



공학석사 학위논문

Comparative assessment of UV advanced oxidation processes: degradation of iodinated contrast media and fate of iodine

UV 고도산화공정에서의 아이오딘화 조영제의 분해와 아이오딘 종의 거동에 관한 비교 연구

2023년 2월

서울대학교 대학원

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Comparative assessment of UV advanced oxidation processes: degradation of iodinated contrast media and fate of iodine

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이 논문을 공학석사 학위논문으로 제출함 2023년 2월

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지호중의 공학석사 학위논문을 인준함 2022년 12월

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Abstract

Comparative assessment of UV advanced oxidation processes: degradation of iodinated contrast media and fate of iodine

Iodinated contrast media (ICM) are widely used in X-ray imaging, and are detected in surface water, groundwater, wastewater, and soil due to their resistance to water treatment. Conventional wastewater treatment plants and drinking water treatment plants remove ICMs with less than 65% efficiency, and toxic byproducts such as iodinated disinfection byproducts may form when reactive iodine species (RIS: I_2 , I_3^- , HOI) react with natural organic matter (NOM). Recently, AOPs utilizing 254 nm UV (UV AOPs) have shown promising removal efficiencies towards several ICM. However, the problems of UV AOPs still entail – possibilities of toxic byproducts formation during AOP treatment, or during post-chlorination.

In this study, various UV AOPs are examined, while using peroxymonosulfate (PMS), peroxydisulfate (PDS), hypochlorite (NaOCl), and hydrogen peroxide (H₂O₂) as oxidants. Along with these single-oxidant processes, mixed-oxidant processes were also tested. Diatrizoate, iohexol, and iopamidol were selected as model compounds for ICM. Degradation efficiencies of these ICMs were analyzed, along with speciation of inorganic iodine (iodide, RIS, iodate) and further, formation of iodinated trihalomethanes (I-THMs) and iodinated haloacetic acids. (I-HAAs). The correlation between RIS concentrations and I-THM / I-HAA formation will be addressed.

Keywords: Iodinated contrast media; Advanced oxidation process; Reactive iodine species; Iodinated disinfection byproducts Student Number: 2021-23781

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Chapter 1. Introduction

1.1. Background

Iodinated contrast media (ICM) are widely used for medical X-ray imaging, and they consist of 10~80% of mass loadings of pharmaceuticals in hospital wastewater and domestic wastewater^{1,2}. Persistence of ICM leads to the global detection in various water systems, including marine systems, surface water, and drinking water^{3–5}. ICMs not only pose adverse health effects from long-term $exposures^{6,7}$, their presence and persistence in water could be problematic, due to being major precursors of iodinated disinfection (I-DBPs) through oxidation. It is known that by-products chlorination/chloramination of ICMs may produce I-DBPs during drinking water treatment⁸, and correlation of ICM and I-DBP concentrations has been found in surface waters and DWTPs⁹. Although I-DBP concentrations are typically lower than other halogenated DBPs in drinking water, I-DBPs are generally known to be more cytotoxic and genotoxic than chlorinated/brominated analogues¹⁰. For instance, in a cell chronic cytotoxicity study, LC₅₀ of I-DBPs were 10~1000 times lower than those of other halogenated DBPs¹¹, thus control of I-DBP formation in waters are deemed to be necessary.

Conventional wastewater treatment plants (WWTPs), where biochemical and physicochemical processes are usually employed, are not very capable of removing ICMs. For instance, zero to negative removal rates were reported in an activated sludge WWTP case study¹². It was also reported that ozonation or granular activated carbon adsorption is not fully capable of removing ICMs, as 30-60% of removal rate was attained with ozone, and iopamidol reached only 70% of removal during granular activated carbon filtration^{13,14}. Even in some advanced oxidation processes

(AOPs), where reactive radicals are generated to decompose pollutants, ICMs were insufficiently removed. In particular, diatrizoate, reached 25% removal efficiency in $O3/H_2O_2$ process, and 36% in UV-C/O₃ process, both with contact time of 18 minutes¹⁵.

Recent studies involving 254 nm-UV AOPs with sulfate- or chlorine-based radical sources, have shown possibilities to completely remove refractory pollutants including ICM. For instance, diatrizoate – one of the most commonly used and persistent ICMs due to its ionic characteristics – was successfully degraded (>99%) within 36 minutes and 1.5 minutes, in UV/S₂O₈²⁻ and UV/Cl₂ processes, respectively^{16,17}. Likewise, iohexol, which is also one of the most commonly used ICMs, was able to be removed 99% within 1.5 minutes in UV/S₂O₈²⁻, and 98% within 5 minutes in UV/Cl₂ process^{18,19}. Iopamidol was also effectively removed with UV/Cl₂ process, where 99% removal was attained within 2.0 minutes²⁰.

Process	Reaction time	Efficiency			
Biochemical processes					
Activated sludge	25-35 h	Negative ³			
Membrane bioreactor	-	Negative ²			
Adsorption					
Powdered	1 day, 23 mg PAC/L	14% 21			
activated carbon	45 min, 20 mg PAC/L	31% 22			
Advanced oxidation processes					
O ₃ /H ₂ O ₂	18 min	25% 15			
UV-A/TiO ₂	1 h	65% ²³			
254 nm-UV AOPs					
UV-C/O ₃	18 min	36% 15			
UV-254/H ₂ O ₂	36 min	60% 16			
UV-254/Cl ₂	6 min	99% ¹⁷			
UV-254/S ₂ O ₈ ²⁻	36 min	99% ¹⁶			

 Table 1. – Diatrizoate removal efficiencies reported in the literature



a) Diatrizoate



Figure 1. List of ICM compounds featured in this research. a) diatrizoate, b) iohexol, c) iopamidol.

1.2. Research objectives

Although UV AOPs have proven their degradation efficiencies towards ICM, the fate of iodine within AOPs has not been extensively studied. It is well known that reactive iodine species (RIS) – mainly HOI, I₂, I₃⁻ – accounts for I-DBP generation for their reactivity towards phenolic structures in natural organic matter (NOM)²⁴. However, generation of RIS within AOPs is not extensively studied, and few data are available to address the transformation of iodine to I-DBP during AOP treatment²⁵. Also, most literatures have evaluated a certain UV AOP for ICM treatment, or have compared two processes in a single experimental setup. Yet, there are few studies that compare multiple processes while assessing the fate of iodine.

Aim of this study is 1) to compare ICM degradation and RIS formation characteristics of various UV AOPs, and 2) to assess I-DBP formation during UV AOP treatment in accordance with RIS concentrations. Diatrizoate, iohexol and iopamidol will be used as a model compound for ICM. Also, this study investigates the reaction characteristics observed in mixed-oxidant AOPs (e.g. UV/NaOCl 0.5 mM + H_2O_2 0.5 mM), and correspondence between RIS formation and I-DBP formation will be addressed.

Chapter 2. Materials and Methods

2.1. Chemicals and Reagents

Sodium diatrizoate hvdrate (≧98%). peroxymonosulfate $(KHSO_5 \cdot 0.5 KHSO_4 \cdot 0.5 K_2 SO_4,$ OXONE®, monopersulfate compound), Potassium iodide (\geq 99%), sodium acetate anhydrous (\geq 99.0%), sodium tetraborate decahydrate ($\geq 99.5\%$), sodium thiosulfate ($\geq 99\%$), 2,6dibromophenol (\geq 99%), EPA 501/601 trihalomethanes calibration mix, EPA 552.2 haloacetic acids calibration mix, and iodoform ($\geq 99\%$) were purchased from Sigma-Aldrich (USA). Hydrogen peroxide (35% solution in water), acetic acid (99.8%), potassium phosphate monobasic (\geq 99%), and potassium phosphate dibasic anhydrous (≧99%) was obtained from Daejung Chemicals & Metals (South Korea). Peroxydisulfate (Potassium persulfate, $\geq 99\%$), sodium hydroxide beads/pellets (\geq 99.99%), and iodine solution (I₂, 1.0N in water) was purchased from Alfa-Aesar (USA). Sodium hypochlorite solution (5.65-6%) and methyl tert-butyl ether ($\geq 99.0\%$) were purchased from Fisher Chemical (USA). Suwannee River natural organic matter (Cat. No. 2R101N) was obtained from International Humic Substance Society (USA).

Iodinated trihlomethanes (I-THM) and iodinated haloacetic acids (I-HAA) standards, including dichloroiodomethane (\geq 95%), chloroiodoacetic acid (\geq 90%) and diiodoacetic acid (\geq 90%) were purchased from CanSyn Chemical Corporation (Canada).

Stock solutions for diatrizoate, iohexol, and iopamidol were prepared with deionized water ($\geq 18.2 \text{ M}\Omega \cdot \text{cm}$) from Milli-Q water purification system (Millipore, USA). Solutions were stored in dark conditions at $4\,^\circ\!\!\mathbb{C}$ prior to their uses.

2.2. Degradation of ICMs in UV Reaction System

The reactor consists of acrylic water jacket, glass reaction cylinder, quartz-tubed UV lamp (TUV 15W SLV/6, Philips®), and thermostatic pump. UV lamp was turned on for 30 minutes prereaction. UV fluence rate at 254 nm was calculated by observing degradation kinetics of atrazine. Pseudo-1st-order rate constant was obtained during UV photolysis of 5 μ M atrazine solution (500 mL), while maintaining pH 7.0 with 10 mM phosphate buffer. UV fluence rate of 28.78 \pm 0.22 J/cm²·s was calculated, based on quantum yield and molar absorption coefficients²⁶.

500 mL of reaction volume containing diatrizoate (or iohexol, iopamidol), oxidants, and 10 mM buffer in the glass reaction tube was irradiated under UV light. Buffer solution types were selected depending on pH conditions – phosphate buffer for pH 6-8, and borate buffer for pH 9. Initial concentration of diatrizoate was 10 ppm for degradation kinetic experiment and inorganic iodine speciation and 50 ppm for THM and HAA analysis. Temperature of the water-jacketed glass reaction tube was maintained at 20°C, and the solutions were continuously stirred at 700 rpm. Samples were collected after certain time of irradiation, where 1 mL of solution was immediately transferred to 2 mL amber glass vial containing sodium thiosulfate or phenol for quenching of oxidants and RIS. These samples were in turn directly analyzed, or diluted for optimal analysis.

2.3. Determination of ICMs

The concentrations of diatrizoate, iohexol, or iopamidol in solution were determined with a single quadrupole liquid chromatography-mass spectrometry (LC-MS, 6120DW, Agilent, USA). The LC system (1260 Infinity II, Agilent, USA) was equipped with ZORBAX Extend C18 column (2.1 \times 150 mm, 1.8 μ m). Mixtures of acetonitrile (solvent A), and 0.1% formic acid in water (solvent B) were used as the mobile phase eluents. Flow rate of 0.2 mL and column temperature of 30° C was maintained. The eluent gradient time profile used for the analysis of diatrizoate, iohexol, and iopamidol was as follows (A:B): 90:10 at t = 0 min, decreased to 5:95 from 0.1 min to 3 min, held at 5:95 for 3 min, increased to 90:10 from 6 min to 8 min, and re-equilibrated to 90:10 from 8 min to 12 min. Electrospray ionization MS in the positive mode was used with fragmentor voltage of 90 V. The following MS settings were used: drying gas (i.e., N2) flow rate of 7.0 L/min, nebulizer pressure of 50 psi, drying gas temperature of 350 °C. Samples for the analyses were quenched with 1.0 mM sodium thiosulfate, to minimize the unwanted reactions between analytes and oxidants.

Degradation products of diatrizoate were analyzed with a LC equipped with quadrupole-time of flight mass spectrometer (LC-Q-TOF-MS, TripleTOF® 5600+, SCIEX, USA). Waters Cortex C18 column (2.1×150 mm, 1.6μ m) was equipped to high-pressure LC system (Ultimate3000, Thermo Scientific, USA), and a mixture of 0.1% formic acid in water (solvent C) and 0.1% formic acid in

acetonitrile (solvent D) was used as mobile phase. Flow rate of 0.2 mL/min and column temperature of 45 °C was maintained. The eluent gradient time profile used for the analysis was as follows (C:D) – 90:10 at t = 0 min, decreased to 20:80 from 0.1 min to 7 min, held at 20:80 from 7 min to 12 min, increased to 90:10 from 12 min to 13 min, and re-equilibrated to 90:10 from 13 min to 20 min. The source conditions of the TripleTOF® 5600+ MS were as follows: nebulizing gas of 50 psi, heating gas of 50 psi, curtain gas of 25 psi, source temperature of 500 °C, declustering potential of -60 V, collision energy of -30 V, and ion spray voltage floating of 4.5 kV. The mass spectra were obtained via full scan and information dependent acquisition scanning in the scan range 50–2000 m/z for MS and MS/MS. The collision energy spread was 10 V. Samples for the analyses were quenched with 1.0 mM sodium thiosulfate, to minimize the unwanted reactions between analytes and oxidants.

2.4. Inorganic Iodine Species Determination

Iodide and iodate concentrations were obtained with ion chromatography (IC, Dionex® ICS-1100, Thermo Scientific, USA) equipped with Dionex® AG-23/AS-23 column, Dionex® DRS 600 suppressor (Thermo Scientific, USA), and Dionex® 7693 autosampler. Samples were prepared by adding 1.0 mM phenol as RIS quencher, to prevent further reactions of RIS to form iodide (I^-) or iodate (IO_3^-). 2.5 mM potassium hydroxide solution was used as eluent, with flow rate of 0.7 mL/min, and suppressor current of 44 mA. I^- and IO_3^- was detected at retention time of 19 minutes and 4 minutes.

Reactive iodine species were quenched with excessive amount (2.5 mM) of 2,6-dibromophenol to form 4-iodo-2,6dibromophenol via electrophilic substitution reaction. Molecular iodine (I₂) and hypoiodous acid (HOI) both was able to produce 4iodo-2,6-dibromophenol with equal stoichiometric ratio., HOI was prepared by adding excessive potassium iodide to HOCl solution. Newly formed 4-iodo-2,6-dibromophenol was quantified with HPLC-UV (YL® 9100, Younglin, South Korea), at wavelength of 212 nm, utilizing ZORBAX Eclipse Plus® C18 column (4.6×250 mm, 5 μ m). 4-iodo-2,6-dibromophenol was detected at retention time of 12 minutes, with isocratic eluent mixture of 85% methanol and 15% of 0.1% acetic acid in water as mobile phase. Flow rate of 1.0 mL/min and column temperature of 30°C was maintained.

2.5. Determination of THM and HAA

THM and HAA samples were prepared with liquid-liquid extraction from aqueous solutions to methyl tert-butyl ether (MtBE), based on EPA method 551.1 and 552.2 (U.S. EPA., 1995a, 1995b). HAA standards were esterified by adding acidic methanol (90:10 methanol sulfuric acid mix) while heating up to 50°C for 2 hours, followed by addition of saturated sodium carbonate solution. Consequently, all of HAAs were converted to haloacetic acid methyl esters (HAAMEs) to improve analytical sensitivity. THM formation potentials (THMFP) and HAA formation potentials (HAAFP) were obtained by measuring the changes of THM or HAA concentrations, prior and after excessive chlorination (5 mg/L) for 3 days.

THM and HAAME concentrations were determined with gas chromatography-mass spectrometry (GC-MS, 5977B, Agilent®, USA). The GC system (7890B, Agilent®, USA) was equipped with HP-5MS column (30 m × 250 μ m × 0.25 μ m, Agilent®, USA), and Agilent® 7693 autosampler. Helium gas was used as mobile phase, and 1 μ L of sample was injected at each run. Injection Oven temperature gradient setting for THM analysis is as follows: 50°C at t = 0 min and held for 3 min, constant increase rate of 10°C/min to 150°C from 3 min to 13 min, hold 150°C for from 13 min to 14 min, and post run of 250°C from 14 min to 17 min. Solvent delay of 1.8 min was applied for this method. Injection Oven temperature gradient setting for HAAME analysis is as follows: 50°C at t = 0 min and held for 5 min, constant increase rate of 10°C/min to 16 min, and post run of 250°C from 16 min to 19 min. Solvent delay of 1.8 min was applied

for this method. Solvent delay of 2.0 min was applied for this method.

Chapter 3. Results and Discussion

3.1. Degradation Kinetics of ICMs in various UV AOPs

All kinetic experiments were triplicated, and degradation reactions of diatrizoate, iohexol and iopamidol in all of AOPs followed pseudo-1st-order kinetics (Fig. S1). Observed rate constants (k_{obs}) were calculated using linear regression analysis, based on the model as in Equation (1).

$$\ln \frac{[ICM]_t}{[ICM]_0} = -k_{obs} \times t \tag{1}$$

where $[ICM]_t$ is the concentration of ICM at certain time past UV reaction; $[ICM]_0$ is the initial concentration of ICM; k_{obs} is the observed pseudo-1st-order rate constant for a single reaction process; and t is the elapsed time. All the experimental data fitted well to the model with $R^2 > 0.98$.

Figure 2 shows the k_{obs} of several UV AOPs consisted of single or dual oxidants, in which total dose of oxidants is 1.0 mM. Notably, degradation rate constants for diatrizoate and iopamidol in UV AOPs where NaOCl was used as oxidant (NaOCl-AOPs) were more than 5 times higher than others, except for UV/NaOCl+H₂O₂ process. It has been reported that •OCl radicals, which can be generated in chlorine-based AOPs, greatly enhance the degradation rates for certain aromatic organics, due to their selective nature ^{17,27}. This phenomenon has been proved by comparing diatrizoate degradation rates in UV/Cl₂ (identical to UV/NaOCl) and UV/NH₂Cl

processes, and 5-fold superior degradation efficiency was observed in UV/Cl₂ process, which was able to produce •OCl radicals in pH 7 ²⁸. Similar results have been observed for iopamidol, where degradation rate was found to follow in the order of UV/Cl₂ > UV/H₂O₂ > UV/NH₂Cl > UV/ClO₂ > UV only ²⁰.

Regardless of the presence of NaOCl, the presence of H_2O_2 could lead to •OCl coupling with •OH (Reaction (2)-(3)), to finally form far-less reactive singlet oxygen (¹O₂) or unreactive triplet oxygen (³O₂) (Reaction (4))²⁹. This could hypothesize the decreased k_{obs} in UV/NaOCl+H₂O₂ process.



Figure 2. Observed pseudo-1st-order rate constants of single/dualoxidant UV AOPs. ([ICM]₀ = 10 ppm, Total oxidant dose = 1.0 mM, phosphate buffer 10 mM, pH 7.0, no NOM addition)

$$H_2 O_2 + h \upsilon \rightarrow 2 \bullet OH \tag{2}$$

•
$$OCl + \bullet OH \rightarrow HOOCl$$
 (3)

$$HOOCl + OH^- \rightarrow O_2 + H_2O + Cl^-$$
(4)

Also, •OH or •SO₄⁻-based processes did not lead to rapid degradation of diatrizoate nor iopamidol, as their k_{obs} were 0.42~0.91 min⁻¹, compared to 3.9~6.0 min⁻¹ from NaOCI-based AOPs mentioned above. These processes do not produce such radicals as •OCI, apparently. Regardless of the reactivity of the radicals produced in these AOPs, UV still seems to be the most dominant factor for diatrizoate degradation, as UV only process still can remove diatrizoate, iohexol and iopamidol with $k_{obs} = 0.37$, 0.27 and 0.28.

On the other hand, such rapid degradation caused by •OCl was not observed during UV AOP treatment of iohexol. It has been reported that in UV AOPs, observed degradation rate constants did not increase more than twice of that of UV only process, though 0.5 mM of HOCl was added to reaction. Also, •OH radical, rather than •OCl radical was suggested to be dominant for iohexol degradation in UV/Cl₂ process, although some intermediate degradation products of iohexol included iodine-abstracted chlorine-substitued ones which are generally the products of •OCl radicals¹⁹. Therefore, it is likely that iohexol or its intermediate products may readily quench •OCl radicals within the molecular structure other than iodine atom attached to aromatic ring. However, there are few studies that fully explains the mechanism.



Figure 3. Scatter plot of k_{obs} without NOM, and k_{obs} with 1 mg/L NOM addition. Dashed red line is a 1-to-1 line of equality (y = x). ([DTZ]₀ = 10 ppm, Total oxidant dose = 1.0 mM, phosphate buffer 10 mM, pH 7.0)



Figure 4. k_{obs} of UV AOPs in various pH conditions. ([DTZ]₀ = 10 ppm, Total oxidant dose = 1.0 mM, buffer 10 mM, no NOM addition)

Addition of Suwannee River NOM (1 mg/L) did not significantly affect degradation rates, as seen in **Figure 3**. Also as in Fig. S1, within pH range of 6~8 where phosphate buffer was equally used, k_{obs} varied less than 2-fold difference, which signifies that pH did not greatly affect the components that lead to diatrizoate degradation.pH was controlled with 10 mM buffer solutions – acetate for pH 5, phosphate for pH 6~8, and borate for pH 9. Degradation rates did not significantly vary in pH ranges 6~9, however drastic decrease of k_{obs} has been observed, only in pH 5. Considering that each of the buffer ions/molecules have different reactivity towards radicals ^{30,31}, acetic acid/acetate ions seem to scavenge the radicals involved in rapid diatrizoate degradation.

pH was controlled with 10 mM buffer solutions – acetate for pH 5, phosphate for pH 6~8, and borate for pH 9. As seen in **Figure 4**, degradation rates did not significantly vary in pH ranges 6~9, however drastic decrease of k_{obs} has been observed, only in pH 5. Considering that each of the buffer ions/molecules have different reactivity towards radicals^{30,31}, acetic acid/acetate ions seem to scavenge the radicals involved in rapid diatrizoate degradation.



3.2. Formation of Inorganic Iodine Species

Figure 5. Inorganic iodine species formed during 30 minutes of diatrizoate degradation. Color of circled dots and lines represent the oxidants used (Green – NaOCl, red – PMS, blue – PDS, yellow – H_2O_2). Straight lines are single-oxidant processes, and dashed lines are dual-oxidant processes. ([DTZ]₀ = 10 ppm, Total oxidant dose = 1.0 mM, phosphate buffer 10 mM, pH 7.0, no NOM addition)



Figure 6. Inorganic iodine species formed during 30 minutes of iohexol degradation. Color of circled dots and lines represent the oxidants used (Green – NaOCl, red – PMS, blue – PDS, yellow – H_2O_2). Straight lines are single-oxidant processes, and dashed lines are dual-oxidant processes. ([DTZ]₀ = 10 ppm, Total oxidant dose = 1.0 mM, phosphate buffer 10 mM, pH 7.0, no NOM addition)



Figure 7. Inorganic iodine species formed during 30 minutes of iopamidol degradation. Color of circled dots and lines represent the oxidants used (Green – NaOCl, red – PMS, blue – PDS, yellow – H_2O_2). Straight lines are single-oxidant processes, and dashed lines are dual-oxidant processes. ([DTZ]₀ = 10 ppm, Total oxidant dose = 1.0 mM, phosphate buffer 10 mM, pH 7.0, no NOM addition)

Concentrations of iodide (Γ), RIS, and iodate (IO_3^-) during ICM degradation are described in **Figures 5-7.** All of the results were triplicated. Generally, NaOCI-based AOPs and PMS-based AOPs successfully oxidized dissolved iodine species to IO_3^- , which is considered as an ideal sink of iodine^{32,33}. On the other hand, H₂O₂-based AOPs showed little to no IO_3^- yield while Γ and RIS were produced, which implies that iodine was not sufficiently oxidized. Γ and RIS was also observed in PDS-based AOPs, however they start to convert to IO_3^- during 15 to 30 minutes of reaction time. **Figure 8** shows the peak concentration of RIS during 30-minute-span. As clearly seen, PDS-based AOPs and H₂O₂-based AOPs mostly produced RIS, while UV only, UV/NaOCl, UV/PMS, and UV/NaOCl+PMS processes did not.



Figure 8. Maximum RIS concentration observed during 30 minutes of ICM degradation, where a) diatrizoate, b) iohexol, and c) iopamidol. Note that RIS was produced in UV AOPs where PDS or H_2O_2 was used, in general. ([ICM]₀ = 10 ppm, Total oxidant dose = 1.0 mM, phosphate buffer 10 mM, pH 7.0, no NOM addition)

It is commonly known that Γ can be easily oxidized to RIS (commonly referred to as free iodine or HOI) with mild oxidants such as NH₂Cl, whereas oxidation reaction of RIS to IO_3^- is extremely slower in same conditions²⁴. However, RIS can be rapidly converted to IO_3^- with strong oxidants such as ozone³⁴, ferrate³⁵, or activated persulfate³⁶. By applying this concept to UV AOPs, it can be considered that PDS and H₂O₂ prevents the generation of highly oxidizing species originating from NaOCl or PMS.

As seen in total inorganic iodine graphs in **Figures 5-7**, rate of iodine abstraction to iodide is mostly faster for diatrizoate, than iohexol and iopamidol. This may attribute to the relatively simple structure of diatrizoate, requiring less time to fully react and release iodine. Also, it is notable that degradation kinetics of these ICMs are not exactly correlated. This can be seen in UV/PMS treatment of iohexol, where its degradation rate is one of the fastest ($k_{obs} = 0.83$) but the rate of inorganic iodine formation is the second slowest.

3.3. THM and HAA Characterization and Correlation with RIS concentrations



Figure 9. a) THM concentrations after 30 minutes of UV AOP treatment, b) additional amount of THM formed (THMFP) after excessive chlorination (5 mg/L NaOCl) for 3 days. ($[DTZ]_0 = 20$ ppm, Oxidant dose 2 mM, no NOM addition, pH 7.0)

Solutions containing 20 ppm ICM, 5 mg/L NOM, and oxidant dose of 2.0 mM were irradiated with UV. NOM was added sufficiently to maintain enough amount of precursors for I-DBPs, and all experiments were duplicated. **Figure 9** shows that I-THM can still be formed during UV irradiation of diatrizoate without NOM (UV only process), however for UV AOPs, sufficient amount of NOM is a prerequisite for I-THM formation. **Figures 10-15** shows the formation of THM and HAA during UV AOP treatment, and also after chlorination of treated waters, in the presence of NOM. The results are summarized in **Figure 16**.

As in **Figure 16**, in terms of total THM and HAA formation, NaOCl-AOPs and PMS-AOPs generally produced non-iodo-THMs and HAAs, as expected from low RIS concentrations found in section **3.2**. On the other hand, H_2O_2 -AOPs and some of PDS-AOPs generally produced less amount of total THMs and HAAs during AOP treatment. However, post-chlorination mostly led to I-THM and I-HAA formation, except for UV/PDS+ H_2O_2 process for iopamidol.

It is notable that I-THMs and I-HAAs were found prechlorination, in H₂O₂-AOPs, PDS-AOPs, or direct UV photolysis (UV only). This result is conceivable for H₂O₂-AOPs, PDS-AOPs, regarding that ample amount of RIS has been detected in these processes. For UV only process, there are possibilities that I⁻ was photochemically activated to radicals (e.g. •I), and NOM was altered by UV irradiation^{25,37}, or iodinated aromatic ring structure could have been cleaved and/or further oxidized to form I-HAA or I-THM. However, specific mechanisms underlying the I-DBP formation during AOP treatment is not extensively studied.





Figure 10. THM and HAA concentrations after 30 minutes of UV AOP treatment of iopamidol ($[ICM]_0 = 20$ ppm, Oxidant dose 2 mM, no NOM addition, pH 7.0)



Figure 11. Additional amount of THM and HAA formed (THM, HAA formation potentials) after excessive chlorination of iopamidol for 3 days ([ICM]₀ = 20 ppm, Oxidant dose 2 mM, no NOM addition, pH 7.0, 5 mg/L NaOCl)



Figure 12. THM and HAA concentrations after 30 minutes of UV AOP treatment of iopamidol ($[ICM]_0 = 20$ ppm, Oxidant dose 2 mM, no NOM addition, pH 7.0)



Figure 13. Additional amount of THM and HAA formed (THM, HAA formation potentials) after excessive chlorination of iopamidol for 3 days ([ICM]₀ = 20 ppm, Oxidant dose 2 mM, no NOM addition, pH 7.0, 5 mg/L NaOCl)



HAA conc. after 30 min AOP treatment (Iopamidol, NOM 5 ppm added)



Figure 14. THM and HAA concentrations after 30 minutes of UV AOP treatment of iopamidol ($[ICM]_0 = 20$ ppm, Oxidant dose 2 mM, no NOM addition, pH 7.0)



Figure 15. Additional amount of THM and HAA formed (THM, HAA formation potentials) after excessive chlorination of iopamidol for 3 days ([ICM]₀ = 20 ppm, Oxidant dose 2 mM, no NOM addition, pH 7.0, 5 mg/L NaOCl)



Figure 16. THM and HAA concentrations after 30 minutes of UV AOP treatment, and additional amount of THM and HAA formed after excessive chlorination (5 mg/L NaOCl) for 3 days. a) diatrizoate, b) iohexol, and c) iopamidol. ([DTZ]₀ = 20 ppm, Oxidant dose 2 mM, NOM 5 mg/L, pH 7.0 maintained with 10 mM phosphate buffer)

I-THM and I-HAA were also found post-chlorination. In particular, UV/PDS and UV/H₂O₂ process show high levels of I-THM and I-HAA after 3 days of chlorination. This is similar to some studies that used H₂O₂ or PDS as oxidant for ICM treatment have also reported the emergence of I-DBPs in AOPs ^{38,39}. In contrast, the use of PMS or NaOCl lowers the I-THM and I-HAA formation potentials, in some cases down to zero (UV PDS vs. UV/PMS+PDS for iohexol and iopamidol).



Figure 17. Total iodine converted to THMs and HAAs – concentrations of total iodine which were converted to I-THMs and I-HAAs, during 30 minutes of AOP treatment and post-chlorination for 3 days. The amount of total iodine in THMs and HAAs were calculated based on the following equation:

 $\begin{aligned} Iodine \ equivalents &= 3 \times [CHI_3] + 2 \times [CHCl_2] + [CHCl_2I] + 2 \times \\ [CHI_2COOH] + [CHClICOOH] + [CH_2ICOOH] \end{aligned}$

Figure. 17 describes the overall percentages of iodine converted to I-THMs and I-HAAs during 30 minutes of AOP and 3-day post-chlorination. These values are conceivable as "maximum percentage of I-THM and I-HAA formed during simultaneous UV AOP-chlorination treatment". In general, I-THM and I-HAA formation capability is large, in order of iopamidol > iohexol > diatrizoate. This is extreme especially for UV/PDS process, where more than 90% of iodine from iopamidol was converted to I-THMs and I-HAAs, whereas less than 2% for iodine from diatrizoate.

UV/PDS+H₂O₂ process, it seems that mixing oxidants has "cancelled-out" I-THM and I-HAA formation abilities, when compared to UV/PDS and UV/H₂O₂ processes. Since UV/PDS+H₂O₂ process yields noticeable amount of RIS just as UV/PDS and UV/H₂O₂, it is thinkable that UV/PDS+H₂O₂ can also yield I-THMs and I-HAAs. It is notable that mixture of two oxidants does not always yield synergistic or antagonistic results.

3.4. RIS formation leading to I-DBP formation?

Based on the results in section **3.2** and **3.3**, it can be inferred that the high RIS concentration somehow correlates to I-DBP formation. However, the correlation is not strong enough – in some cases high yield of I-THM and I-HAA was observed regardless of relatively low RIS concentration (Iohexol and iopamidol in UV/H₂O₂ process). Also, it should be considered that there could be several other pathways for RIS and I-DBP formation. On one hand, it is highly reasonable that Γ or RIS can be oxidized to IO_3^- in oxidative conditions of UV AOPs. Yet, there can be other factors that may affect the distributions of iodine species.

For instance, IO_3^- can be photolytically degraded with UV, and consequent possibilities for I-THM formation has been reported (Tang et al., 2021; Tian et al., 2017). This phenomenon can also be observed in UV AOPs, where weak oxidants are used, e.g. UV/H₂O₂ or UV/NH₂Cl processes. What's interesting is, increased H₂O₂ or NH₂Cl dosage leads to faster iodate degradation and increased I-THM formation in the presence of NOM (Tian et al., 2019; Zhang et al., 2016). This may indicate that photolytic reduction of IO₃⁻ to RIS and oxidation of RIS to I-DBP occur simultaneously.

Contrarily, I-DBP can also undergo degradation in UV AOPs. UV irradiation and UV/H₂O₂ process is capable of removing I-THM, while yielding I⁻ as a major end product (Xiao et al., 2015). Opposed to the researches mentioned in the paragraph above, addition of H₂O₂ promoted I-THM degradation in this study. Additionally, degradation of iodoform (CHI₃) was available in UV/chlorine process, while UV rays and •OH being major reactive counterparts (A. Q. Wang et al., 2017). Together considering that iodate yield and I-DBP yield are in negative correlation (Section **3.2** and **3.3**), it seems that reactions governing I-DBP formation in UV AOPs are in competitive relationship and rather complex -1) oxidation of RIS to iodate, 2) photodegradation of iodate, 3) photodegradation of I-DBP and 4) oxidants promoting or hindering I-DBP formation.

On the other hand, NOM is another precursor for I-DBPs and NOM can be categorized into humic-like, fulvic-like, or protein-like substances. It is known that dissolved organics with high content of humic or fulvic-like substances are likely to produce I-THM and I-HAAs during chlorination of iopamidol (Ackerson et al., 2018). Also, water with different NOM characteristics has different DBP formation potentials, and UV AOP may change the distribution of these components, resulting in shifts in molecular weights of dissolved organics (Xia et al., 2018).

PMS-based processes produce •OH and •SO₄⁻ radicals which can also be generated from PDS (•SO₄⁻ source) and H₂O₂ (•OH source). However, the amount of RIS, I-THMs and I-HAAs formed are significantly different, as seen in section **3.2** and **3.3**. This finding also suggests that there are possible reactions that may alter the oxidative conditions of AOP, other than reactions arising from radicals.

Chapter 4. Conclusions

Degradation efficiencies, iodine species formation, and I-THM/I-HAA formation for diatrizoate, iohexol and iopamidol have been compared, for single- and dual-oxidant AOPs using NaOCl, PMS, PDS, and H₂O₂. NaOCl-based AOPs were highly capable of removing diatrizoate and iopamidol, seemingly due to selective reactions, while H₂O₂ may hinder this selectivity. While NaOCl-based AOPs and PMS-based AOPs were able to fully oxidize iodine species to IO_3^{-1} , which is a desirable sink of iodine, PDS-based AOPs and H₂O₂-based AOPs seemed to have lower oxidation potentials. These processes yielded RIS, which is less oxidized form than IO_3^- and reactive towards NOM to form I-DBP. I-THM and I-HAA analysis roughly correlated with this results - I-THMs and I-HAAs were generally found in PDS-AOPs and H₂O₂-AOPs. Although some correlations have been observed, there are numerous side reactions in UV AOPs that attribute to I-DBP formations, such as dissociation of IO₃⁻ or I-DBPs. Also, possible reactions between two oxidants, or oxidant and NOM may exist. Therefore, future studies may have to be implemented in a more controlled-manner to extensively address the fate of iodine in AOPs.

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え 록

아이오딘화 조영제(iodinated contrast media, ICM)는 X선 영상의학에 보편적으로 사용되고, 많은 사용량으로 인해 병원 하수, 지표수, 지하수, 토양 등에서 검출된다. 그러나 현재 정 수처리장 및 및 하수처리장에서의 제거 효율은 65% 이하로 낮으며, 수처리 과정에서 생성될 수 있는 reactive iodine species(RIS: I2, I3-, HOI)가 용존유기물(NOM)과 반응하여 아이 오딘화 소독부산물이 생성될 수 있다. 최근에는 254 nm의 UV 를 이용한 고도산화공정에서 ICM의 높은 제거율에 대한 가 능성이 보고되었으나. 여전히 처리 도중 또는 후소독처리 시 소독부산물이 생성되는 문제점이 있다. 본 연구에서는 254 nm UV와 함께 peroxymonosulfate(PMS), peroxydisulfate(PDS), hypochlorite(NaOCl), hydrogen peroxide(H₂O₂) 등의 산화제를 이 용한 여러 고도산화공정의 적용 가능성을 검토한다. 산화제를 단독 또는 배합하여 설계한 고도산화공정에서 ICM을 효과적 으로 분해하고, 분해 후 존재하는 아이오딘 종들의 분포를 iodide (I-), RIS, iodate (IO₃)로 범주를 나누어 파악한다. 이들로 인해 처리수에서의 생성될 수 있는 아이오딘화

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trihalomethanes (I-THM)와 아이오딘화 haloacetic acids (I-HAA)의 발생량 및 소독부산물 생성 포텐셜을 공정별로 구하고, 이들 의 농도와 RIS 농도의 연관성을 탐구한다.

주요어: 아이오딘화 조영제, 고도산화공정, 254 nm UV, 아이오딘화 소독부산물

학 번: 2021-23781