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Comparison of UV-induced AOPs (UV/Cl₂, UV/NH₂Cl, UV/ClO₂ and UV/H₂O₂) in the degradation of iopamidol: Kinetics, energy requirements and DBPs-related toxicity in sequential disinfection processes

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HIGHLIGHTS

- Removal efficiency of iopamidol followed the order of UV/Cl₂ > UV/H₂O₂ > UV/NH₂Cl > UV/ClO₂.
- EE/O of iopamidol degradation followed the trend of UV/ClO₂ > UV > UV/NH₂Cl > UV/Cl₂ > UV/Cl₂.
- The pH behaviors of UV-based AOPs upon iopamidol in 5–9 exhibited quite differently.
- UV/Cl₂ and UV/NH₂Cl enhanced classical DBPs and I-THMs while UV/ClO₂ and UV/H₂O₂ exhibited elimination effect.
- The risk ranking of DBPs-related toxicity was UV/NH₂Cl > UV/Cl₂ > UV > UV/H₂O₂ > UV/ClO₂.

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ABSTRACT

The UV-induced advanced oxidation processes (AOPs, including UV/Cl₂, UV/NH₂Cl, UV/ClO₂ and UV/H₂O₂) degradation kinetics and energy requirements of iopamidol as well as DBPs-related toxicity in sequential disinfection were compared in this study. The photodegradation of iopamidol in these processes can be well described by pseudo-first-order model and the removal efficiency ranked in descending order of UV/Cl₂ > UV/H₂O₂ > UV/NH₂Cl > UV/ClO₂ > UV. The synergistic effects could be attributed to diverse radical species generated in each system. Influencing factors of oxidant dosage, UV intensity, solution pH and water matrices (Cl⁻, NH₄⁺ and nature organic matter) were evaluated in detail. Higher oxidant dosages and greater UV intensities led to bigger pseudo-first-order rate constants (K₁) in these processes, but the pH behaviors exhibited quite differently. The presence of Cl⁻, NH₄⁺ and nature organic matter posed different effects on the degradation rate. The parameter of electrical energy per order (EE/O) was adopted to evaluate the energy requirements of the tested systems and it followed the trend of UV/ClO₂ > UV > UV/NH₂Cl > UV/H₂O₂ > UV/Cl₂. Pretreatment of iopamidol by UV/Cl₂ and UV/NH₂Cl clearly enhanced the production of DBPs-related toxicity.
classical disinfection by-products (DBPs) and iodo-trihalomethanes (I-THMs) during subsequent oxidation while UV/ClO₂ and UV/H₂O₂ exhibited almost elimination effect. From the perspective of weighted water toxicity, the risk ranking was UV/NH₂Cl > UV/Cl₂ > UV > UV/H₂O₂ > UV/ClO₃. Among the discussed UV-driven AOPs, UV/Cl₂ was proved to be the most cost-effective one for iopamidol removal while UV/ClO₂ displayed overwhelming advantages in regulating the water toxicity associated with DBPs, especially I-THMs. The present results could provide some insights into the application of UV-activated AOPs technologies in tradeoffs between cost-effectiveness assessment and DBPs-related toxicity control of the disinfected waters containing iopamidol.

1. Introduction

At present, due to the worldwide outbreak of atypical pneumonia, caused by COVID-19, which is limitedly known to be sensitive to UV light and effectively killed by chlorine-based disinfectants, disinfection has never been valued so seriously by everybody [1,2]. Some investigators have proposed that COVID-19 might have potential risks of water mediated transmission, which presents much stricter requirements and objectives for water disinfection [2]. However, more than 600 kinds of disinfection by-products (DBPs) have been accidentally found when chemical disinfectants are used to kill aquatic pathogens. The vast majority of DBPs have not been chemically or biologically characterized and only less than 100 kinds were resolved in quantitative occurrence or toxicity research centers [3]. DBPs are inevitably formed when commonly used disinfectants (Cl₂, O₃, ClO₂ or NH₂Cl, etc) react with naturally occurring organic matters in source waters during disinfection [3,4]. 11 types of DBPs, such as trihalomethanes (THMs) and haloacetic acids (HAAs), have been controlled in USA while 74 emerging DBPs are not regulated because of their medium occurrence levels or toxicological properties [3,4]. Besides, primary treatment with disinfectants is often followed by post disinfection to maintain disinfectants residues in water supply systems [5,6]. The occurrence of some emerging DBPs (for example, nitrogen-containing DBPs, iodo-DBPs (I-DBPs)) with highly enhanced toxicity might be unavoidable in this process [3,6].

The comparative toxicity order of different DBPs categories is iodination > bromination > chlorination [7]. This indicates that the more toxic I-DBPs are more worthy of studying on the health risk assessment in drinking water disinfection [3,8]. Among I-DBPs, which have attracted more and more attention nowadays, iodoacetic acid (IA) is an emerging drinking water pollutant with high toxicity. Studies have shown that IA is the most genotoxic DBPs in mammals [9,10]. Iodo-THMs (I-THMs) are the most detected I-DBPs species in drinking water. In addition to their far higher toxicity than conventional THMs, I-THMs could also cause other problems to potable water [11]. For example, iodof orm has been considered as an important contributor to the incidents of bad tastes and odors, owing to its lowest organoleptic threshold concentration (0.03–1 μg L⁻¹) in all THMs [12]. In fact, it was estimated that up to 25% of bad taste and odor events in French drinking water were caused by iodof orm [13,14]. Therefore, the regulation of I-DBPs is of great significance in lowering drinking water toxicity during disinfection. To achieve this goal, control measures on the transformation of iodine sources are extremely practical and operable.

Iopamidol is proved to be the most important organic iodine source of I-DBPs in drinking water [15,16]. The UV transformation characteristics of iopamidol to I-DBPs in subsequent oxidation processes have been reported in our previous work [17]. The degradation features and pathways of iopamidol in three UV-based advanced oxidation processes (AOPs, UV/Cl₂, UV/S₂O₈²⁻ and UV/H₂O₂) were also studied [17,18]. Some investigators demonstrated that processes of O₃/H₂O₂ and UV/ClO₂ could also reduce iodinated X-ray contrast media (ICM) including iopamidol [19,20]. Wang et al. studied the UV/Cl₂ degradation of iohexol (another important ICM) and I-THMs formation in the following chlorination [21]. Despite of so many reports on ICM degradation, most works concentrated on influence factors and destruction mechanisms in UV/Cl₂ and UV/H₂O₂, while UV/NH₂Cl and UV/ClO₂ have never been considered yet. Although the degradation of iopamidol by UV/Cl₂ and UV/H₂O₂ have been reported [17,18], the required electrical energy are still unknown and no effective measures haven been proposed to restrain its transformation to noxious I-DBPs. Thus, this study aimed to make overall comparisons of the UV-induced AOPs with respect to degradation characteristics, energy consumption and toxicity evaluation, especially the never touched processes of UV/NH₂Cl and UV/ClO₂.

Recently the UV-initiated AOPs, which combine UV irradiation with common oxidants (such as Cl₂, NH₂Cl, H₂O₂, S₂O₈²⁻, HSO₄⁻) or synthesized photocatalysts have attracted increasing interests in water treatment and environmental remediation fields [17,18,22–25]. Various highly reactive radicals can be formed in these integrated systems, which can apparently promote the degradation rate of organic contaminants compared with UV alone [17,18,24–26]. Research on iohexol indicated that UV/Cl₂ had more advantages than UV in controlling I-THMs [21]. Other studies on UV/Cl₂ also showed that higher Cl₂ concentrations could not only degrade ICM more effectively but also reduce the formation of I-THMs [27–29]. The UV photolysis of NH₂Cl can form Cl⁻ and NH₂ while the former could directly or indirectly degrade many pollutants by forming ·OH (30–32). Although UV/NH₂Cl might inhibit the degradation of organic compounds and promote the DBPs formation in actual waters, the removal effect was fairly satisfactory [23,33]. H₂O₂ can also be UV photolyzed directly to form ·OH and the highly reactive ·OH is considered to play the most important role as it could attack organic compounds by inducing a series of oxidation reactions [34–38]. However, the evolution of iopamidol in these UV-based AOPs and their effects on the formation of I-DBPs in subsequent oxidation are still not clear.

The four UV-based systems related here (UV/Cl₂, UV/NH₂Cl, UV/ClO₂ and UV/H₂O₂) are quite different in oxidation ability, application convenience as well as performance-to-price ratio. Generally speaking, the free radicals involved in these processes mainly include reactive oxygen species (ROS), reactive chlorine species (RCS) and nitrogen-containing radicals. There are great differences in the reaction selectivity between these two kinds of radicals towards organic compounds, which make the oxidized intermediates of the same target compound quite different and then have a significant impact on the DBPs-related toxicity of waters in subsequent oxidation. Few studies have specifically concerned the related water toxicity associated with DBPs derived from these intermediates. So it is of important guiding significance in practical applications for these processes to study the degradation efficiency and energy requirements of pollutants in these AOPs, as well as their effects on water toxicity. Considering the high UV photosensitivity of ICM [15,17,18], there is clearly much work to be done to examine the removal characteristics of iopamidol by different UV-based AOPs and their influence on the transformation of nontoxic iodinated medicine to toxic I-DBPs.

The objectives of present work are (1) to compare the removal efficiency and degradation kinetics of iopamidol by four UV-induced AOPs (UV/Cl₂, UV/NH₂Cl, UV/ClO₂ and UV/H₂O₂) in terms of oxidation dosage, UV intensity, solution pH and water matrixes (Cl⁻, NH₄⁺ and nature organic matter (NOM)); (2) to evaluate the energy consumption of these systems using electrical energy per order (EE/O) parameter; (3) to estimate DBPs (including classical DBPs and I-THMs) formation and
the related toxicity during subsequent oxidation. The current research could provide some insights into the application of UV-mediated AOPs technologies in tradeoffs between cost-effectiveness assessment and toxicity control associated with DBPs, especially 1-THMs, of the disinfection waters containing iopamidol.

2. Experimental materials and methods

2.1. Chemicals and reagents

All the reagents used in this research were at least analytical purity except as noted. Iopamidol (99.6%) was obtained from U.S. Pharmacopeia. The calibration standards for 18 kinds classical DBPs (including dibromochloromethane (DBCM), bromodichloromethane (BDCM), chloroform (TCM), bromoform (BF), dibromoiodopropane (DCP), trichloroacetonitrile (TCP), bromochloroacetonitrile (BCAN), dichloroacetonitrile (DCAN), dichloroacetonitrile (TCAN), dichloroacetamidine (DBAN), trichloroacetdehyde (TCAL), trichloronitromethane (TCMN), dibromomethane (DBE), trichloroethylene (TCE), trichloroacetaldehyde, tetrachloroethylene and dibromochloropropane), \( \text{KH}_2\text{PO}_4 \geq 99.0\% \), iodometric (TIM, CHIpo, 99%), \( \text{Na}_2\text{CO}_3 \geq 99.0\% \), \( \text{NaOH} \geq 98\% \), \( \text{NaHCO}_3 \geq 98\% \), \( \text{NaHCO}_3 \geq 99.0\% \) and NaOCl (available Cl\(_2\) as 4.00–4.99%) were all acquired from Sigma-Aldrich (St. Louis, MO, USA). Acetonitrile and methyl tert-butyl ether (MtBE) were obtained from J.T. Baker (USA). The standards of 1-THMs including dibromochloromethane (DBCM), bromodichloromethane (DCIM, \( \text{CHClI}_2 \)), chlorodichloromethane (DCDM, \( \text{CHCI}_2\text{Cl} \)), dichloroiodomethane (DCIM, \( \text{CHClI}_2 \)), chlorodichloromethane (CDIM, \( \text{CHClI}_2 \)), and bro-mochloroiodomethane (BCIM, \( \text{CHBrClI} \)) were all bought from CanSyn Chemical Corp. (Canada). \( \text{H}_2\text{O}_2 \), \( \text{Na}_2\text{SO}_4 \), \( \text{K}_2\text{TiO}(\text{ClO}_2)_2 \), \( \text{NaCl} \), benzoic acid (BA), tert-butanol (TBA), \( \text{H}_2\text{SO}_4 \) and other chemicals of analytical purity were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ultra-pure water generated from a Milli-Q water purification system (Millipore, USA) were used to prepare all the solutions here.

\[ \text{NH}_2\text{Cl} \text{ and NaOCl (molar ratio of } \text{Cl}_2/\text{N} = 0.8:1) \text{ at } \text{pH} \geq 8.5 \text{ were newly mixed to prepare } \text{NH}_2\text{Cl} \text{ solution} \]  

Stock solution of \( \text{ClO}_2 \text{ was generated freshly to ensure the purity using the modified method detailed previously} \]  

The water matrix of real water was used as NOM sources in this study. The real water samples were acquired from the river running through our university and purified by 0.45 µm membranes (Millipore Corp., Billerica) before used. The main water characteristics of real waters were given in Table S10.

2.2. Procedures of experiments

The experiments on the degradation of iopamidol by different UV-based processes (UV alone, \( \text{UV/Cl}_2 \), \( \text{UV/Na}_2\text{Cl} \), \( \text{UV/ClO}_2 \) and \( \text{UV/H}_2\text{O}_2 \)) were carried out in a photoreactor equipped with four Hg UV lamps of 254 nm, the output rate was 4.0 L min\(^{-1}\), the drying gas flow rate was 120 m\(^3\)/h, the capillary voltage was 4500 V and the mass range was recorded from m/z 100 to 1000 Da in a positive-ion mode.

Standard buffer solutions (\( \text{pH} = 4.01, 7.00, 9.21 \)) were frequently applied to calibrate the pH meter for pH measurement (F20-FiveEasy, Mettler Toledo, Switzerland). \( \text{UV-C} \) luxometer (Photoelectric Instrument Factory of Beijing Normal University, Beijing, China) placed into a quartz sleeve inside the reactor was used to measure the exposed light intensity, which were altered by turning on 1, 2, 3 and 4 lamps (measured to be 2.43, 4.94, 7.34 and 9.76 mW cm\(^{-2}\), respectively).

3. Results and discussions

3.1. Degradation efficiency of iopamidol by different UV-induced processes

The degradation of pollutants by \( \text{UV/Cl}_2 \) \( [17,18,26,27,45,46] \), \( \text{UV/Na}_2\text{Cl} \) \( [30,47–49] \), \( \text{UV/ClO}_2 \) \( [50–52] \) and \( \text{UV/H}_2\text{O}_2 \) \( [53–56] \) processes are developed and the kinetics could be depicted by pseudo-first-order model with regard to the compound concentration, as explicated in Eq. (1).

\[ \dfrac{dC}{dt} = k_{\text{obs}}t \]  

The following Eq. (2) can be acquired by integrating Eq. (1):
\[
\ln \frac{C_i}{C_0} = k_{obs} t = (k_{radicals} + k_{UV} + k_{oxidant}) t
\]

where \(k_{obs}\) represents rate constant of the pseudo-first-order reaction, \(t\) is the corresponding reaction time, \(C_0\) and \(C_i\) stand for the initial and instantaneous concentrations of iopamidol. The total decomposition of iopamidol can be attributed to the degradation contribution of reactive radicals (\(k_{radicals}\)), UV irradiation (\(k_{UV}\)) and the oxidant itself (\(k_{oxidant}\)), respectively, viz.,

\[
k_{obs} = k_{radicals} + k_{UV} + k_{oxidant}
\]

[17,30,47,51,56]. Our previous studies have reported the oxidation rate constants of iopamidol by Cl₂ and NH₂Cl, which revealed the negligible degradation of the target compound after 300 s reaction (the same data shown in Fig. S1) [57]. It was also found that both \(H_2O_2\) and \(ClO_2\) can not oxidize iopamidol evidently (data also shown in Fig. S1) within 300 s [17,18]. Hence the values of \(k_{oxidant}\) in the respective system can be neglected. Therefore, the \(k_{obs}\) can be simplified as:

\[
k_{obs} = k_{radicals} + k_{UV}
\]

The UV degradation of iopamidol has also been proposed to follow pseudo-first-order kinetics [15]. To compare these UV-induced AOPs, the degradation of iopamidol was thus evaluated firstly, as depicted in Fig. 1. As presented in Fig. 1, linear regression curves of different UV-based processes were determined (\(R^2 > 0.99\)) and the respective slopes (representing \(k_{obs}\), listed in Fig. S2) were then obtained. Comparatively, iopamidol underwent mildly direct photolysis by UV alone (\(k_{obs}\) calculated to be 0.002551 s\(^{-1}\)). The combination of UV radiation with oxidants (Cl₂, NH₂Cl, ClO₂ and \(H_2O_2\)) can markedly promote the degradation rate of iopamidol. The negligible direct oxidation of Cl₂, NH₂Cl, ClO₂ and \(H_2O_2\) towards iopamidol (Fig. S1) enabled the comparison among UV-based systems as depicted in Fig. S2. Obviously, among the five processes, \(k_{obs}\) followed the order of \(UV/ClO_2 > UV/H_2O_2 > 0.01330 \text{ s}^{-1} > UV/ClO_2\) (0.01079 \text{s}^{-1}) > \(UV/Cl_2\). The data might provide useful referential information for applications of iopamidol degradation in water works. Of course, more influence factors other than degradation efficiency should be taken into account in applying these UV-induced AOPs.

### 3.2. Degradation of iopamidol by four UV-induced AOPs

The degradation of iopamidol by four UV-induced AOPs were comprehensively investigated in terms of oxidant dosage, UV intensity, solution pH and water matrixes (Cl⁻, NH₄⁺ and NOM). The results obtained were plotted in Figs. 2–5 and Figs. S4–S11 applying the pseudo-first-order kinetics discussed in Section 3.1. The calculated \(k_{obs}\), \(t_{1/2}\) (half-life) and the determination coefficient (\(R^2\)) were shown in Figs. S4–S11 and Tables S6–S9 for comparison. Each curve was comprised of at least six experimentally data and the respective \(R^2\) values were relatively high (\(R^2 > 0.95\)) to give enough analytical accuracy. The data might provide useful referential information for applications of the UV-mediated AOPs technologies relating to operational parameters as oxidant dosage, UV intensity, pH and water matrixes.

![Fig. 1. Pseudo-first-order kinetics plot of iopamidol by different UV-based processes](image-url)

\(UV\) alone, \(R^2=0.9756\)
\(UV/Cl_2\), \(R^2=0.9991\)
\(UV/NH_2Cl\), \(R^2=0.9940\)
\(UV/ClO_2\), \(R^2=0.9917\)
\(UV/H_2O_2\), \(R^2=0.9918\)
3.2.1. Degradation of iopamidol by UV/Cl2 process

The UV/Cl2 degradation of iopamidol with different influencing factors was plotted in Fig. 2 and S4-S5. The reactive radicals and related reactions included in UV/Cl2 were summarized in Table S2. $k_{\text{obs}}, t_{1/2}$ and iopamidol degradation after 300 s reaction under different conditions were provided in Table S6.

As shown in Fig. 2(a) and S4(a), increasing Cl2 concentrations from 0 to 1000 μM resulted in substantial enhancement of $k_{\text{obs}}$. Since the increase of Cl2 concentrations led to higher productions of radical species towards iopamidol [26,27], the observed positive correlation between Cl2 dosages and the removal rate can be expected. But the degradation role of $\cdot OH$ was not sensitive to Cl2 dosages. In fact, during the UV/Cl2 degradation of micropollutants, Wu et al. have proved that the concentration of $\cdot OH$ almost kept unchanged as Cl2 dosages added, but that of Cl increased linearly and that of ClO added with the increasing rate gradually slowed down [27]. It is the added RCS that contributed to the faster removal of iopamidol at higher Cl2 doses. The conclusion coincided with other scholars’ findings [18,26,27].

As given in Fig. 2(b) and S4(b), the degradation rate of iopamidol increased remarkably with UV intensity, from which the fine linearity between $k_{\text{obs}}$ and UV intensity can be inferred ($R^2 = 0.9079$, the fitting
line was $k_{\text{obs}} = 0.00545 \text{[UV]}$. This stated the vital role of UV intensity in the UV/Cl$_2$ degradation of iopamidol. The results can be attributed to the increased degradation contributions of both radicals (including RCS and -OH) and UV photolysis (Eq. (2)) at higher UV intensities.

The influence of pH on the UV/Cl$_2$ degradation of iopamidol was supplied in Fig. 2(c) and S4(c). It seemed that pH conditions had a great influence on the degradation rate of iopamidol. Among the inquired pHs, the highest $k_{\text{obs}}$ appeared at pH 7. The data were distinct from other scholars which reported that the highest reactivity towards pollutants in UV/Cl$_2$ exhibited at low pHs, where -OH was the dominant radical contributor to the degradation [26,27,60,61]. Kong et al. have demonstrated that it is the indirect radicals (Cl$_2^-$ and ClO-) not primary radicals (-OH and Cl-) that were responsible for the degradation of iopamidol at pH 7 [18]. The $k_{\text{obs}}$ rank of pH behavior was pH 7 > pH 8 > pH 6 > pH 9 > pH 5. Solution pH can greatly affect the
dissociation of HOCl (reaction (6) in Table S2). The formations of Cl· and ·OH were reduced as pH increased because of the weakened photolysis of chlorines and the enhanced radical scavenging [27]. The decreased kobs as pH fluctuated around 7 can be ascribed to the combined consequence of the declined radical productions and the simultaneous consumption of ·OH by OH− (reaction (3) in Table S2) [18].

The effect of water matrices (Cl−, NH4+ and NOM) on the UV/Cl2 oxidation of iopamidol was plotted in Fig. S5. The presence of Cl−displayed negligible effect on the degradation rate, because the concentrations of OH− and Cl· were reported to be constant with Cl− present [17]. Besides, the concentrations of Cl− tested did not affect the species distributions of ClO2− [17,18]. The degradation of iopamidol was greatly inhibited by the appearance of NH4+ (Fig. S5(b)), but the inhibition was not correlated with the NH4+ concentrations. This can be attributed to the reaction of NH4+ and ClO2− to form chloramines, yet the yields of chloramines posed negligible influence on the degradation rate [27]. Meanwhile, as Fig. S5(c) listed, the presence of NOM in real waters also exhibited certain inhibitory effect on the UV/Cl2 degradation of iopamidol, as NOM could act as inner scavenger of reactive radicals as well as ClO2− [17]. Furthermore, the degradation of iopamidol in the presence of NOM can not be described by the pseudo-first-order model. So the degradation curves were given instead of linear fitting plots.

The findings of this part indicated that UV/Cl2 was an emerging alternative AOPs for the removal of iopamidol. The decomposition of iopamidol was favorable to higher Cl2 dosages and UV intensities as well as neutral pH conditions. Cl− showed negligible effect while NH4+ and NOM exhibited inhibitory effect on the degradation of iopamidol. But the highly reactive RCS in UV/Cl2 might lead to diverse intermediates as the major mechanisms may not be the Cl−substitution and RCS were inclined to attack organics by the electron transport instead of H-abstraction and addition in comparison with ·OH [18,62]. The oxidation of these intermediates in subsequent disinfection might pose non-ignorable toxicity effect on the treated waters.

3.2.2. Degradation of iopamidol by UV/NH2Cl process

The UV/NH2Cl degradation of iopamidol with different influencing factors was shown in Fig. 3 and S6–S7. The involved radicals and related reactions included in UV/NH2Cl were sorted in Table S3. kobs, 1/2 and iopamidol degradation after 300 s reaction under different conditions were provided in Table S7.

As shown in Fig. 3(a) and S6(a), the synergistic degradation of iopamidol may result from the formation of ·OH and ·Cl in solution [23], and the productions of these species were promoted as the concentrations of NH2Cl added. However, the relevant rate growth slowed down obviously. This could be attributed to the transformation of primary radicals to nitrogen-containing radicals (NH· and NHCl−, etc.), which was considered to have lower oxidative capacity and could be ignored in the degradation of iopamidol (reactions (2), (5) (10) and (12) in Table S3) [23,30,63]. Moreover, chloramines could also eliminate ·OH and the reaction was more easily to occur than that between ·OH and HClO (reactions (5) and (12) in Table S3) [30,64]. The results were consistent with previous studies [23,31].

The data in Fig. 3(b) showed that the degradation rate of iopamidol was distinctly improved as UV intensity added. As depicted in Fig. S6(b), the linear correlation between kobs and UV intensity was obtained (R2 = 0.9419, the fitting line was kobs = 0.007609 [UV]), which stated the critical significance of UV intensity. As UV intensity enhanced, the radicals (Cl·, ·OH and NHCl−, etc.) originated from the decomposition of NH2Cl increased, and the simultaneous UV photolysis was also intensified. The dual action upon iopamidol resulted in the higher kobs. The radicals contributed as high as 76.35% to the total degradation in UV/NH2Cl (Fig. 1). The increase of UV intensity provided much more reactive radicals and UV photons to iopamidol degradation. The results agreed well with former reports [30,65].

The pH behavior of UV/NH2Cl degradation upon iopamidol was provided in Fig. 3(c) and S6(c). It was observed that solution pH also displayed a significant effect on the degradation rate. The highest kobs in the pH range of 5–9 appeared at pH 7, which was consistent with that of UV/Cl2 system. This might be ascribed to the homologous radicals of ·OH and ·Cl in both processes [32,66–68]. kobs followed the order of pH7 > pH6 > pH5 > pH8 > pH9 and the tendency was slightly different from that in UV/Cl2. The phenomena may be explained by the self-degradation of NH2Cl and the equilibrium transfer of various chloramine forms (reactions (13)–(16) in Table S3) during the variation of pH [69,70]. Besides, ·OH could consume ·Cl at higher pHs more quickly (reaction (2) in Table S3) [16]. Our previous reports have confirmed that the chloramination of iopamidol was also based on the action of free chlorines (HOCl and ClO−, especially the more reactive ClO2− towards iopamidol) from the NH2Cl dissociation [57]. Under alkaline conditions, the self-degradation of NH2Cl (reaction (16) in Table S3) shifted to the right, resulting in great inhibition to reaction (15) in Table S3. At the acidic pHs, the main chloramine species were NHCl2 and reaction (13) in Table S3 shifted leftward, thus the kobs were higher than those in alkaline solutions. The consequences were caused by both transformation of chlorine species and equilibrium of HOCl and ClO−. This may be interpreted by the most production of ClO− at neutral pH, while at pH 5–6 and pH 8–9, the conversion to ClO− was greatly restrained, so the kobs decreased obviously.

The effect of water matrices including Cl−, NH4+ and NOM on the UV/NH2Cl degradation of iopamidol was plotted in Fig. S7. As depicted in Fig. S7, no significant difference of kobs was observed among different concentrations of Cl− as well as NH4+ and it seemed that the degradation rate was not affected by the presence of both Cl− and NH4+. However, the degradation of iopamidol was markedly inhibited with the addition of NOM, which might be due to the consuming competition of NOM towards the indirect free chlorines and then radicals of ·OH and ·Cl. The results of this section suggested that the UV/NH2Cl degradation rate of iopamidol could be accelerated with higher NH2Cl dosages and UV intensities or adjusting pH to near-neutral conditions. The presence of both Cl− and NH4+ showed negligible influence on the degradation rate but NOM exhibited distinctly inhibitory effect. Nevertheless, the nitrogen-containing radicals during the UV excitation of NH2Cl might participate in the subsequent reaction towards the intermediates of the parent compound and thus result in other health risks to the treated waters, for example, the inclined formation of much more toxic nitrogen-containing DBPs.

3.2.3. Degradation of iopamidol by UV/ClO2 process

The degradation of iopamidol by UV/ClO2 with different influencing factors was shown in Fig. 4 and S8–S9. The reactive radicals and related reactions included in UV/ClO2 were listed in Table S4. kobs, 1/2 and iopamidol degradation after 300 s reaction under different conditions were provided in Table S8.

As shown in Fig. 4(a) and S8(a), kobs increased with the increasing ClO2 concentrations from 0 to 1000 μM due to the added yields of radicals. Although UV/ClO2 showed the least additive effect in the degradation rate compared with other UV-based AOPs, the roles of radicals were also nonnegligible in this system. The formation of ·OH has been proposed in UV/ClO2 assisted decolorization of methylene blue as well as color and chemical oxygen demand removal [50,52]. As listed in Table S4, two distinctive photodissociation channels have been suggested (reactions (1)–(2)) [71–73], the newly generated O3(ID) atom may combine with atmospheric O2 to reform O3 (reaction (4)) [74] and react fast with H2O to produce ·OH (reaction (7)) [75]. But according to the data here, the radical yields were too low to present an outstanding promotion on the degradation rate. The formation of highly energetic ·O and ·O3 in UV/ClO2 might influence the oxidation mechanisms of iopamidol and then lead to totally different oxidation products in comparison with those in UV/Cl2.
As illustrated in Fig. 4(b) and S8(b), the UV/ClO₂ degradation rate of iopamidol increased linearly with UV intensity, the fitting line of which can be deduced as \( k_{obs} = 0.00252 \cdot [UV] \) \( (R^2 = 0.9856) \). Greater \( k_{obs} \) was obtained at higher UV intensities, because photons and radicals attacking the triiodinated compound increased with the number of photons entering into the iopamidol samples added. This result was in accordance with the published studies [50–52].

The pH impact on \( k_{obs} \) was also evaluated in the range of 5–9 and displayed in Fig. 4(c) and S8(c). The degradation rate gradually increased with solution pH but the \( k_{obs} \) added limitedly with pH ascending from 7 to 9. The higher \( k_{obs} \) were noticed under neutral and basic media at pH 7–9 but decreased in acidic media at pH 7–5. Our previous study has confirmed that pH can not affect the UV photolysis rate of iopamidol and there is no dissociated form of iopamidol at all investigated pHs [15]. Such pH behavior here might be the integrated degradation results of multi-radicals as \( \cdot OH \), \( \cdot O \), Cl−, and ClO₂−, especially the highly reactive RCS, the reactivity of which was inhibited in acidic conditions [18]. For example, the \( k_{obs} \) at pH 5 was calculated to be 0.002377 s⁻¹, which implied the negligible contribution of radicals in UV/ClO₂ with UV photolysis alone calculated to be 0.002551 s⁻¹. The present results were in accord with the published literature on UV/ClO₂ decolorizing of azure C dye [51].

The influence of water matrices (Cl−, \( NH_4^+ \) and NOM) was provided in Fig. S9. It can be concluded that Cl− slightly accelerated the degradation rate while \( NH_4^+ \) resulted in noticeable promotions of \( k_{obs} \), while the effect of NOM can be neglected. The presence of Cl− might induce a series of reactions by \( \cdot OH \) (reactions (12)–(17) in Table S2), which finally led to the formation of more reactive Cl− and ClO₂− towards iopamidol. Although the transformation of \( \cdot OH \) to RCS was quite limited, the promotion of degradation rate can be observed. Studies has demonstrated that \( NH_4^+/NH_3 \) could be oxidized to \( NO_2^- \) and \( NO_3^- \) by \( \cdot OH \) (reactions (5)–(15)), then the generation of \( \cdot O \) from the UV photo-reduction of \( NO_2^- \) (reactions (16)–(18)) [76–77]. The highly reactive \( \cdot O \) might be responsible for the enhanced degradation.

\[
\begin{align*}
NH_4^+ + H_2O &\rightarrow NH_3 + H_3O^+ \text{ pka } 9.246 \\
\text{NH}_3 + \cdot OH &\rightarrow NH_2^- k = 1 \times 10^8 M^{-1}s^{-1} \\
\text{NH}_2^-+OH &\rightarrow NHOH k = 9.5 \times 10^8 M^{-1}s^{-1} \\
\text{NH}_2OH + \cdot OH &\rightarrow NOH + H_2O k = 9.5 \times 10^8 M^{-1}s^{-1} \\
\text{NH}_2O_2+\cdot OH &\rightarrow HNO_2 + H_2O \\
\text{NH}_2O_2+\cdot NO &\rightarrow NO + H_2O \\
\cdot NO + \cdot OH &\rightarrow HNO_2 k = 8.9 \times 10^8 M^{-1}s^{-1} \\
\text{NO}_2^- + \cdot OH &\rightarrow \cdot NO_2 + OH^- k = 1.1 \times 10^9 M^{-1}s^{-1} \\
\cdot NO_2^- + \cdot OH &\rightarrow NO_3^- + H^+ k = 1 \times 10^9 M^{-1}s^{-1} \\
2\cdot NO_2^- + H_2O &\rightarrow NO_2^- + NO_3^- + H^+ k = 6.5 \times 10^8 M^{-1}s^{-1} \\
\text{NO}_2^- + h\nu &\rightarrow \cdot NO_3 + O^- \\
O^- + H_2O &\rightarrow \cdot OH + OH^- k = 1.8 \times 10^9 M^{-1}s^{-1} \\
\text{NO}_2^- + h\nu &\rightarrow NO_2^- + O-
\end{align*}
\]

The findings stated that the removal of iopamidol can be achieved by the combination of UV and ClO₂, and the degradation rate was favorable to higher ClO₂ dosages and UV intensities as well as basic pHs. The presence of Cl− and \( NH_4^+ \) in UV/ClO₂ can clearly promote \( k_{obs} \) while the effect of NOM can be neglected. Although the radicals generated in UV/ClO₂ were partly similar to those in UV/Cl₂, \( k_{obs} \) of the former was far smaller. The difference might lead to quite different degradation pathways and intermediates, which could affect the formation of toxic DBPs in subsequent disinfection. The destruction mechanisms of UV/ClO₂ on contaminants still need further investigations.

### 3.2.4. Degradation of iopamidol by UV/H₂O₂ process

The degradation of iopamidol by UV/H₂O₂ with different influencing factors was shown in Fig. 5 and S10–S11. The reactive radicals and related reactions included in UV/H₂O₂ were summarized in Table S5. \( k_{obs} \) in Table S5 and iopamidol degradation after 300 s reaction under different conditions were provided in Table S9.

As depicted in Fig. 5(a) and S10(a), the data suggested that the elimination rate of iopamidol (\( k_{obs} \)) gradually increased with added \( H_2O_2 \) dosage but the relationship was not linear. The results can be ascribed to the increased radicals (Table S5, mainly referring to \( \cdot OH \)) in solution at higher \( H_2O_2 \) dosages upon the same UV intensity. This conclusion was consistent with the published reports [18].

As shown in Fig. 5(b) and S10(b), the degradation rate of iopamidol increased remarkably with UV intensity. It can also be seen that \( k_{obs} \) was directly proportional to UV intensity and the good linear fits can be observed \( (R^2 = 0.9842) \), the fitting equation as \( k_{obs} = 0.016736 [UV] \), the relationship of which suggested the critical importance of UV intensity. Much more radicals can be generated at higher UV intensities by the enhanced photolysis of \( H_2O_2 \) [35,56]. Furthermore, UV photolysis alone contributed 19.18% of the total iopamidol degradation in UV/H₂O₂ (Fig. 1). The joint action of both aspects led to the promoted \( k_{obs} \) at higher UV intensities. The results agreed broadly with previous studies by other scholars [54,56].

The pH effect on the UV/H₂O₂ degradation of iopamidol was plotted in Fig. 5(c) and S10(c). The \( k_{obs} \) distinctly decreased with pH increasing from 5 to 9. The increasing \( OH^- \) in alkaline conditions caused the consumption of \( \cdot OH \) and the simultaneous formation of \( O^\cdot \) (reactions (9) and (10) in Table S5) [78]. It is supposed that \( \cdot OH \) acts as electrophile while \( O^\cdot \) behaves as nucleophile in their respective reaction with organic molecules [79]. So as pH increased, the less reactive and more selective radical of \( O^\cdot \), rather than \( \cdot OH \), became the major radical towards iopamidol [59,79], which then displayed a tardy degradation rate. Besides, the \( I^- \) originated from the UV deiodination also slightly inhibited the removal of iopamidol [17]. These dual effects resulted in a distinct decrease of \( k_{obs} \) under basic pHs. The pH behavior here was in correspondence with other relative reports [17,18].

The effect of water matrices of Cl−, \( NH_4^+ \) and NOM on the UV/ \( H_2O_2 \) degradation of iopamidol was given in Fig. S11. It was seen from Fig. S11 that Cl− showed slightly enhancement on \( k_{obs} \) while \( NH_4^+ \) resulted in obvious accelerations. The explanations could also be attributed to the formation of RCS and \( \cdot O \), which were initiated by \( \cdot OH \), as discussed in Section 3.2.3. Besides, NOM displayed weakly inhibitory effect on the degradation rate as the organic matter present in real waters interfered with the photooxidation of iopamidol.

The results of this section revealed that the promotion of UV/H₂O₂ degradation rate of iopamidol could be realized by enhancing \( H_2O_2 \) dosages and UV intensities or adjusting pH to acidic conditions. The occurrence of Cl− and \( NH_4^+ \) can also noticeably promote \( k_{obs} \) while NOM exhibited slight inhibition. Utilization of greater UV intensity can be a preferred operation with more facility. However, these measures might also greatly improve the prime cost of this technology. In actual operation, it can be applied flexibly under full cost-effective assessment.

### 3.3. Energy calculations

As discussed above, the removal effectiveness and major factors of different UV-driven AOPs on iopamidol were investigated comprehensively. As all these photodegradation processes are electric-energy-intensive, it is necessary to introduce a scale-up parameter correlated with the electric energy, which can represent a primary fraction of the operating costs with regard to these techniques [25,80]. Therefore, the concept of EE/O proposed by the international union of pure and applied chemistry (IUPAC) was then employed to provide a cost-effective
evaluation for the concerned systems \cite{81}, EE/O (kWh m\(^{-3}\) order \(^{-1}\)) is defined as the electrical energy (kWh) required to decompose the contaminants by one order magnitude in 1 m\(^3\) of polluted water \cite{25,81,82}. The whole EE/O is constituted by the electrical energy from UV light (EE/O\(_{\text{UV}}\)) and the equivalent electrical energy for oxidant consumption \((EE/O_{\text{oxidant}})\), values of which can be calculated by Eqs. (19)-(21) \cite{81,83}.

\[
\begin{align*}
EE/O &= EE/O_{\text{UV}} + EE/O_{\text{oxidant}} \quad (19) \\
EE/O_{\text{UV}} &= \frac{P \times t \times 1000}{V \times \log \frac{C_0}{C_t}} \quad (20) \\
EE/O_{\text{oxidant}} &= \frac{Eq_{\text{oxidant}} \times [\text{oxidant}] \times 1000}{\log \frac{C_0}{C_t}} \quad (21)
\end{align*}
\]

where \(P\) represents power of the electronic energy input of the UV device (kW, as listed in Text S2); \(V\) is the volume of the solution (L); \(t\) is the photodegradation time (h); [oxidant] means the utilized dosages of oxidant (mol L\(^{-1}\)); \(\log \frac{C_0}{C_t}\) is the logarithm of the initial and instant concentrations of the contaminant; \(k_{\text{obs}}\) is the pseudo-first-order rate constant of the iopamidol degradation (s\(^{-1}\)); \(Eq_{\text{oxidant}}\) is the electric energy consumption to generated per mole of oxidant equivalently \((Eq_{\text{Cl}_2} = 1.6210 \text{ kWh mol}^{-1}, Eq_{\text{ClO}_2} = 3.452 \text{ kWh mol}^{-1}, Eq_{\text{NH}_2\text{Cl}} = 1.3900 \text{ kWh mol}^{-1}, Eq_{\text{H}_2\text{O}_2} = 0.3586 \text{ kWh mol}^{-1}\), the calculations of the unit conversion were detailed in Text S2). Then the calculated values and compositions of EE/O for iopamidol degradation by different UV-based processes were shown in Fig. S2 and Tables S6-S9.

As shown in Fig. S2, \(k_{\text{obs}}\) followed the order of \(UV/Cl_2 \gg UV/H_2O_2 \gg UV/NH_2Cl \gg UV/ClO_2 \gg UV\). However, the total EE/O followed the almost contrary trend of \(UV/ClO_2 \gg UV > UV/NH_2Cl > UV/H_2O_2 > UV/Cl_2\). As EE/O increases, the energy efficiency of a system decreases \cite{84}. \(UV/Cl_2\) was observed to be the most cost-effective one for iopamidol degradation among the tested AOPs. Contrarily, \(UV/ClO_2\) was the highest energy consumption system owing to the biggest equivalent electrical energy of ClO\(_2\) and the lowest degradation rate. Compared with direct UV photolysis, \(EE/O_{\text{UV}}\) decreased obviously in the discussed processes due to the contribution of various radical species in \(k_{\text{obs}}\). \(EE/O_{\text{UV}}\) dominated the total EE/O, which proved the significant role of UV intensity in all of these UV-mediated AOPs.

As presented in Tables S6-S9, the necessary UV energy \((EE/O_{\text{UV}})\) decreased with the growing oxidant dosages, while the \(EE/O_{\text{oxidant}}\) increased instead. Then the proportions of \(EE/O_{\text{UV}}\) and \(EE/O_{\text{oxidant}}\) changed accordingly. The optimal oxidant dosages in \(UV/Cl_2\), \(UV/NH_2Cl\), \(UV/ClO_2\) and \(UV/H_2O_2\) for their lowest EE/O values were estimated at 200, 300, 100 and 200 \(\mu\)M, respectively, which corresponded to the UV intensity of 2.43 mW cm\(^{-2}\). With the increased UV intensity, the total EE/O reduced gradually in \(UV/NH_2Cl, UV/ClO_2\) and \(UV/H_2O_2\) but obviously added in \(UV/Cl_2\). This indicated that it is unnecessary to enhance UV intensity in the \(UV/Cl_2\) degradation of iopamidol when taking into consideration of energy optimization. Under specific UV intensity and oxidant dosage with different pHs, the minimum of EE/O appeared when \(k_{\text{obs}}\) reached its maximum in each process. The results of current study can provide a few usefully cost-effective concerns in the application of these UV-driven AOP technologies.

3.4. DBPs-related toxicity evaluation in sequential disinfection processes

It can be concluded from the above results that the four UV-induced AOPs were all capable of degrading iopamidol effectively compared with UV alone. Our previous research has confirmed the formation of I\(^-\) released from iopamidol and its intermediates during UV irradiation, which then resulted in an enhanced conversion of classical DBPs to highly toxic I-DBPs during subsequent oxidation \cite{15}. Other scholars have also verified deiodination as the vital pathways and the evolution of inorganic iodine (I\(^-\) and HOI) in the degradation of iopamidol by UV/H\(_2\)O\(_2\) and UV/Cl\(_2\) \cite{17,18}. The I\(^-\) present in these UV based systems can be oxidized to HOI, which further reacted with degradation intermediates of iopamidol and probably led to the formation of undesirable I-DBPs \cite{13,15,17}.

The organic oxidation products of iopamidol by UV, UV/H\(_2\)O\(_2\) and UV/Cl\(_2\) have been identified and the destruction mechanisms mainly include deiodination, hydroxylation, chlorination and H-abstraction \cite{15,17,18}. The degradation intermediates of iopamidol by UV/Cl\(_2\), UV/NH\(_2\)Cl, UV/ClO\(_2\) and UV/H\(_2\)O\(_2\) were also analyzed here and the results were shown in Table S11 and Fig. S12. It was seen that the deiodinated and hydroxylated products were all detected in the four processes. The chlorinated products were both observed in UV/Cl\(_2\) and UV/NH\(_2\)Cl, while chlorine substitutions and hydroxy substitutions of iodine atoms might simultaneous take place, which resulted in much more intermediates than other two systems. The detected products of UV/ClO\(_2\) and UV/H\(_2\)O\(_2\) were similar except for slight monochlorinated products (products 8 and 12 in Table S11). It should also be pointed out that amino group substituted products (such as product 2 in Table S11) were noticed in UV/NH\(_2\)Cl, which might pose serious influence on the formation of nitrogen-containing DBPs. These oxidized intermediates can provide sufficient organic carbon source and may then facilitate the subsequent attack by oxidants to form DBPs.

The main parameters (TOC, TN and \(UV_{254}\)) of iopamidol solutions after treated by different processes were presented in Table S10. It can be seen that removals of TOC and \(UV_{254}\), which both decreased in the order of \(UV/Cl_2 > UV/H_2O_2 > UV/ClO_2 > UV > UV/NH_2Cl\), were little though there were radicals within all systems. The TOC data provided valuable information on the mineralization extent of samples. The results can be explained by the fact that the reactivity of radicals was firstly consumed by iopamidol and its derivates, while the irradiation time was not enough to realize the distinct conversion of these compounds to plant accessible forms, i.e., \(CO_2, H_2O, NH_2Cl, NO_3^-\). \(UV_{254}\) is an optical parameter indicating the chromophores with conjugated double bond functional groups (C=C, C=C, C=N) and aromatic rings of dissolved organic matter in solution \cite{46}. Scholars have revealed that RCS were prone to attack aromatics containing hydroxyl or amino groups while ·OH mainly led to deiodination and addition reactions \cite{17,18}. The results of TOC and \(UV_{254}\) evidenced reactivities of RCS and ·OH in the respective system. Besides, the changes of TN were not notable in all samples except that of UV/NH\(_2\)Cl, the sharp increase of which could be ascribed to reactions of nitrogen-containing radicals (NH\(_2^-\) and NH\(_3^-\), etc).

The variations of these parameters in each sample indicated the reactivity features of these UV-based AOPs and may pose different effects on DBPs formation. The distinct reactivity of radicals resulted in varied oxidation products by deiodination, hydroxylation, chlorination and H-abstraction, etc. Thus the DBPs-related toxicity of waters in subsequent oxidation processes displayed quite differently. Nevertheless, the influence of these processes on the DBPs formation and the solution toxicity during the subsequent disinfection are still unknown. This information has important indicative significance in evaluating the application of these technologies. Therefore, investigations on the formation of classical DBPs and I-THMs during various UV-based AOPs and sequential disinfection of iopamidol were carried out and the results were exhibited in Fig. 6. To facilitate comparison, the total production of classical DBPs and I-THMs as well as the iodine conversion of iodomethyl to I-THMs were also calculated in Table S12.

As seen from Fig. 6, five classical DBPs (including TCN, DCAN, TCAN, TCAL and TCNM) and three I-THMs (including DCIM, CDIM and TIM) were detected. It should be noted that certain amounts of nitrogen-containing DBPs (including DCAN, TCAN and TCNM) were observed. Though their concentrations were not remarkable, the corresponding impact on the toxicity of disinfected waters should not be ignored due to their higher toxicity than carbon-containing DBPs \cite{85}. The attack of radicals in these systems led to the cleavage of asymmetric side chain at the amide bond of the hydroxylated products of
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In these five UV-activated systems, $I^-$ could be released by UV deiodination of iopamidol [15]. However, the following reactions between $I^-$ and various reactive species might result in the evolution of iodine speciation and thus affected the final formation of I-THMs in subsequent oxidation. The reaction rates of ROS and RCS towards iopamidol were quite different [17,18,87], and RCS were noticed to be more selective and efficient [17]. Consequently, the relevant products in subsequent reactions with $I^-$ and the deiodinated intermediates of iopamidol differed greatly. The chlorinated intermediates of iopamidol by RCS were more liable to form I-THMs. On the contrary, ROS were more reluctant to induce I-THMs formation than RCS in the subsequent oxidation not only due to its reaction with $I^-$ as reactions (22)-(23) but also the formation of hydroxylated products [79,87].

$\cdot OH + 2I^- \rightarrow HOI^- \quad k = 1.1 \times 10^{10} M^{-1} s^{-1}$ \hspace{1cm} (22)  

$\cdot OH + I^- \rightarrow HO^- \quad k = 1.1 \times 10^{10} M^{-1} s^{-1}$ \hspace{1cm} (23)

For the subsequent chlorination, these UV-based processes can repress the total formation of classical DBPs to some extent, but have different impact on the I-THMs formation. Pretreatment of iopamidol by these processes can considerably inhibit the DCAN formation, and thus dramatically reduced the overall toxicity of the solution, which showed the control effect of toxicity in the order as $UV/Cl_2 > UV/ClO_2 > UV/Cl_3 > UV > UV/NH_2Cl$. The sum production rank of classical DBPs was $UV/Cl_2 < UV/ClO_2 < UV < UV/NH_2Cl < UV/Cl_3$, as expressed in Fig. 6(a) and Table S12. UV/Cl_3 led to the greatest yields of classical DBPs, which may be attributed to its strongest oxidation ability towards iopamidol. This can also be evidenced by the fastest degradation rate (Fig. 1) and the most reduction between deiodination of iopamidol [15]. However, the following reactions be-

![Fig. 6. Formation of classical DBPs (a), I-THMs (b) and the toxicity weighted concentrations of all DBPs measured during various UV-based AOPs of iopamidol (UV fluence = 1458 mJ cm$^{-2}$, pH = 7. [phosphate buffer] = 10 mM, [iopamidol]$_0$ = 10 μM, [Cl]$_0$ = [NH$_2$Cl]$_0$ = [ClO$_2$]$_0$ = [H$_2$O$_2$]$_0$ = 200 μM) followed by different disinfection processes (pH = 7. [Cl]$_0$ = [NH$_2$Cl]$_0$ = [ClO$_2$]$_0$ = 100 μM, t = 7 d). Error bars represent one standard deviation of triplicate measurements. Capital letters A, B, C, D, E and F indicate pretreatment by none, UV alone, UV/Cl$_2$, UV/NH$_2$Cl, UV/ClO$_2$ and UV/$H_2$O$_2$ processes, respectively, the subscript numbers 1, 2 and 3 represent subsequent oxidation by Cl$_2$, NH$_2$Cl and ClO$_2$, respectively.](image)

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and I-THMs in UV/NH₂Cl, UV/Cl₂ and UV. The occurrence of TCAL and DCAN were more susceptible to the oxidation by NH₂Cl [90,91]. Much more I-THMs (especially TIM) were formed in the following chloramination than chlorination, which was consistent with research results of other scholars [13,15]. As listed in Table S10, although UV/NH₂Cl slightly reduced TOC and UV₅₅₄, it resulted in sharp increase in TN, which consequently led to much more DCAN [92]. Besides, trace productions of classical DBPs and I-THMs were observed in UV/H₂O₂ and UV/ClO₂, which displayed minor inhibition in comparison with other three processes. The tendency of iodine conversion (Table S12) was similar to that in chlorination and UV/NH₂ClI should be avoided before both disinfection processes. The data also demonstrated that although all these UV-assisted AOPs can realize the removal of iopamidol, the systems dominated by ROS (UV/H₂O₂ and UV/ClO₂) seemed to have more advantages than those by RGS (UV/Cl₂ and UV/NH₂Cl) in controlling DBPs during subsequent oxidation. Therefore, when considering the control of DBPs, the ROS systems should be given much more attention. The results also revealed far greater disinfection risk of NH₂Cl than Cl₂, especially in I-THMs formation, which can provide referential value for the application of chlorine-based disinfectants.

It can also be seen from Fig. 6 that among three subsequent processes, ClO₂ produced the least DBPs, thus presented the smallest water toxicity. The data provided some evidences that ClO₂ could be a green disinfectant in controlling DBPs as Cl₂ and NH₂Cl alternatives [93]. ClO₂ alone could not oxidize iopamidol and produced none DBPs [15], but the pretreatment of UV-based processes induced a certain amount of DBPs. The iodine conversion to I-THMs followed the order of UV/NH₂Cl > UV/H₂O₂ > UV/Cl₂ > UV > UV/ClO₂, which clearly stated the elimination effect of UV/ClO₂ and the formation risk of UV/NH₂Cl. But the water toxicity descended in the order of UV/Cl₂ > UV > UV/NH₂Cl > UV/H₂O₂ > UV/ClO₂. Small molecular organic compounds in UV/Cl₂ were favored to form more DBPs in the subsequent ClO₂ oxidation thus engendered the most toxic conditions. Certain amounts of TCAN and TIM were detected in sequential treatment of UV/H₂O₂ and ClO₂, which resulted in a marked increase in DBPs-related toxicity compared with subsequent chlorination and chloramination. Besides, it should be specially pointed out that UV/ClO₂ can degrade iopamidol effectively with hardly any I-THMs formed during subsequent oxidation.

Up to present, iopamidol is reported to be the most important organic iodine source for I-DBPs [15,16,94] and the fate of iodine in iopamidol has critical significance in evaluating the relevant toxicity of waters. It was concluded that during the subsequent chlorination and chloramination, the iodine conversion in UV/NH₂ClI turned out to be the highest while those in UV/ClO₂ were quite low. As for the I-THMs-related safety in subsequent disinfection, the advantage of ClO₂ over Cl₂ and NH₂ClI was obviously noticed. The results can provide application value for these UV-induced techniques in treatment with iopamidol-contaminated waters as well as the toxicity control relating to I-THMs.

From the perspective of weighted water toxicity after subsequent oxidation, the risk ranking was UV/NH₂Cl > UV/Cl₂ > UV/H₂O₂ > UV/ClO₂. Based on our results, more concerns must be drawn in the utilization of UV/NH₂ClI and UV/Cl₂I UV/NH₂ClI in particular, as these treatments might greatly enhance the water toxicity in the following disinfection. In fact, ammonia nitrogen pollution in surface waters is generally serious while Cl₂ is the most widespread conventional disinfectant in most plants. Hence the safety issue concerning DBPs on the UV combination with NH₂ClI and Cl₂ should be addressed. Meanwhile, UV/ClO₂ displayed overwhelming advantage in controlling the water toxicity problems associated with DBPs, especially I-THMs, compared with other UV-driven AOPs.

4. Conclusions

The degradation of iopamidol by four UV-induced AOPs can be described by pseudo-first-order model. The calculated kₘₚ ranked in the order of UV/Cl₂ > UV/H₂O₂ > UV/NH₂Cl > UV/ClO₂ > UV. The synergistic effects could be attributed to different radical species generated by UV irradiation of oxidants. The removal rate of iopamidol was favorable to higher oxidant dosages and greater UV intensities. However, the pH behaviors of kₘₚ in these processes exhibited quite differently. The kₘₚ for UV/Cl₂ was pH₇ > pH₂ > pH₁ > pH₉ > pH₅ while that in UV/NH₂ClI was pH₇ > pH₅ > pH₂ > pH₈ > pH₉. kₘₚ in UV/ClO₂I gradually increased with solution pH whereas in UV/H₂O₂I it distinctly decreased. The effects of typical water matrices including Cl⁻, NH₄⁺ and NOM on the degradation of iopamidol in these processes were also investigated. The concept of EE/O was employed here to provide a cost-effective evaluation for the tested AOPs and the constitutes of EE/O were then quantified. EE/O followed the trend of UV/ClO₂ > UV > UV/NH₂ClI > UV/H₂O₂ > UV/Cl₂I Pretreatment of iopamidol by UV/Cl₂I and UV/NH₂ClI clearly enhanced the formation of classical DBPs and I-THMs while UV/ClO₂ and UV/H₂O₂I exhibited almost elimination effect. From the perspective of weighted water toxicity, the risk ranking was UV/NH₂ClI > UV/Cl₂ > UV/H₂O₂ > UV/ClO₂I. The results of current study can provide useful cost-effective concerns and DBPs-related toxicity evaluation in the application of these UV-driven AOP technologies.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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