm{CO(NHCl)_2} \rightleftarrows \mathrm{ClHNCONCl^-} + \mathrm{H^+} \qquad \mathrm{p}K_a = 5.1 \pm 1.4 \tag{8}$$

$$\mathrm{ClHNCONCl^-} + \mathrm{HOCl} \rightarrow \mathrm{ClHNCONCl_2} + \mathrm{OH^-} \tag{9}$$

Furthermore, the deprotonation of monochlorourea occurs and the proportion of deprotonated monochlorourea increases as pH increases in the pH 7.5-10 region (Reaction (10)). The formation of dichlorourea is accelerated by the chlorination of deprotonated monochlorourea (Reaction (11)). The generated dichlorourea exists as a deprotonated state in this pH range, promoting the production of trichlorourea. Therefore, the simultaneous deprotonation of mono- and dichlorourea accelerates the chlorination to form trichlorourea more rapidly.

$$\mathrm{H_2NCONHCl} \rightleftarrows \mathrm{HNCONHCl^-} + \mathrm{H^+} \qquad \mathrm{p}K_a = 9.7 \pm 1.1 \tag{10}$$

$$\mathrm{HNCONHCl^-} + \mathrm{HOCl} \rightarrow \mathrm{CO(NHCl)_2} + \mathrm{OH^-} \tag{11}$$

Trichlorourea exists as the deprotonated state in pH 3-10 because the pK_a of trichlorourea is 0.5 ± 1.8. The deprotonated trichlorourea would rapidly react with chlorine to form tetrachlorourea. The previous investigations suggested that the C-N bond of tetrachlorourea breaks immediately by hydrolysis.[15, 31] Therefore, the chloroureas would decompose rapidly once the trichlorourea is produced.

Moreover, the difference in degradation rates at the chlorine doses of 400 μM and 800 μM in the pH 3-7.5 region could be another evidence for the deprotonation of dichlorouea (see the inset of Figure 9b). The relative peak intensity of dichlorourea was higher at 800 μM of chlorine than at 400 μM of chlorine (Figure 11). This indicates that the increase in chlorine dose increased the amount of dichlorourea produced during the first step of the pH swing. Therefore, more generated dichlorourea would increase the amount of deprotonated dichlorourea at the second step of the pH swing, consequently promoting the degradation of (chloro-)ureas.

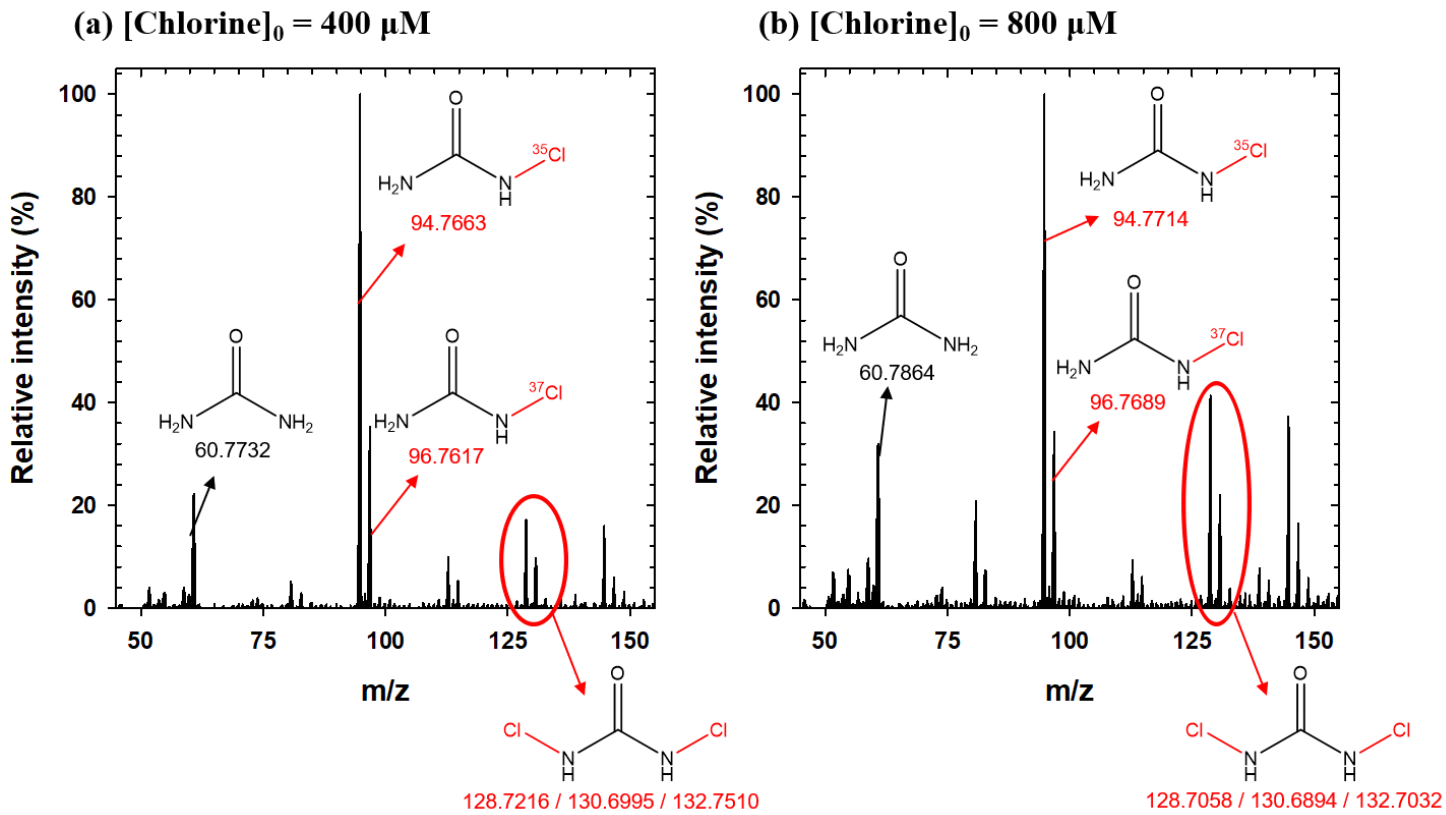

Figure 11. ESI-MS spectra of chlorinated products of urea after 10 minutes of reaction at different chlorine doses under acidic conditions, (a) $[\text{Chlorine}]_0$ = 400 µM and (b) $[\text{Chlorine}]_0$ = 800 µM ($[\text{Urea}]_0$ = 100 µM; pH 3).

3.4 Product formation of urea chlorination

The previous studies suggested that chloramines (NCl_3, $NHCl_2$, NH_2Cl), NH_4^+, and NO_3^- are produced during chlorination of urea.[14, 15, 32, 33] The hydrolysis of tetrachlorourea and further chlorination produce NCl_3, and $NHCl_2$ and NH_2Cl are produced by the hydrolysis of NCl_3.[15] NH_4^+ and NO_3^- are produced by the reaction between the chloramines.[34-36] In this study, the concentrations of NH_4^+ + chloramines, NO_3^-, and total nitrogen were measured at various conditions (Figure 12-14).

The concentration of (chloro-)ureas decreased with reaction time at pH 3 (Figure 1a), whereas the total nitrogen concentration remained almost constant during the reaction for 150 minutes in the pH 3 closed system (Figure 12a). However, in the pH 3 open system, the total nitrogen concentration decreased with a similar trend to the decrease in (chloro-)ureas concentration (Figure 12b). These results indicated that the products formed by the chlorination of urea at pH 3 are volatile.

Moreover, NH_4^+ + chloramines increased rapidly in the first 10 minutes and remained almost constant in the pH 3 closed system (Figure 12a), while a small amount of NH_4^+ + chloramines was detected only at 10 minutes in the pH 3 oopen system (Figure 12b). These results show that the volatile products formed by the chlorination of urea are chloramines. A small amount of NO_3^- was detected for 150 minutes in the pH 3 closed system (Figure 12a) or NO_3^- was not detected in the pH 3 open system (Figure 12b). These results means that NO_3^- formation through the oxidation of chloramines hardly occurs at pH 3.

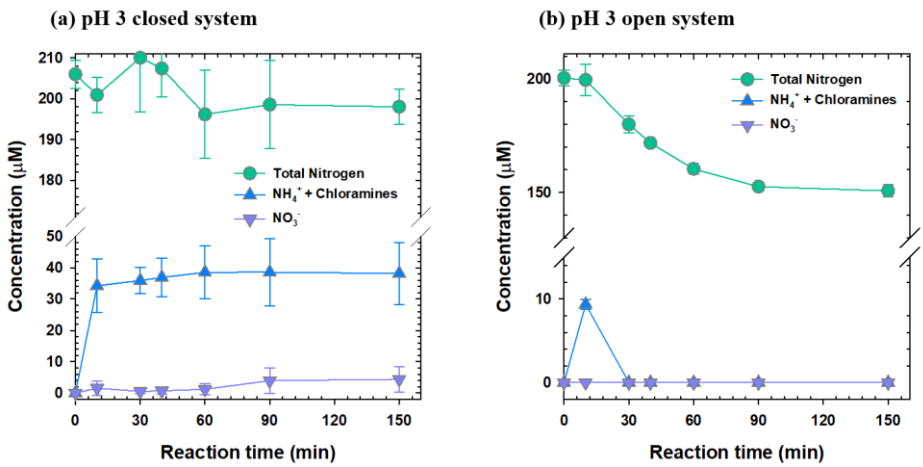

Figure 12. Concentrations of NH_4^+ + chloramines, NO_3^-, and total nitrogen as a function of time in (a) pH 3 closed system and (b) pH 3 open system ($[Urea]_0$ = 100 μM; $[Chlorine]_0$ = 400 μM; pH 3).

The total nitrogen concentration decreased with reaction time in both the pH 7 closed and open systems, with little difference in total nitrogen concentration between the two systems (Figure 13a, b). The concentrations of NH_4^+ + chloramines and NO_3^- also showed little difference between the two systems. These results indicate that the volatilization of chloramines has no significant effect at pH 7 and gaseous nitrogen compounds could be produced through the chlorination of urea at pH 7. Furthermore, contrary to the results in the pH 3 closed system (Figure 12a), the concentration of NO_3^- was higher than that of NH_4^+ + chloramines in the pH 7 closed system (Figure 13a). This result is consistent with the previous study that the NO_3^- formation through chloramines was accelerate as pH increased.[36]

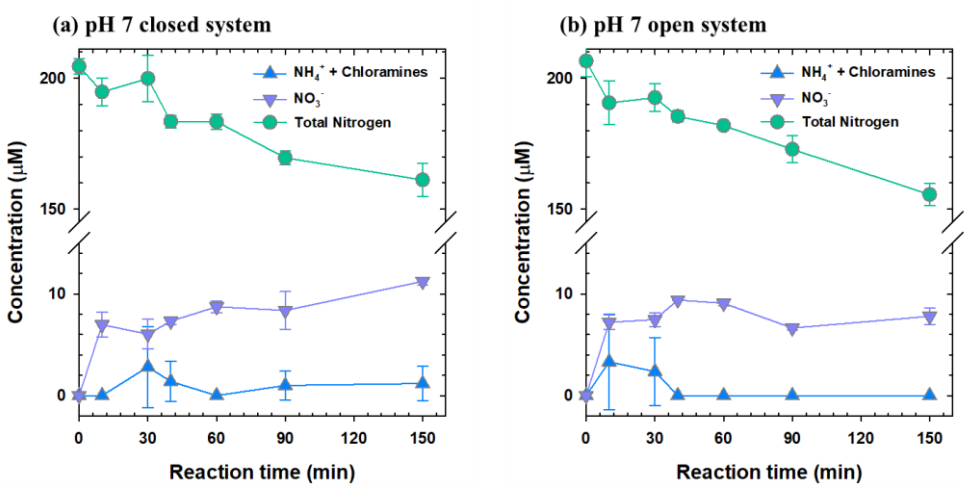

Figure 13. Concentrations of NH_4^+ + chloramines, NO_3^-, and total nitrogen as a function of time in (a) pH 7 closed system and (b) pH 7 open system ($[Urea]_0$ = 100 μM; $[Chlorine]_0$ = 400 μM; pH 7).

The total nitrogen concentration rapidly decreased in the second step in the pH swing closed system (Figure 14a), which was aa similar trend to the degradation of (chloro-)ureas (Figure 1a). However, the sum of NH_4^+ + chloramines and NO3- concentrations in the second step hardly changed (Figure 14a). These results imply that gaseous nitrogen compounds were generated in the second step of the pH swing, which is consistent with the previous investigations.[35, 37, 38] These investigation suggested that N_2 or N_2O could be produced from the base decomposition of trichloramine (Reaction (12)),[37] the reaction between dichloramine and trichloramine (Reaction (13)),[38] and the hydrolysis of dichloramine (Reactions (14)-(15)).[35]

$$2NCl_3 + 6OH^- \rightarrow N_2 + 3OCl^- + 3Cl^- + 3H_2O \quad (12)$$

$$NHCl_2 + NCl_3 + 3OH^- \rightarrow N_2 + 2HOCl + 3Cl^- + H_2O \quad (13)$$

$$NHCl_2 + H_2O \rightarrow HNO + 2H^+ + 2Cl^- \quad (14)$$

$$2HNO \rightarrow N_2O + H_2O \quad (15)$$

NH_4^+ + chloramines decreased with the reaction time in the second step, while the amount of NO_3^- increased in the pH swing closed system (Figure 14a). This result is also consistent with the previous investigation that chloramines oxidize to NO_3^- in neutral pH.[36] The small amount of NH_4^+ + chloramines were measured and the concentration of NO_3^- was not detected in the pH swing open system (Figure 14b), because chloramines volatilized in the first step of the pH swing.

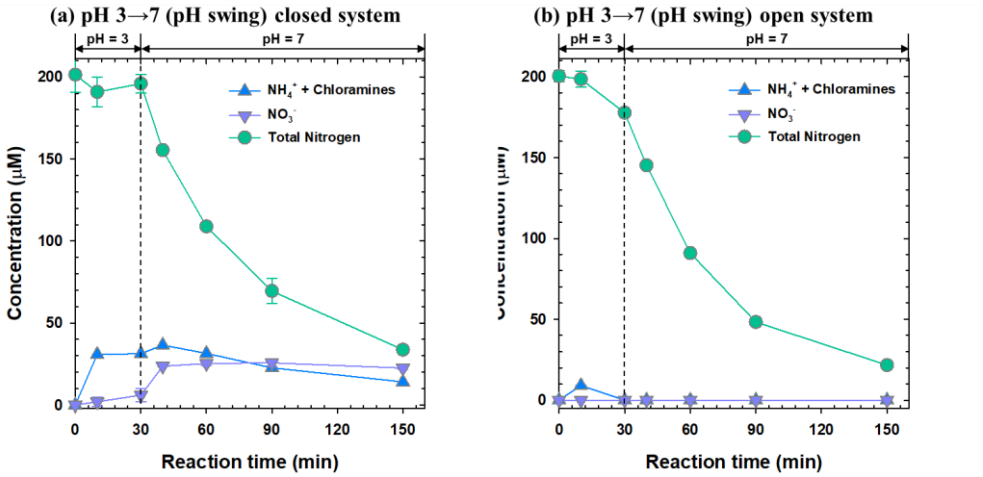

Figure 14. Concentrations of NH_4^+ + chloramines, NO_3^-, and total nitrogen as a function of time in (a) pH 3→7 closed system and (b) pH 3→7 open system; The black dashed line indicates the point when pH was elevated from 3 to 7 ($[Urea]_0$ = 100 μM; $[Chlorine]_0$ = 400 μM; pH = 3 for first 30 min and pH was elevated to 7).

The concentrations of chloramines under six different conditions were measured to check the volatilization of chloramines (Figure 15). The difference in the chloramines concentrations between the closed system and open system was greatest at pH 3, and it was negligible at pH 7. This result shows that the volatilization of chloramines decreased and other nitrogen compounds such as NO_3^-, N_2, or N_2O were produced from chloramines as the pH increased.

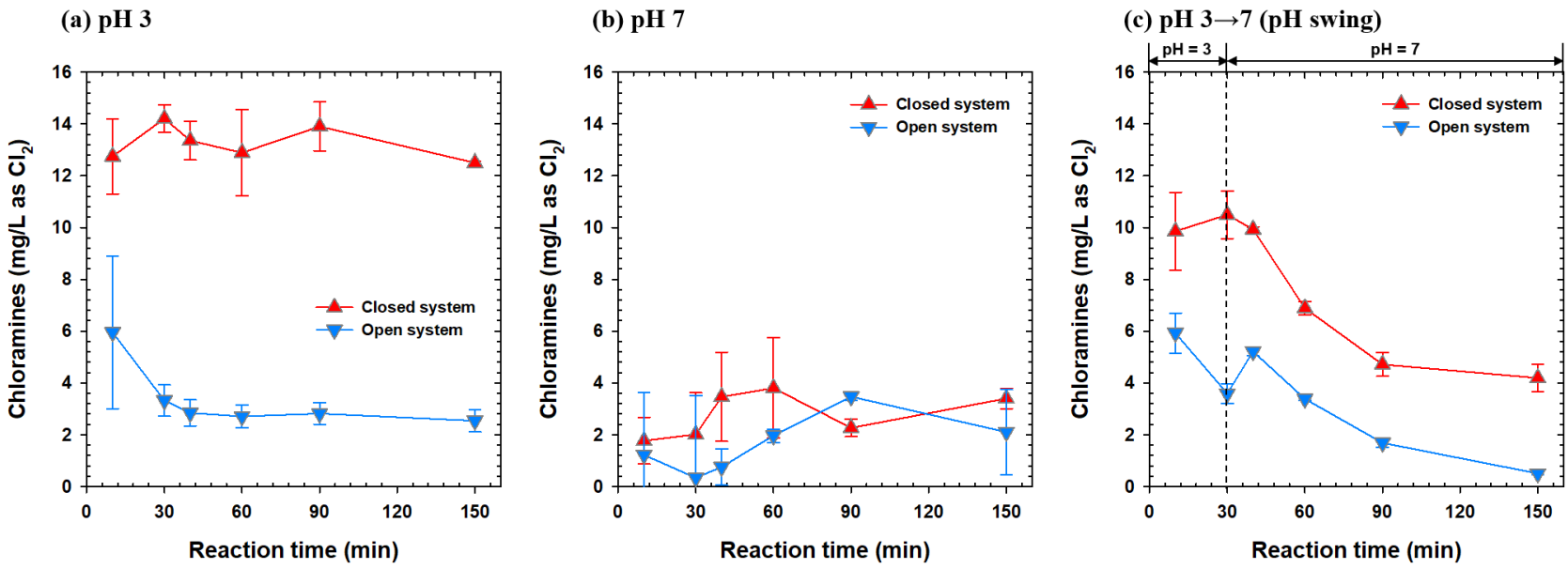

Figure 15. Concentrations of chloramines as a function of time at (a) pH 3, (b) pH 7, and (c) pH 3→7 (pH swing); The black dashed line indicates the point when pH was elevated from 3 to 7 ($[Urea]_0$ = 100 μM; $[Chlorine]_0$ = 400 μM; pH 3 for first 30 minutes and pH was elevated to 7 for the pH swing system).

3.5 Proposed pH-dependent mechanism for chlorination of urea

The pH-dependent reaction mechanism of urea and chlorine was proposed in Figure 16 based on the experiment results. The first chlorination of urea is promoted at pH 3 due to the presence of Cl_2, and further chlorination occurs as monochlorourea reacts with residual chlorine. The second chlorination to form dichlorourea speeds up as pH rises, especially at basic condition, because of the high pK_a of monochlorourea. The third chlorination is accelerated at a lower pH than the second chlorination because the pK_a decreases as the number of substituted chlorines increases. However, the fourth chlorination is hardly affected by pH because the pK_a of trichlorourea is very low. After all of H in urea was substituted with Cl, tetrachlorourea was decomposed to produce chloramines.[15, 31] Chloramines could be hydrolyzed or oxidized to form various nitrogen compounds depending on the pH.

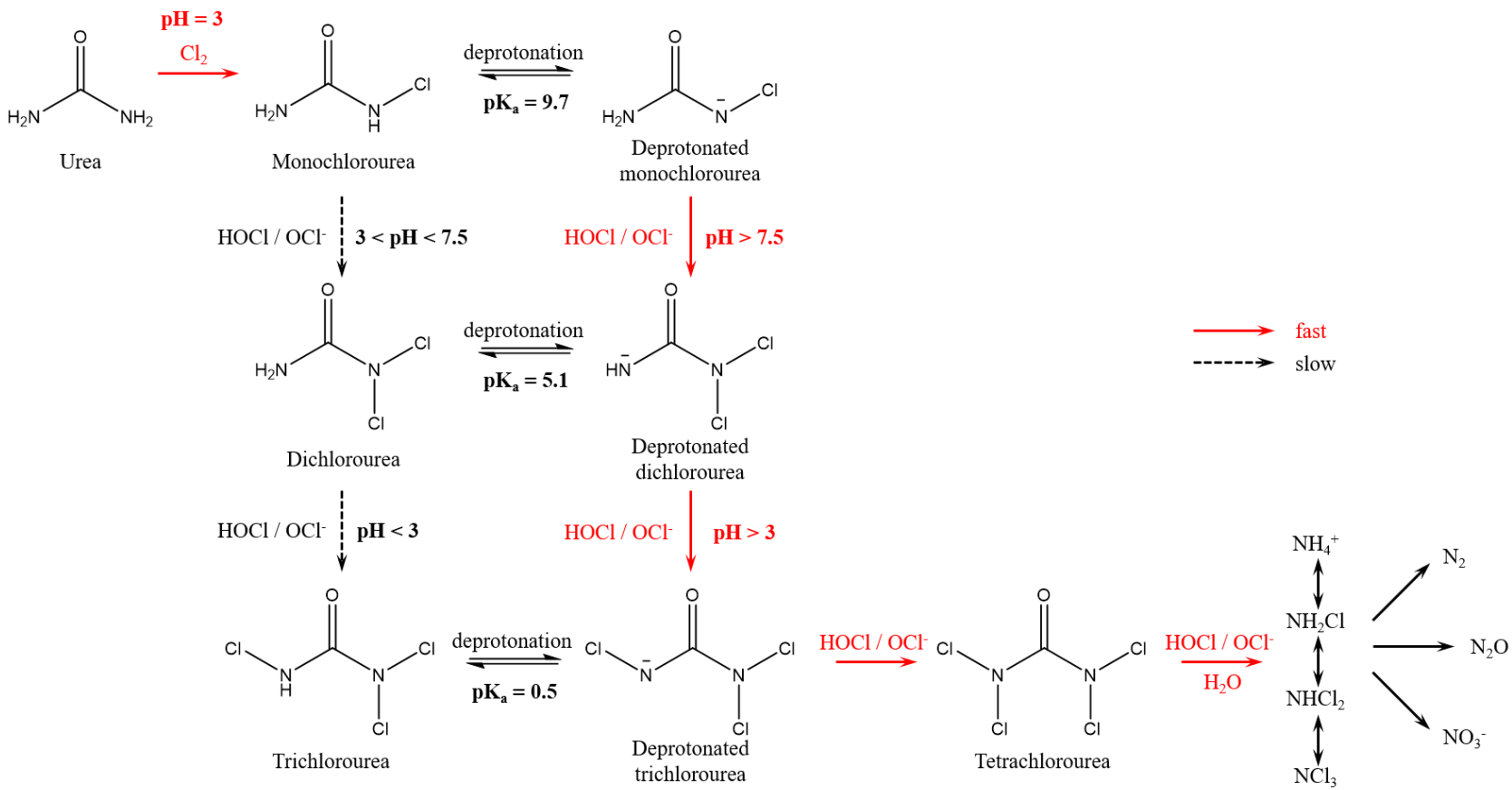

Figure 16. Proposed reaction pathways for the chlorination of urea depending on pH.

Chapter 4. Conclusions

This study demonstrated that the pH swing method can greatly enhance the urea degradation rate by chlorine. The pH swing is the method in which the urea reacted with chlorine at pH 3 for 30 minutes and then at pH 7 for 120 minutes. The reaction of urea and chlorine to form monochlorourea occurred rapidly at acidic pH, and the rate of subsequent reactions to degrade chloroureas increased as pH raised. This method could be applied to sewage treatment to reduce nitrogen and prevent eutrophication. However, the reaction time to degrade urea by pH swing is yet too long for the practical application. The reduction of reaction time by changing the acid pretreatment pH or increasing the chlorine dose is needed for the application.

Moreover, the pH swing method could be applied to degrade urea in raw water used for ultrapure water production. Urea is not easily removed through the ultrapure water production process, so the remaining urea increases the TOC of ultrapure water.[9, 39] The application of the pH swing method would efficiently degrade urea in raw water, but the addition of acid, base, and oxidant increases the conductivity of water. Therefore, it is necessary to add appropriate amounts of acid, base, and oxidant that do not exceed the ultrapure water conductivity requirements while maintaining the degradation efficiency of urea.

The kinetic study, analysis of intermediates, and pK_a calculations provide new insight into the chlorination mechanism of urea depending on pH. The deprotonation of the chloroureas, which were produced during the acid pretreatment, could promote chlorination after the pH increase. The concentrations of NH_4^+ + chloramines, NO_3^-, and total nitrogen were measured under various conditions. The formation of the

gaseous nitrogen compounds during the chlorination by the pH swing was indirectly confirmed, but further studies are needed to determine the exact products and analyze each quantitatively.

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국문 초록

요소는 염소와 반응하여 수소가 염소로 치환된 클로로우레아(chlorourea)를 생성하고, 염소로 모두 치환된 요소는 가수분해에 의해 분해된다. 요소를 산성 조건에서 30 분 동안 염소와 반응한 다음 (1 단계), pH 7 에서 120 분 동안 반응하는 (2 단계) pH 스윙을 이용한 염소화를 통해 요소의 분해를 크게 향상시켰다. 요소는 pH 3 과 pH 7 에서 각각 20%와 16%가 분해되었으나, pH 스윙을 이용한 경우에는 92%가 분해되었다. pH 스윙에 의한 요소의 분해 효율은 염소 주입량이 증가함에 따라 증가하였다. 또한, 요소의 분해 속도는 pH 스윙 2 단계의 pH 가 3 에서 10 으로 증가함에 따라 증가했으며, 클로로우레아의 종 변화가 분해 속도 향상 원인임을 확인하였다. pH 스윙을 이용한 경우, 2 단계의 pH 가 증가함에 따라 탈양성자화된(deprotonated) 모노클로로우레아(monochlorourea) 와 디클로로우레아(dichlorouera)가 증가해 염소화 속도를 가속화했다. 디클로로우레아의 탈양성자화는 pH 3-7.5 영역에서 분해 속도를 가속화했고, 모노클로로우레아와 디클로로우레아의 동시 탈양성자화는 pH 7.5-10 영역에서 분해 속도를 크게 향상시켰다. 또한, 다양한 pH 조건에서 폐쇄형과 개방형 시스템일 때 요소의 염소화를 통해 형성된 생성물을 각각 분석하였다. 클로라민(chloramine)이 휘발성이기 때문에 폐쇄형 시스템보다 개방형 시스템에서 더 낮은 농도의 생성물이

측정되었다. 또한, 암모늄(NH_4^+)과 클로라민은 pH 가 증가함에 따라 산화되어 질산염(NO_3^-)을 형성하였다.

주요어: 요소, 산화, 염소화, pH 스윙, pH 의존적 반응 기작, 탈양성자화

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