Advancement of Urea Elimination Using Pre-Halogenation Processes in UV_{254}/Bromine and UV_{254}/Chlorine Systems

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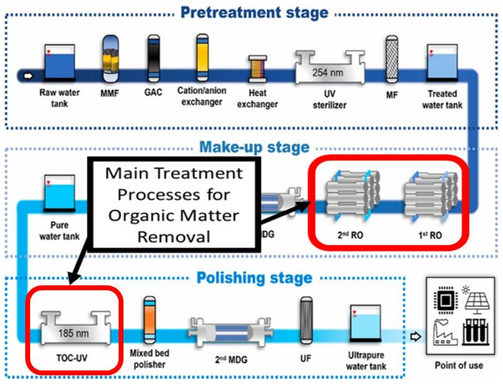
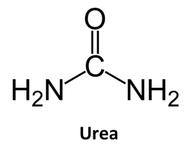
Introduction

Urea Issue in Ultrapure Water





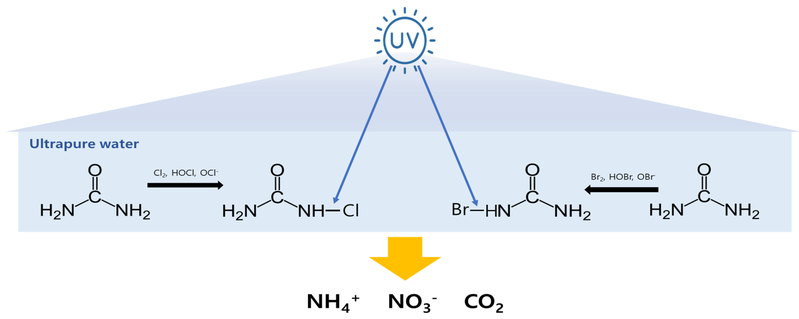
Urea

Treatment	Removal
Reverse osmosis	Low
Ion exchange	None
Activated carbon	None
UV oxidation	Low

❖ Ultrapure water, characterized by its exceptionally high purity and extremely low conductivity, is essential for high-tech industries such as semiconductor and display manufacturing.

❖ The removal of urea in ultrapure water treatment is challenging due to its neutrality, hydrophilicity and small molecular size.

UV_{254}/Br & UV_{254}/Cl Processes for Efficient Urea Elimination

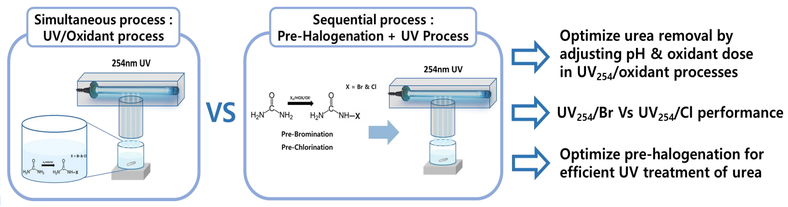


❖ Chlorine and bromine are widely used as oxidizing agents in water treatment, reacting with urea to form halogenated urea.

❖ UV-based technologies remove contaminants through direct photodegradation or indirect oxidation, facilitated by reactive species or radicals generated in the presence of oxidants.

❖ Urea itself has weak UV absorption, but halogenation increases its UV absorptivity by forming more UV-reactive N-Br and N-Cl bonds. Under UV irradiation, these halogenated compounds ultimately degrade into NO_3^-, NH_4^+, and CO_2.

Research Objectives



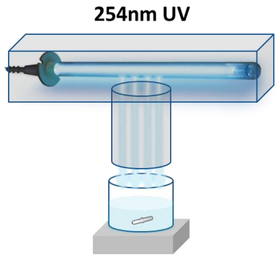
❖ To evaluate the efficiency of UV/oxidant processes for urea elimination by examining the effects of varying oxidant dosages and pH conditions, with the goal of optimizing process performance.

❖ To investigate the UV_{254}/bromine (UV/Br) process, which remains under explored, and compare its performance with the conventional UV_{254}/chlorine (UV/Cl) process.

❖ To assess the feasibility of pre-bromination and pre-chlorination for the formation of halogenated urea species prior to UV irradiation, aiming to enhance removal efficiency compared to simultaneous UV/Br and UV/Cl processes.

Methods

UV/Oxidant Processes: Sequential & Simultaneous Process



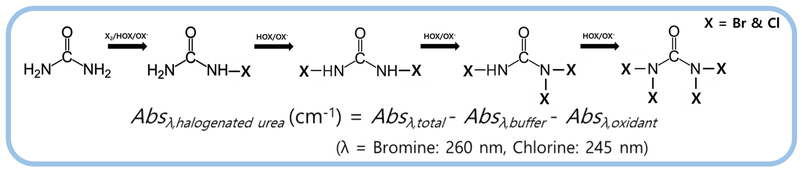
- $[urea]_0$ = 20 μM
- pH = 3, 7 (phosphate buffer)
- UV fluence rate = 3.35 mW/cm²

❖ **Simultaneous Process :** Experiment was conducted in 5 mM buffer with $[urea]_0$ = 20 μM and $[bromine]_0$ or $[chlorine]_0$ = 20 - 200 μM, along with simultaneous UV irradiation.

❖ **Sequential Process :** Experiment was conducted in 5 mM buffer with $[urea]_0$ = 20 μM and $[bromine]_0$ or $[chlorine]_0$ = 10 - 40 μM, along with sequential UV irradiation.

❖ Samples were taken at designed time intervals and quenched using sodium thiosulfate.

Determination of Maximum Halogenated Product Formation



❖ Reaction dynamics between bromine/chlorine and urea were analyzed through time-course UV absorption monitoring.

❖ Corrections were applied to the absorbances of halogenated urea to account for contributions from the buffer, bromine/chlorine and urea (negligible), following the equation.

Analysis Methods

❖ **Total Urea Concentration (Urea + Halogenated Ureas)**
– Diaceytl monoxime (DAMO) method

❖ **Bromine & Chlorine Concentration**
– N,N'-diethyl-p-phenylenediamine (DPD) colorimetric method

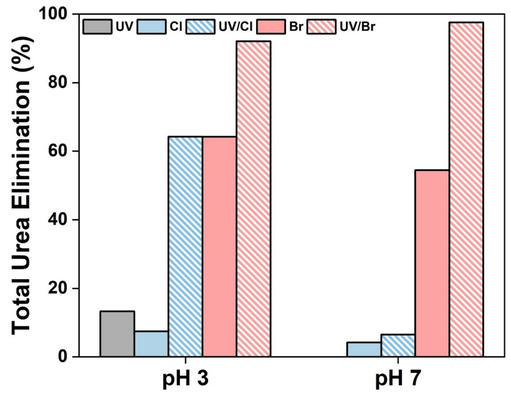
❖ **Bromourea(s) Monitoring**
– Spectroscopic method at 260 nm

❖ **Chlorourea(s) Monitoring**
– Spectroscopic method at 245 nm

UV-VIS Spectrophotometer

Results & Discussion

Effect of pH on Total Urea Elimination in Simultaneous UV/Oxidant Process



❖ Bromine alone exhibited higher efficacy overall, while chlorine alone and UV alone were not effective across all tested pHs.

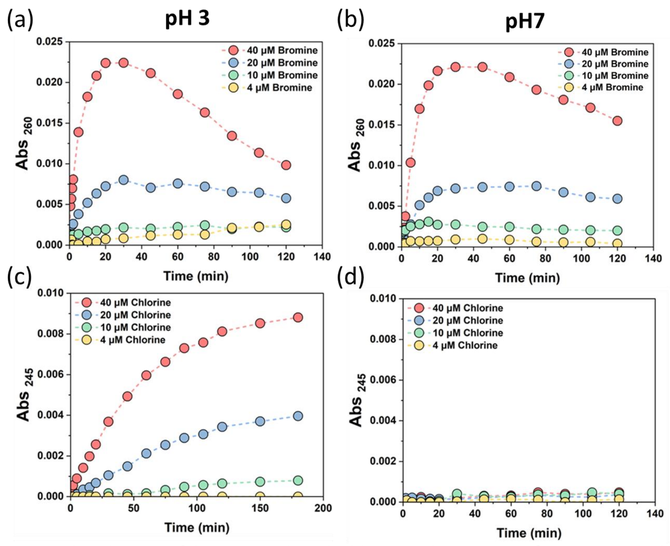
❖ **Acidic condition (pH 3):** Chlorine alone achieved 7% elimination and UV/Cl achieved 64% elimination.
→ The formation of chloroureas occurs more readily under acidic condition, enhancing total urea elimination at pH 3 with UV irradiation.

❖ **Neutral condition (pH 7):** Bromine alone achieved 55% elimination and UV/Br achieved 98% elimination, and with UV/Br yielded higher removal than in acidic conditions.

▶ **Application of UV further enhanced the elimination.**

Figure 1. Effects of pH on total urea elimination during UV/Br, UV/Cl, UV, Br, Cl processes after 30 min. $[urea]_0$ = 20 μM; $[bromine]_0$ and $[chlorine]_0$ = 100 μM at pH 3 and 7.

Absorbance Monitoring of Halogenated Product Formation (pH 3 & 7)



❖ **Bromination:** When $[bromine]_0 > [urea]_0$, the halogenated products were unstable and noticeable decrease in absorbance was observed after 30 min. Conversely, when $[bromine]_0 \leq [urea]_0$, halogenated product formation reached its peak and remained stable. This trend was consistently observed under both pH 3 & pH 7 conditions.

❖ **Chlorination:** At pH 3, when $[chlorine]_0 \geq [urea]_0$, halogenated products were gradually formed and remained stable for up to 180 min. In contrast, when $[chlorine]_0 < [urea]_0$, halogenated product formation was minimal. At pH 7, halogenated product formation was minimal across all oxidant concentrations. This explains the higher treatment efficiency of UV/Cl at pH 3 than pH 7 (Figure 1).

▶ **pH and oxidant concentration significantly influenced the formation of halogenated products.**

Figure 2. Absorbance of brominated and chlorinated urea transformation products monitored at 260 nm and 245 nm with varying oxidant concentration. $[urea]_0$ = 20 μM ; $[bromine]_0$ and $[chlorine]_0$ = 4, 10, 20, 40 μM at pH 3 and 7. (a) bromine at pH 3, (b) bromine at pH 7, (c) chlorine at pH 3, (d) chlorine at pH 7.

Effect of pH on Total Urea Elimination in Sequential & Simultaneous UV/Oxidant Process

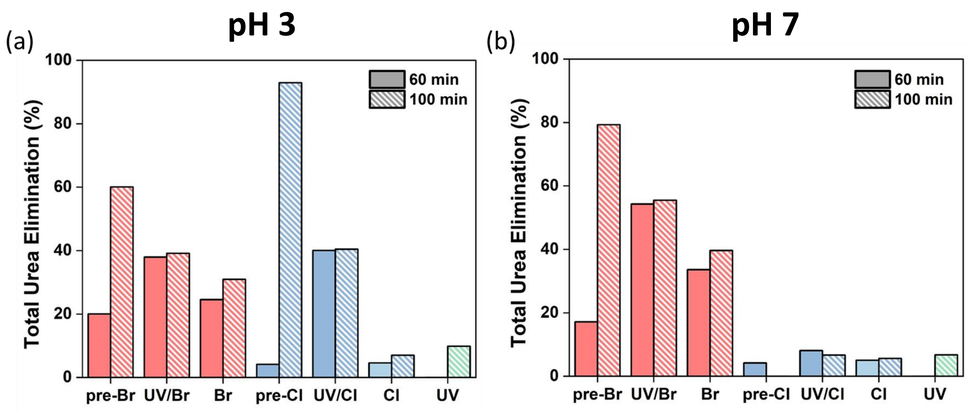


Figure 3. Effects of pH on total urea elimination during pre-bromination + UV (pre-Br), pre-chlorination + UV (pre-Cl), UV/Br, UV/Cl, UV, Br, Cl processes after 100 min. $[urea]_0$ = 20 μM; $[bromine]_0$ and $[chlorine]_0$ = 40 μM at (a) pH 3 and (b) pH 7. Pre-oxidation time was 60 min for pre-Br and pre-Cl processes, followed by 40 min UV irradiation.

❖ **Acidic condition (pH 3):** The pre-chlorination + UV (pre-Cl) process achieved the highest elimination efficiency (92%), followed by pre-bromination + UV (pre-Br) (60%). In the case of pre-Br, the elimination efficiency increased by 40% after UV treatment, whereas for the pre-Cl process, the efficiency exhibited a significant increase of 89% following UV exposure.

❖ **Neutral condition (pH 7):** Bromine-containing processes show higher elimination efficiency than chlorine-containing processes. The pre-bromination + UV (pre-Br) process achieved the highest elimination efficiency (79%), followed by UV/Br (56%). In the case of pre-Br, the elimination efficiency increased by 62% after UV treatment. The pre-chlorination + UV (pre-Cl) process exhibited minimal elimination. As indicated in Figure 2, it is likely due to the minimal formation of chlorinated urea species at pH 7.

▶ **The pre-halogenation + UV processes exhibited higher elimination efficiency compared to the UV/oxidant and oxidant-only processes.**

Conclusions

❖ The pre-halogenation + UV process demonstrated superior urea removal efficiency compared to conventional UV/bromine, UV/chlorine, and oxidant-only treatments.

❖ pH significantly influenced both urea removal efficiency and halogenated product formation. Bromine-containing processes exhibited higher removal efficiency and increased product formation under neutral conditions, whereas chlorine-containing processes were more effective and promoted product formation under acidic conditions. This trend was consistently observed in pre-halogenation experiments, highlighting the pH-dependent characteristics of each oxidant.

❖ These findings indicate that pre-bromination + UV presents a promising alternative to chlorine for advanced urea removal in water treatment. While pre-chlorination with UV enhanced efficiency under acidic conditions, extreme pH may not be suitable for ultrapure water production. In contrast, pre-bromination with UV at neutral pH demonstrated superior and more practical performance.

Acknowledgement

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