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Degradation of iohexol by UV irradiation: kinetics, pathways and iodinated trihalomethanes formation during post-chlorination

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ABSTRACT

The photodegradation of iohexol by UV irradiation and the formation of iodinated trihalomethanes (I-THMs) during subsequent chlorination were investigated in this study. Iohexol can be photodegraded by UV with pseudo-first order kinetics and the quantum yield was determined to be 0.0385 mol einstein^{-1}. The degradation rate of iohexol was linear along with the increase of UV intensity while effects of solution pH and Br$^-$ were negligible. The main photodegradation intermediates including deiodinated and hydroxylated products were identified by UPLC-ESI-MS. Then the UV photodestruction pathways of iohexol were proposed. The I-THMs formation in UV-chlorination of iohexol was evaluated in terms of UV fluence, pH, Br$^-$ concentration and raw water matrix. The increase of UV fluence and Br$^-$ concentration significantly enhanced the I-THMs formation and iodine substitution factor (ISF) while effect of pH was negligible. Raw freshwater matrix can appreciably influence the photodegradation rate of iohexol and I-THMs formation due to the presence of natural organic matter and Br$^-$. It was found that the UV removal of iohexol in real waters was depressed while I-THMs formation and ISF values were greatly enhanced. The results of the current study led to some practical concerns on toxic I-THMs in the UV application of iohexol-containing raw waters.

Keywords: Iohexol; UV irradiation; Iodinated trihalomethanes (I-THMs); Chlorination

1. Introduction

A great variety of pharmaceuticals and personal care products (PPCPs) have been widely used and therefore are frequently detected in aquatic environment as emerging contaminants [1–3]. As representative PPCPs that catch scholars' attention, iodinated X-ray contrast media (ICM) have been detected in effluents of wastewater treatment plants and surface waters at elevated concentrations [4–8]. A study in U.S. drinking water sources found that ICM were detected at several ng L^{-1} to 2.7 µg L^{-1} (iopamidol) and 120 ng L^{-1} (iohexol) [9]. The occurrence of ICM in German was also reported at µg L^{-1} level and the maximum reached as high as 100 µg L^{-1} [8]. Iopamidol and iohexol are the most frequently detected ICM in waters reported to date [5,9]. ICM are not toxic in themselves, but their presence can lead to the formation of iodinated disinfection by-products (I-DBPs) [9]. Besides, when chlorinated, ICM, especially iohexol, generated an enhanced level of CHO cell cytotoxicity and genotoxicity [10].

I-DBPs, including iodo-acids and iodo-trihalomethanes (I-THMs), are believed to be much more toxic than their chlorinated and brominated analogues [11,12]. Besides, the occurrence of I-THMs (especially iodoform) in drinking water may cause serious taste and odor problems [13].

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The concentrations of I-THMs were reported at μg L^{-1} level in chloraminated and chlorinated drinking waters in the United States and Canada [8]. Therefore, many studies focused on the formation of I-DBPs have been developed, making it a hot point and academic front in water treatment area [9,14–18]. The iodine sources contributing to the I-DBPs formation incorporate iodide (I^-) [13, 19–21], iodine-based disinfectants [22], and ICM [9,15,16]. I^- can be oxidized to HOI by oxidant and then I-DBPs were formed in the presence of natural organic matter (NOM) [13,19–21]. Iodoform can generate during disinfection of source waters by iodine tincture or iodine tablets [22]. ICM have been evidenced to be effective organic iodine source to form I-DBPs [9,16]. Moreover, the nontoxic ICM (iopamidol) could release I^- from UV photodegradation and transform to harmful I-DBPs in sequential oxidation processes [15]. Research on the transformation of potentially toxic ICM to I-DBPs by different treatment is of practical significance to water quality regulation.

UV irradiation has many advantages over chemical disinfection, such as producing no common halogenated DBPs, decreasing the treatment cost and inactivation a wide range of waterborne pathogens [23,24]. Lots of UV degradation studies have been reported and results showed that higher UV intensity and lower initial contaminant concentration led to greater degradation rate while the pH effect was negligible [3,15,25–27]. But the major deficiency of UV disinfection is that it can not maintain a disinfectant residual [24,28], thus the chlorine-based oxidants are often added to resupply residual disinfection ability after UV process.

The extremely stable structure of ICM makes these triiodinated compounds persistent to conventional water treatment processes [5–7], even ozonation can only remove 35–55% of non-ionic ICM [4]. Due to the strong oxidative capacity of hydroxyl radicals, advanced treatment processes have proved successful in degrading ICM [4,15]. But our previous study revealed the degradation effectiveness of UV process on the triiodinated compounds [15], which are attributed to iodine element in structure. Besides, UV also exhibits enhanced effect on the formation of chloropicrin, N-nitrosodimethylamine, halobenzoquinones, haloacetic acids and even I-DBPs [15,29–33]. Therefore, it is important to investigate the UV degradation effects of representative ICM-iohexol, on the I-DBPs formation during subsequent oxidation.

The main aim of this research was to investigate the UV photodegradation features of iohexol and the I-THMs formation during subsequent chlorination. The factors of UV fluence, solution pH, Br^- concentration as well as the raw water matrix and UV degradation mechanism of the triiodinated compound were also studied. This study could be of some relevance to understand the transformation of non-toxic iodinated organic compounds as ICM to toxic I-DBPs in UV-chlorination processes.

2. Materials and methods

2.1. Chemicals

All chemicals were at least of analytical grade except as noted. Iohexol (CAS No: 66108-95-0) was purchased from Sigma-Aldrich (USA) in more than 99.0% purity and used as received. Iodoform (CHI_3, 99%), sodium hypochlorite (NaOCl) solution (available chlorine 4.00–4.99%), NaOH (≥ 98%), KH_2PO_4 (≥ 99.0%), Na_2CO_3 (≥ 99.0%), $NaHCO_3$ (≥ 99.0%), KI (≥ 99.0%) were also purchased from Sigma-Aldrich. Five I-THMs standards, including chlorodiiodomethane ($CHClI_2$, 90–95%), dichloroiodomethane ($CHCl_2I$, ≥ 95%), bromochloroiodomethane (CHBrClI, ≥ 95%), dibromoiodomethane ($CHBr_2I$, 90–95%) and bromodiiodomethane ($CHBrI_2$, 90–95%) were obtained from CanSyn Chemical Corp. (Canada). Methyl tert-butyl ether (MtBE) and acetonitrile were obtained from J.T. Baker (USA). Formic acid solution (49–51%) was purchased from Fluka (St. Louis, MO, USA) and atrazine was obtained from Dr. Ehrenstorfer (German) in chromatographical purity (>99.0%). Analytical grade reagents including $Na_2S_2O_3$, H_2O_2, $K_2TiO(C_2O_4)_2$, H_3PO_4 and H_2SO_4 were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All solutions were prepared with ultra-pure water produced from a Milli-Q water purification system (Millipore, USA).

The raw waters of Yangtze River and Huangpu River were collected from Yangshupu drinking water treatment plant (Shanghai, China) and Minhang No. 2 drinking water treatment plant (Shanghai, China), respectively. Then the raw water samples were filtered through 0.45 μm acetate membrane filters (Millipore, USA) immediately and stored in the dark at 4°C until usage. The characteristics of HR and YR were provided in Table 1.

The chemical and physical properties of iohexol and iopamidol were presented and compared in Table 2. It can be seen from Table 2 that, although the iodine content is a bit smaller, iohexol has greater molecular weight and molar extinction coefficient than its analogue. The different chemical and physical properties of iohexol might virtually influence its UV photodegradation features.

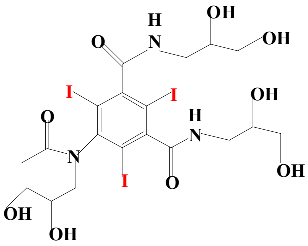
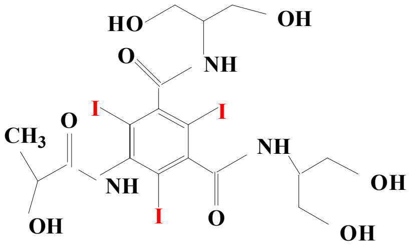
2.2. UV irradiation

The photodegradation experiments were conducted using a bench-scale UV quasicollimated beam setup housed with four low pressure Hg UV lamps.The system contained a 9 L stainless steel reactor (i.d. = 20 cm, height = 32 cm) with a 400 mL quartz tube (i.d. = 4.5 cm) fixed in the center. The temperature of the UV system was controlled at 25°C by connecting the system to a low temperature water bath (DKB-1915, Jinghong, Shanghai, China) and circulating the

Table 1
Characteristics of raw water samples

Parameters	Yangtze River raw water	Huangpu River raw water
pH	7.29	7.75
Turbidity	9.44	27.5
NH_4–N (mg/L)	0	0.12
UV_{254}	0.046	0.107
TOC (mg/L C)	2.003	4.261
Br^- (μg/L)	47.22	92.96
TN (mg/L N)	1.732	2.614
NO_3^-–N (mg/L)	1.105	0.095

Table 2
Chemical and physical properties of iohexol and iopamidol

Items	Iohexol	Iopamidol
CAS number	66108-95-0	60166-93-0
Molecular formula	$C_{19}H_{26}I_3N_3O_9$	$C_{17}H_{22}I_3N_3O_8$
Molecular weight	821.14	777.09
Melting point	174–180°C	Decomposes at about 300°C without melting
Solubility	2.16 g/L	120 g/L
log P	–3.05	–2.42
Molar extinction coefficient	27620 M^{-1} cm^{-1}	22700 M^{-1} cm^{-1}
Mass content of iodine	46.36%	48.99%
Chemical structure		

water by a diaphragm pump (Model DP0700, Puricom, Taiwan, China). Four UV lamps (TUV 11 W T5 4P-SE, Philips, Netherlands) with quartz sleeves were symmetrically fixed in the center of the reactor. The UV intensity was changed by turning on different numbers of UV lamps and detected using a light intensity meter (UV-C luxometer, Photoelectric Instrument Factory of Beijing Normal University, Beijing, China) at 254 nm. The UV intensity of 1.53, 3.02, 4.45 and 5.96 mW cm^{-2}, were measured with UV lamps of 1, 2, 3 and 4, respectively. The determination of UV fluence rate values as 6.891×10^{-7}, 14.159×10^{-7}, 18.879×10^{-7}, 25.487×10^{-7} einstein s^{-1} L^{-1}, using atrazine actinometer [34] and path lengths as 7.225, 6.405, 6.616, 6.443 cm using H_2O_2 actinometry [35] were detailed elsewhere in our previous study [15]. The UV fluence (mJ cm^{-2}) delivered to the sample was calculated as the UV intensity multiplied by the exposure time [36,37].

2.3. Experimental procedures

The iohexol solutions were beforehand buffered using 10 mM phosphate (for pH 5–8) or 10 mM carbonate (for pH 9) buffer. Solution pH was adjusted with small volume of H_2SO_4 and/or NaOH. Br^- was spiked into iohexol solution before exposed to established UV intensity for 5 min. In UV degradation experiment, a 200-mL solution spiked with 10 µM iohexol and buffered at certain pH with temperature controlled at 25±1°C was subjected to UV irradiation. 1 mL of solution was rapidly transferred into a UPLC vial at different time-points, and then the samples were analyzed by ultra performance liquid chromatography (UPLC) immediately.

The analyses of iohexol photodegradation intermediates experiments were carried out during UV irradiation at a concentration of 25 µM so as to enhance production for higher analytical resolution. At the scheduled time, the samples were collected and analyzed by UPLC-ESI-MS as soon as possible.

In order to reveal the I-THMs formation features in chlorination process after UV irradiation of the samples, a completely removal of iohexol within 10 min UV exposure was applied in this study. After exposed for 10 min at certain UV intensity, the stock chlorine was spiked into solutions to the desired concentration. Then the I-THMs formation experiments were conducted in triplicate under headspace-free conditions in 40-mL glass screw-cap amber vials with PTFE-lined septa in dark at temperature (25 ±1°C) in a thermostatic biochemical incubator. At the scheduled time of 7 d, the reaction was quenched using NH_4Cl at 1.2 times of oxidants concentration and the samples were then extracted for the I-THMs analysis.

2.4. Analytical methods

The solution pH was measured by a regularly calibrated pH meter (FE20-FiveEasy, Mettler Toledo, Switzerland) using standard buffer solutions (Mettler Toledo; pH = 4.01, 7.00, 9.21). The chlorine concentration was calibrated by the N, N-diethyl-p-phenylenediamine (DPD) colorimetric method [38]. The UV intensity changed by turning on different numbers of UV lamps were measured as 1.53, 3.02, 4.45 and 5.96 mW cm^{-2}, respectively, by placing a light intensity meter (UV-C luxometer, Photoelectric Instrument Factory of Beijing Normal University, Beijing, China) into a quartz sleeve. The UV absorbance was measured via a 1-cm quartz cell at wavelength of 254 nm using a UV-Vis spectrophotometer (SQ-4802 UNICO, Shanghai).

Iohexol and I^- released from photolysis of iohexol were both analyzed using UPLC (Waters, USA) equipped with a XTerra® MS C18 column (4.6 × 250 mm i.d., 5 µm film thickness, Waters, USA) by an UV detector at wavelength of 245 nm and 223 nm [15,39,40], respectively. The mobile phase for iohexol was consisted of 5%/95% (v/v) acetonitrile and Milli-Q water at a flow rate of 0.80 mL min^{-1}. The mobile phase for I^- was consisted of 2%/98% (v/v) acetonitrile and KH_2PO_4 solution (0.09 M) at a flow rate of 0.80 mL min^{-1}. The injection volume was 10 µL. The detection limits of iohexol and I^- were 10.0 and 5.0 µg L^{-1}, respectively.

Method for quantifying I-THMs was developed by modifying USEPA Method 551.1 [15,41]. Samples were extracted with MtBE and the extracts were analyzed using a gas chromatograph (GC-2010, Shimadzu, Japan) equipped with an electron capture detector (ECD) and a HP-5 capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness, J&W, USA). The injector and detector temperature were 200 and 290°C, respectively, and the flow rate of the nitrogen carrier gas was 30 mL/min with pressure of 69.8 kPa. The temperature program for the regular DBPs analyses was as follows: hold at 37°C for 10 min, ramp to 50°C at 5°C/min and hold for 5 min, and finally ramp to 260°C at 15°C/min and hold for 10 min. The temperature program for the iodinated DBPs analysis method was as follows: hold at 40°C for 10 min and then ramp to 260°C at 15°C/min and hold for 10 min.

Photodegradation intermediates of iohexol during UV irradiation were identified by UPLC-ESI-MS consisted of an Accela U-HPLC system and a TSQ Quantum mass spectrometer (ESI source, Thermo Scientific Inc.,USA). An XTerra® MS C18 column (250 mm × 2.1 mm, i.d., 5 mm film thickness, Waters, USA) was used for product analysis. Acetonitrile (10%) and 1% formic acid solution (90%) were used as the mobile phase at a flow rate of 0.25 mL min^{-1}. MS chromatograms were obtained both in total ion current (TIC) mode, using full scans (m/z 200–900) for mass spectra acquisition and in the selected ion monitoring (SIM) mode.

3. Result and discussion

3.1. UV degradation kinetics

The UV degradation kinetic model of organic substances has been reported by many researchers and the concentration decrease of the organic compound by UV versus time can be expressed as the following equation [15,26,27,41]:

$$-\frac{dC_t}{dt} = \Phi I_0\left[1-\exp(-2.3L\varepsilon C_t)\right] \tag{1}$$

Then Eq. (2) can be obtained by integrating Eq. (1):

$$\ln\left(\frac{10^{\varepsilon LC_0}-1}{10^{\varepsilon LC_t}-1}\right) = 2.3\Phi I_0 L\varepsilon t = k_{obs}t \tag{2}$$

The parameters C_0 and C_t indicate the concentrations of the target compound at the UV irradiation time of $t = 0$ and $t = t$ (M); I_0 is the UV fluence rate value (einstein s^{-1} L^{-1}); Φ represents the quantum yield of the compound (mol $einstein^{-1}$); ε is the molar extinction coefficient of the compound (M^{-1} cm^{-1}); L is the optical path length (cm). As expressed in Eq. (2), plot of the left term of the equation towards the irradiation time should be a straight line, the slope of which is the pseudo-first order rate constant ($k_{obs} = 2.3\Phi I_0 L\varepsilon$).

Hence, according to the phodegradation results of iohexol, the fitting lines under different UV intensities are shown in Fig. 1.

As displayed in Fig. 1, the linear fits of iohexol photodegradation under different UV intensities were excellent enough to utilize the above kinetic model ($R^2 > 0.98$). Moreover, faster degradation of iohexol was observed at greater UV intensity. In Fig. 1, this phenomenon corresponds to the increasing slopes of the fitting lines with UV intensity. The results are consistent with other scholars' reports on the photooxidation of other organic materials [15,26–27]. It can also be seen from Fig. 1 that the photodegradation effectiveness of iohexol by UV irradiation was proved, which can be attributed to the photosensitivity of the triiodinated compound. The k_{obs} and iohexol degradation after 5 min UV exposure under different UV intensities are provided in Table 3.

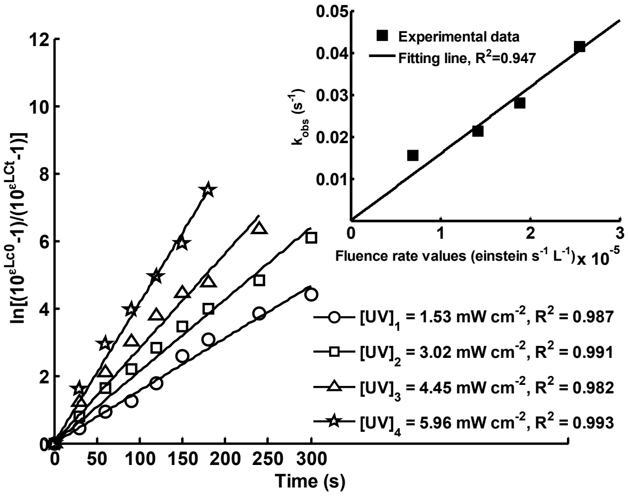


Fig. 1. Pseudo-first order kinetics plot of iohexol photodegradation under different UV intensity of 1.53, 3.02, 4.45, 5.96 mW cm^{-2}, respectively. (pH = 7, [phosphate buffer] = 10 mM, $[iohexol]_0$ = 10 µ M.)

Furthermore, the regression analysis of k_{obs} and UV fluence rate values was also plotted in Fig. 1, the equation of which can be fitted as $k_{obs} = 1592.7\ I_0$. Then, according to the ε of iohexol (27620 M^{-1} cm^{-1}) [3], values of I_0, and L of the UV reactor, the Φ of iohexol at 254 nm can be calculated as 0.0385 mol $einstein^{-1}$, which was similar to the former value estimated by Pereira et al. (Φ = 0.0403 mol $einstein^{-1}$) [3]. The quantum yield of iohexol evaluated in this study was a bit bigger than iopamidol (Φ = 0.03318 mol $einstein^{-1}$, ε = 22700 M^{-1} cm^{-1}), which was consistent with their molar extinction coefficient difference. The experimental data also indicated that iohexol showed more removal than iopamidol by UV irradiation.

3.2. Effect of pH and Br^- on iohexol photodegradation

Study on the photodecomposition of iohexol by UV irradiation was further extended to the effect of solution pH and Br^- and the first-order rate constants under different conditions are summarized in Table 3.

As shown in Table 3, the k_{obs} of iohexol photodegradation and degradation percent after 5 min UV exposure were not much affected by the increase of solution pH from 5 to 10. The results indicated that solution pH has no remarkable influence on the UV photodegradation rate of iohexol. The data is directly related to the fact that the undissociated molecule of iohexol in solution would lead to constant

Table 3
First order rate constants of iohexol degradation during UV irradiation

Concentration of Br^- (μM)	UV intensity (mW cm^{-2})	pH	k_{obs} (s^{-1})	$t_{1/2}$ (s)	Iohexol degradation after 5 min UV exposure (%)	R^2
0	1.53	7	0.0155	154.4	82.65	0.987
0	3.02	7	0.0212	101.8	97.01	0.991
0	4.45	7	0.0281	78.96	100.00	0.982
0	5.96	7	0.0415	52.29	100.00	0.993
0	3.02	5	0.0215	100.4	99.57	0.972
0	3.02	6	0.0214	100.9	99.21	0.975
0	3.02	7	0.0212	101.8	97.03	0.963
0	3.02	8	0.0213	101.4	98.49	0.956
0	3.02	9	0.0211	102.8	96.87	0.968
0	3.02	10	0.0210	102.8	96.46	0.973
10	3.02	7	0.0213	101.4	98.35	0.993
25	3.02	7	0.0212	101.9	97.03	0.977
50	3.02	7	0.0212	101.9	97.00	0.986
100	3.02	7	0.0214	100.9	98.86	0.988
200	3.02	7	0.0213	101.4	98.41	0.982
0.591 [a]	3.02	7	0.0185	116.7	90.56	0.969
1.163 [b]	3.02	7	0.0143	151.0	80.37	0.972

Notes:

[a] The concentration of Br^- was obtained from the raw water samples of Yangtze River.

[b] The concentration of Br^- was obtained from the raw water samples of Huangpu River.

monochromatic absorption coefficient [26]. This is consistent with our previous research on the UV photodegradation of iopamidol [15].

It can also be seen from Table 3 that no significant difference of k_{obs} was observed among different Br^- concentrations. As bromide would not transform under UV light from low pressure mercury vapor lamps [43], the increase of Br^- concentrations could not change the monochromatic absorption coefficient of the solution and so was the photodegradation rate of iohexol. The Br^- separated in waters may not be involved in the UV phototransformation pathways of iohexol. It is also deduced from our experimental results that changing the acidity or basicity and Br^- concentrations of waters will not improve the UV degradation efficiency of iohexol.

3.3. UV photodestruction pathways of iohexol

The nuclear magnetic resonance spectra has revealed that the UV-light energy could cause the structural dissolved humic substances change from high-molecular-weight matter to more aliphatic contents with more carboxyl and carbonyl carbon atoms [37]. Previous reports on the degradation of ICM have verified the deiodinated and hydroxylated intermediates during advanced oxidation/reduction processes, simulated solar radiation as well as UV irradiation [15,45,46]. The UV degradation intermediates of iohexol were analyzed by UPLC-ESI-MS and the proposed structures for the products are summarized in Fig. 2.

The product of 695 was characterized as substitution of one iodine atom by a hydrogen atom on the aromatic ring of iohexol. The stepwise deiodination of iohexol was demonstrated by the simultaneous degradation of iohexol and release of I^- in Fig. 3. Our previous research has proved the stepwise deiodination and hydroxylation of the triiodinated compound by UV irradiation at the iodo sites in benzene ring [15]. Similarly, the ions of 695, 569, 585 and 601 were identified as partially or completely hydroxylated intermediates of three iodo sites in iohexol. Other ions of 819, 693, 709, 583, 599, 489 and 473 were postulated as the ketone products by hydrogen atom abstraction reactions from side chains of the deiodinated intermediates of iohexol [15,45,46]. In general, the UV photodestruction pathways of iohexol were proposed and presented in Fig. 2.

3.4. Effect of UV fluence on I-THMs formation during post-chlorination

Report has proven that the photodegradation of iopamidol by UV irradiation would not be accompanied by the mineralization of total organic carbon (TOC) in solution [15]. Therefore, the photooxidation intermediates of iohexol after UV irradiation might provide organic carbon source for DBPs formation during subsequent chlorination. Meanwhile, I^- released from the UV deiodination of iohexol could be active iodine source for the formation of toxic I-DBPs in subsequent oxidation process [10,11]. Thus the I-THMs formation from chlorination of iohexol pretreated by different UV intensities is exhibited in Fig. 4.

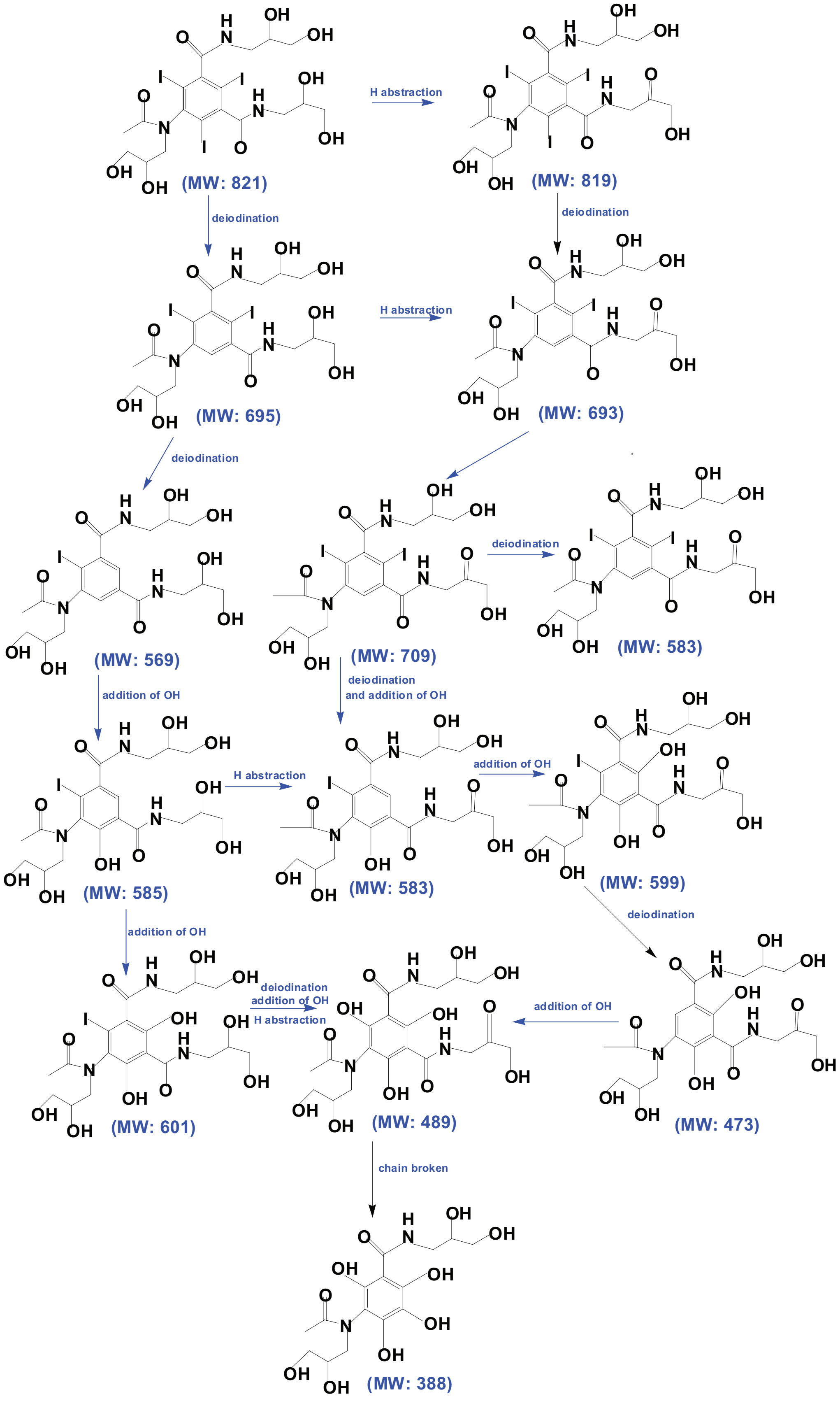


Fig. 2. Proposed destruction pathways of iohexol during UV irradiation.

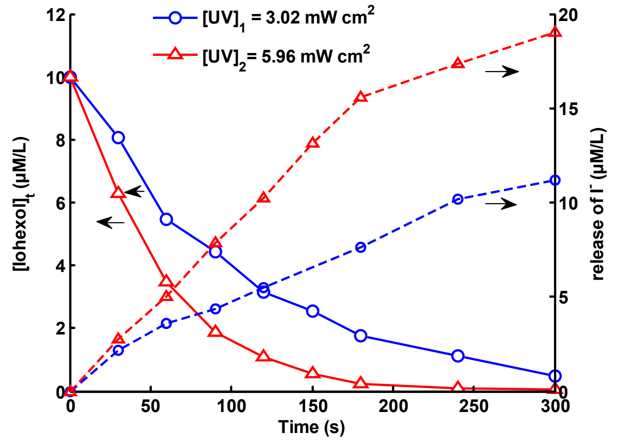


Fig. 3. Simultaneous degradation and deiodination of iohexol with UV intensity of 3.02 and 5.96 mW cm^{-2}, respectively. (pH = 7, [phosphate buffer] = 10 mM, [iohexol]$_0$ = 10 μM.)

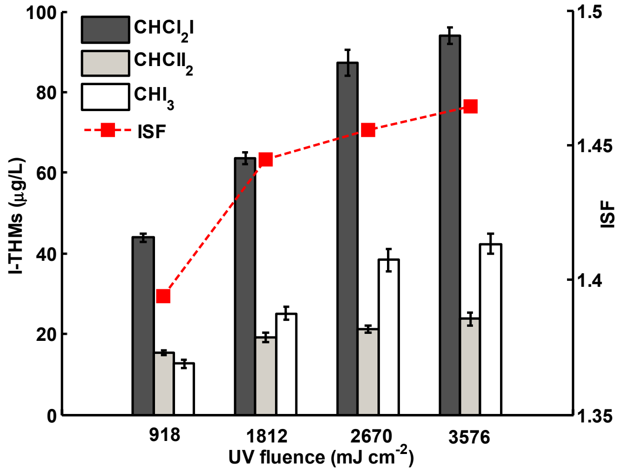


Fig. 4. Effect of UV fluence on the I-THMs formation during irradiation of iohexol followed by chlorination process. Error bars represent standard deviation of three replications. (UV fluence = 918, 1812, 2670 and 3576 mJ cm^{-2}, pH = 7, [phosphate buffer] = 10 mM, [iohexol]$_0$ =10 μM, [Cl$_2$]$_0$ = 100 μM, t =7 d).

It should be pointed out that no I-THMs was measured during the chlorination of iohexol without UV irradiation. However, as shown in Fig. 4, UV irradiation induced the formation of three kinds of I-THMs (including $CHCl_2I$, $CHClI_2$ and CHI_3) to the following chlorination process. Furthermore, the increase of UV fluence significantly enhanced the formation of all the detected I-THMs. The UV irradiation of iohexol resulted in the generation of I$^-$ in solution and then HOI can be formed after spiking with Cl_2, afterwards I-THMs were formed from the oxidation of the photodegradation products by HOI [13,19], which is shown in Eq. (3) [47]. Although $CHCl_2I$ constituted the majority of I-THMs, the formation of CHI_3 might cause serious taste and odor problems in drinking water as its organoleptic threshold concentration lay as low as 0.03–1 μg L^{-1} [13,48].

$$HOCl + I^- \rightarrow HOI + Cl^- \quad k_0 = 4.3\times10^8\, M^{-1}s^{-1} \tag{3}$$

$$ISF = \frac{[CHCl_2I]+[CHBr_2I]+[CHClBrI]+2\times[CHClI_2]+2\times[CHBrI_2]+3\times[CHI_3]}{[CHCl_2I]+[CHBr_2I]+[CHClBrI]+[CHClI_2]+[CHBrI_2]+[CHI_3]} \tag{4}$$

Like the application of bromine substitution factor (BSF), iodine substitution factor (ISF) was introduced in this study to provide a direct measure of iodine content of the total halogen incorporated into each group of I-THMs [40, 49]. Therefore, ISF can be calculated by Eq. (4) to compare the iodination degrees of the detected I-THMs with different UV fluence. It can be seen from Fig. 4 that ISF constantly increased with elevating UV fluence, which clearly indicated an enhancive iodine substitution of the total I-THMs formation.

3.5. Effect of pH and Br$^-$ on I-THMs formation during post-chlorination

As discussed in Section 3.2, pH and Br$^-$ posed no distinct effect on the photodegradation rate of iohexol. However, what we care about most is whether these factors would influence I-THMs formation in the following oxidation process. Accordingly, the effect of Br$^-$ on I-THMs formation during subsequent chlorination is shown in Fig. 5.

It was found that the effect of pH on I-THMs formation as well as ISF were negligible, which can be attributed to the fact that variations of pH values didn't change the amount of I$^-$ formed from the photodegradation of iohexol (data not shown). As shown in Fig. 5, however, the effect of Br$^-$ concentration on the I-THMs formation in UV-chlorination of iohexol was distinct. Not only the I-THMs yields but also the species of I-THMs were significantly increased. The introduction of Br$^-$ to solution led to the enhanced formation of brominated I-THMs, which increased with the Br$^-$ concentrations. Meanwhile, although the sum formation of $CHCl_2I$ and $CHClI_2$ was depressed at higher Br$^-$ concentrations, the CHI_3 formation was obviously enhanced. As Br$^-$ concentrations gradually increased, the total yields of I-THMs considerably elevated and the I-THMs species with more iodine atoms ($CHClI_2$, $CHBrI_2$ and CHI_3) increased, which caused increasing ISF values evidently. The results agreed with previous studies concerning Br$^-$ effect on I-THMs of different experimental conditions [40,50]. Overall, the increase of ISF primarily resulted from the more powerful oxidation capacity of HOBr and HOI shown as Eqs. (5) and (6) in the presence of Br$^-$ [51,52]. Our conclusions also suggested that the naturally occurring Br$^-$ in iohexol-containing raw waters, especially for the sea water intrusion areas [11], could highly enhance the formation risk of toxic I-THMs.

$$HOCl + Br^- \rightarrow HOBr + Cl^- \quad k_1 = 1550\ M^{-1}s^{-1} \tag{5}$$

$$HOBr + I^- \rightarrow HOI + Br^- \quad k_2 = 5.0\times10^9\, M^{-1}s^{-1} \tag{6}$$

3.6. Effect of the raw water matrix on iohexol photodegradation and I-THMs formation during post-chlorination

It is known that the presence of natural water components might affect the degradation rate and phototrans-

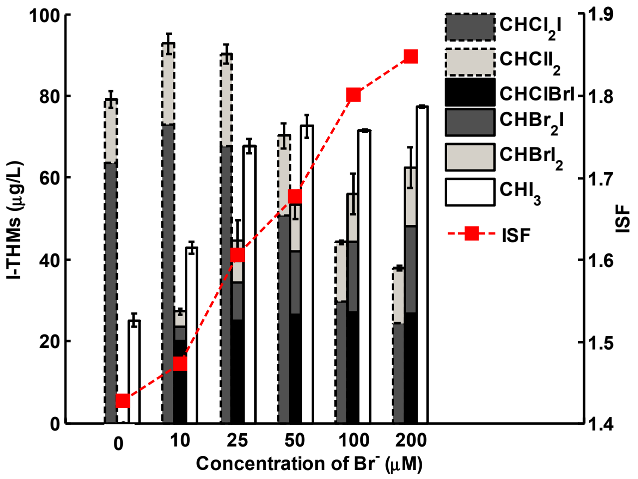


Fig. 5. Effect of Br^- concentration on the I-THMs formation during UV irradiation of iohexol followed by chlorination process. Error bars represent standard deviation of three replications. (UV fluence = 1812 mJ cm^{-2}, $[Br^-]_0$ = 0, 10, 25, 50, 100 and 200 μM, pH = 7, [phosphate buffer] = 10 mM, $[iohexol]_0$ = 10 μM, $[Cl_2]_0$ = 100 μM, t =7 d).

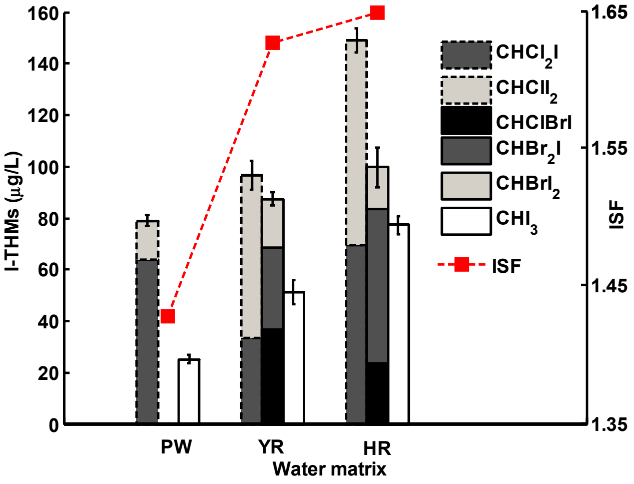


Fig. 6. Effect of the raw water matrix on the I-THMs formation during UV irradiation of iohexol followed by chlorination process. Error bars represent standard deviation of three replications. (UV fluence = 1812 mJ cm^{-2}, pH = 7, [phosphate buffer] =10 mM, $[iohexol]_0$ = 10 μM, $[Cl_2]_0$ = 100 μM, t = 7 d, the abbreviates of "PW", "YR" and "HR" represent the water matrix of Pure Water, Yangtze River raw water and Huangpu River raw water, respectively.)

formation of organic compounds by UV irradiation [34]. Accordingly, two raw waters spiked with 10 μM iohexol were studied for the photodegradation and I-THMs formation during subsequent chlorination. The k_{obs} of iohexol photodegradation and degradation percent after 5 min UV exposure in the two raw water matrix were calculated and are given in Table 3. The results obtained on the effect of raw water matrix on I-THMs formation in UV-chlorination of iohexol are shown in Fig. 6.

It can be inferred from Table 3 that the raw water matrix exhibited a negative effect on iohexol removal rates and the k_{obs} was observed in decreasing order as follows: PW > YR > HR. This is because that UV energy absorbed to iohexol decreased due to the consumption of UV energy by NOM in raw waters [2]. The more severe competition circumstances with NOM for UV energy in HR than YR led to the smaller degradation rate in the latter raw water matrix. Some scholars have also reported that NOM present in natural waters can reduce the effective fluence rate and consequently the rate of photodegradation [2,34]. Our results were consistent with these conclusions.

However, as for the I-THMs formation during subsequent chlorination, the raw water matrix displayed contrarily. As shown in Fig. 6, much more I-THMs were measured in HR and YR, especially brominated I-THMs, which were corresponding to the occurrence of Br^- in these two raw waters (Table 1). The distinct higher I-THMs formation observed in real source waters might be due to the fact that NOM are important precursors in the formation of I-DBPs [9,16]. Although the degradation rate and transformation of iohexol in HR were the smallest of all (Table 3), it inhabited comparatively the most I-THMs (Fig. 6) because of its greatest NOM content (Table 1). Therefore, the important roles of NOM on I-THMs formation in UV irradiation and sequential chlorination processes should be concerned. Similar conclusion can also be drawn from the comparison of ISF increased in the order as PW < YR < HR in Fig. 6. The results revealed that though the NOM presence in actual source waters could weaken the iohexol removal by UV irradiation, it might conversely contribute to the substantial enhancement of toxic I-THMs formation in the following chlorination process.

4. Conclusions

Iohexol can be photodegraded by UV irradiation with pseudo-first order kinetics and the quantum yield was evaluated as 0.0385 mol $einstein^{-1}$. The degradation rate of iohexol was linearly increased with UV intensity. But pH and Br^- both have no remarkable influence on the UV photodegradation rate of iohexol.

Based on the deiodinated and hydroxylated intermediates identified by UPLC-ESI-MS analyses, the destruction pathways of iohexol by UV irradiation were proposed.

The increase of UV fluence and Br^- concentrations significantly enhanced the formation of I-THMs and ISF during post-chlorination. However, the effect of pH was negligible.

The raw water matrix exhibited a negative effect on iohexol removal rates and the k_{obs} was observed in decreasing order as follows: PW > YR > HR. Nevertheless, the I-THMs formation and ISF during UV-chlorination of iohexol were significantly promoted due to the presence of NOM and Br^- in the raw water samples.

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