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Transformation of X-ray contrast media in reverse osmosis brines by advanced oxidation processes

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ABSTRACT

The transformation of two X-rays contrast media iopromide (IOPr; non-ionic) and diatrizoate (DTZ; ionic) in reverse osmosis (RO) brines during UVA-TiO_2 oxidation was investigated. The scavenging effect of chlorides, alkalinity and fulvic acid (HA) was comparatively evaluated against ultrapure water. The transformation of both compounds followed a pseudo-first reaction order, but rate of IOPr oxidation was higher than DTZ regardless of the water matrix. In ultrapure water, 98% IOPr transformation was achieved compared to only 42% for DTZ after a 6 h experiment. In contrast, transformation was significantly reduced in RO brines with only 18 and 9% transformation for IOPr and DTZ, respectively, whereas chlorides displayed very low to none scavenging effect, fulvic acid and alkalinity decreased rate constants by about 50% due to competitive radicals scavenging. The scavenging effect of HA was more evident for DTZ than IOPr. The ratio of deiodination/transformation was higher in DTZ, indicating that the initial transformation involves deiodination, e.g. takes place predominantly in the triiodinated skeleton. In contrast, the ratio of deiodination/transformation was lower in IOPr, indicating that the initial transformation proceeds without deiodination, e.g. takes place predominantly in the side chains. Finally, in both cases, kinetic experiments showed that oxidation leads to iodide evolution without iodate formation.

Keywords: Wastewater effluents treatment; X-ray contrast media; Advanced oxidation processes (AOP's); UVA-TiO_2; Brines desalination

1. Introduction

In the last two decades, an increasing number of articles reporting presence of micropollutants in the aquatic environment, such as pharmaceuticals, hormones and personal care products, have been published [1–5]. These micropollutants are introduced into the environment in different ways; the most predominant is via wastewater treatment plant (WWTP) effluents. Thus, a proper post-treatment of effluents is necessary to avoid their release along the water stream. Reverse osmosis (RO) is a technology that has possibilities for purification of effluents by removing most organic and inorganic species while concentrating

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them in the brines [6,7]. The organic fraction of RO brines is mainly composed of soluble microbial products and exopolymeric substances resulting from microbial activity during biological treatment and natural organic matter, mainly humic-like and hydrophobic compounds present in the source water [8], and trace concentration of micropollutants [9]. The inorganic fraction of RO brines contains mainly chlorides and bicarbonates. A proper brines treatment is necessary to avoid discharge of the micropollutants into the environment [10,11]. Several methodologies have tested the removal of micropollutants from brines, including biological activated carbon column followed by capacitive deionization process [12], electrochemical treatment [13,14], flocculation–coagulation [15], non-thermal plasma (NTP) [11], ozonation/sonolisys [16] and different advanced oxidation processes (AOPs) [10,17,18]. However, these techniques achieve only partial transformation or mineralization in RO brines due to the pronounced scavenging capacity of the water matrix. We recently reported that applying UVA-TiO_2 about 70% of the quenching in RO brines can be attributed to the organic fraction, and about 30% to the inorganic fraction, and especially bicarbonate alkalinity [19].

In this work, the comparative pattern of oxidation by UVA-TiO_2 of two X-rays contrast media (ICM) diatrizoate (DTZ; an ionic ICM) and iopromide (IOPr; a non-ionic ICM) in different water matrixes is presented. ICM, widely used for diagnostic imaging, are eliminated mostly unmetabolized via urine or faeces [20]. Conventional WWTPs are not able to remove them effectively. These compounds have been found in WWTP effluents at concentrations varying between 6–10 μgL^{-1} for IOPr and 3–5 μgL^{-1} DTZ, respectively [1,20,21]. The transformation of these compounds in water using TiO_2 as catalyst has been reported previously. For DTZ, it was found more than 65% transformation in ultrapure water (UPW) during the first hour in UVA-TiO_2 system [22], whereas IOPr transformation exhibited a rate constant of 0.19 min^{-1} during ultraviolet (UV) (Solar simulator)-TiO_2 [23].

However, information regarding UVA/TiO_2 oxidation of these ICM in RO brines is scarcer.

2. Material and methods

2.1. Materials

Sodium DTZ and IOPr with purity ≥ 99% were purchased from Sigma-Aldrich and US Pharmacopeia, respectively. TiO_2 used was Degussa P-25. Fulvic acid sodium salts (HA), technical grade, was purchased from Sigma-Aldrich. Eluents and standards were at least of analytical grade.

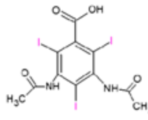
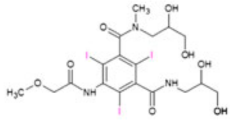
2.2. Water matrixes

Experiments were carried out in fresh RO brines, synthetic solutions and UPW. Water matrixes were spiked with DTZ and IOPr (~100 ± 15 μM) as indicated. The properties of the model compounds are presented in Table 1.

2.2.1. RO brines

The brines were obtained from the two-stage RO Technion pilot plant located in a commercial WWTP site, with a treatment capacity of secondary wastewater effluents of 10 $m^3 h^{-1}$. The pilot plant characteristics are detailed elsewhere [11]. For this study, fresh RO brines (2-fold concentrated) were obtained from the first RO stage. A schematic diagram of the desalination process is presented in Fig. 1. The characteristic composition of the RO brines applied in this study was described previously [19].

Table 1
Properties of the tested model compounds

Compound	Chemical name	Empirical formula	Structural formula	Mw	pKa	pKow
Diatrizoaic acid	3,5-Diacetylamino-2,4,6-triiodobenzoic acid	$C_{11}H_9I_3N_2O_4$		635.9	3.4[a]	0.45[a]
Iopromide	1-N,3-N-bis(2,3-dihydroxypropyl)-2,4,6-triiodo-5-[(2-methoxyacetyl)amino]-3-N-methylbenzene-1,3-dicarboxamide	$C_{18}H_{24}I_3N_3O_8$		791.1	9.9[b]	−2.3[b]

[a] From Ref. [7].

[b] From Ref. [25].

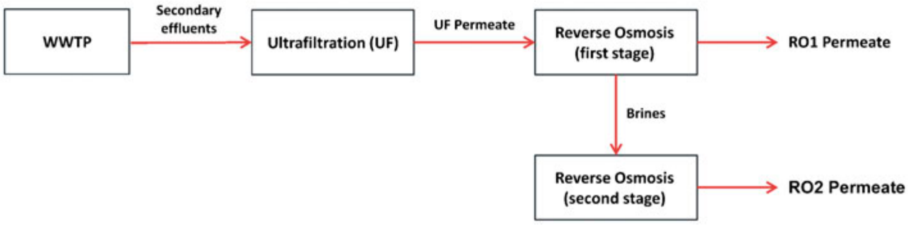


Fig. 1. Schematic process diagram of the secondary effluents-desalination process applied to generate the brines used in this study.

2.2.2. Synthetic solutions

Synthetic solutions were prepared in UPW, adding either chlorides (600 mgL^{-1}), bicarbonate alkalinity (370 mgL^{-1} as $NaHCO_3$), or HA (4 mgL^{-1} as C), at a similar concentration as they are present in RO brines first stage. In spite of its low concentration, HA was chosen to represent organic matter due to its relative high influence on DTZ transformation, as observed in our previous work [19].

2.2.3. Ultrapure water

(18.2 MΩ cm) was generated in a Purelab classic system (Elga).

2.3. Photocatalysis experiments

Experiments were carried out at room temperature in 500-ml glass reactors containing 180 ml solution spiked with the model compounds and 1 g L^{-1} TiO_2, as detailed in our previous work [19]. The reactors were irradiated from the top with UVA lamp (Eversun, 40 W) with maximum intensity at 350 nm. Measured light intensity was 990 µWcm^{-2}. At fixed sampling times, samples were collected for analysis, supplemented with excess $NaHCO_3$ to facilitate TiO_2 removal, centrifuged and filtered with 0.45-µm syringe-driven filter units (Millipore) prior to the analysis.

2.4. Analytic techniques

DTZ and IOPr determination were performed using liquid chromatography with electrospray tandem mass spectrometry as detailed elsewhere [7], in an Agilent 1200 HPLC system (Hewellet Packard) coupled through an ion spray interface to an API 3200 triple quadrupole mass spectrometer (Applied Biosystems). Reverse-phase HPLC was performed on a LiChroCART® Purospher STAR RP-18 (Merck) endcapped column (4.6 mm × 15 cm) with 5 µm pore size. The compounds were detected in multiple-reaction monitoring mode.

Anions concentrations (chloride, iodide) were measured in an 881 compact IC Pro ion chromatograph (Metrohm) equipped with Metrohm A supp 5–150 (with 4 µm pore size) column. A solution of 3.2 mM sodium carbonate and 1.0 mM sodium bicarbonate in 5% acetonitrile was used as eluent.

Dissolved organic carbon was analyzed on a total organic carbon analyzer (multi N/C 2000, Analytic Jena), and ultraviolet absorbance (UV) at a wavelength of 254 nm (A_{254}) was measured in a UV–visible spectrophotometer (Agilent 8453 series) with a 1-cm quartz cell. Alkalinity was measured according to standard methods 2320 [24].

In order to perform an iodine–iodide mass balance of the transformation/deiodination, concentrations of DTZ and IOPr were expressed as in a molar basis, as

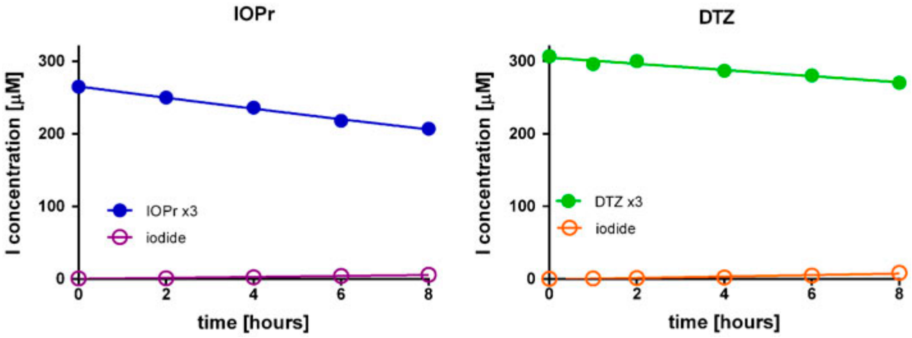


Fig. 2. Transformation and deiodination of IOPr and DTZ in RO brines during UVA-TiO_2 oxidation. Symbols represent actual data. Lines represent fit to first-order kinetics.

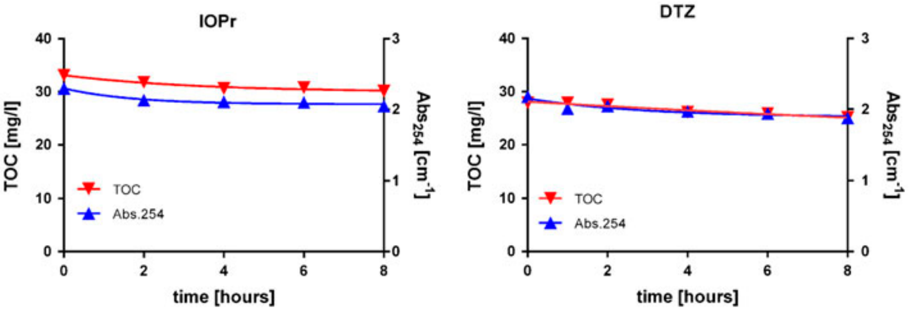


Fig. 3. Mineralization and UV-absorption at 254 nm during UVA-TiO$_2$ oxidation of IOPr and DTZ in RO brines. Symbols represent actual data. Lines represent fit to first-order kinetics.

μM iodine. Since both model compounds contain three iodine atoms per molecule, their iodine concentration is three times their molar concentration.

3. Results

The transformation and deiodination of the model compounds in RO brines are presented in Fig. 2. IOPr displayed a twofold higher degree of transformation than DTZ after 6 h of experiment (18 and 9% transformation, respectively). In contrast, initial deiodination/transformation ratio measured after 2 h oxidation was 3.3-fold higher for DTZ (0.2) than that of IOPr (0.06), indicating deiodination as the primary oxidation pathway for DTZ. As shown in Fig. 3, the levels of mineralization (10 and 9%) and absorption at 254 nm (9 and

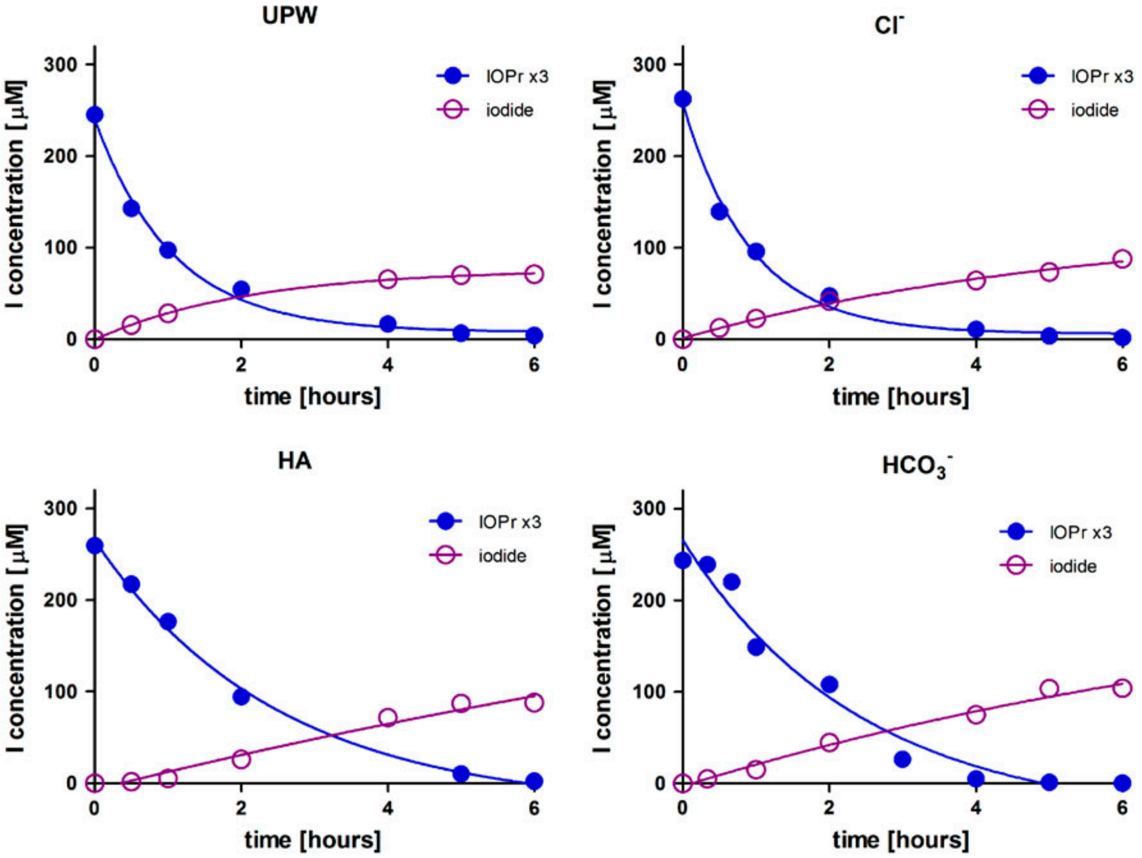


Fig. 4. Transformation and deiodination of IOPr during UVA-TiO$_2$ treatment of synthetic solutions. UPW: ultrapure water; Cl$^-$: chlorides solution; HA: fulvic acid solution; HCO$_3^-$: bicarbonate alkalinity solution. Symbols represent actual data. Lines represent fit to first-order kinetics.

8% decrease), corresponding to the transformation of the background organic compounds, were similar in both cases.

Experiments in UPW were performed in order to evaluate the oxidation patterns without interference of the water matrix (Figs. 4 and 5). In UPW, IOPr reached practically 100% transformation in 6 h corresponding to 30% mineralization, whereas DTZ achieved only 42% corresponding to 18% mineralization, again depicting the relative higher resistance to oxidation of DTZ. The pseudo-first-order rate constant for IOPr ($1.4.10^{-2}\,\text{min}^{-1}$) was roughly one order ofmagnitude higher than that of DTZ ($2.3.10^{-3}\,\text{min}^{-1}$). In line with the results obtained in RO brines, an almost 5-fold higher deiodination/transformation ratio was observed for DTZ (0.64) compared to IOPr (0.13), measured in the first 30 min of the experiment.

To test the influence of RO brines components, synthetic solutions containing chlorides, fulvic acid or bicarbonate alkalinity in UPW were tested (see Figs. 4 and 5). At the end of the experiments, an almost complete transformation was observed for IOPr regardless of water matrix, whereas transformation was less than 40% for DTZ. In all the water matrixes tested in this study, DTZ and IOPr transformation leads in iodide formation; presence of iodate was not observed. No significant differences in the initial rate of transformation, measured after 2 h, were found in the presence of chlorides for either IOPr or DTZ compared to UPW. In contrast, about 40–50% decrease in the initial rate of transformation of IOPr was found for either HA or bicarbonate alkalinity compared to about 50–60% for DTZ.

4. Discussion

The presented work shows that the transformation of IOPr and DTZ during UVA-TiO_2 oxidation followed a similar pattern and profile of oxidation regardless of the water matrix tested. These, along with a relatively low mineralization after 6 h irradiation (20–30%) obtained in UPW, in which the model compounds were the only organic matter present in the reactions, indicate that partial transformation

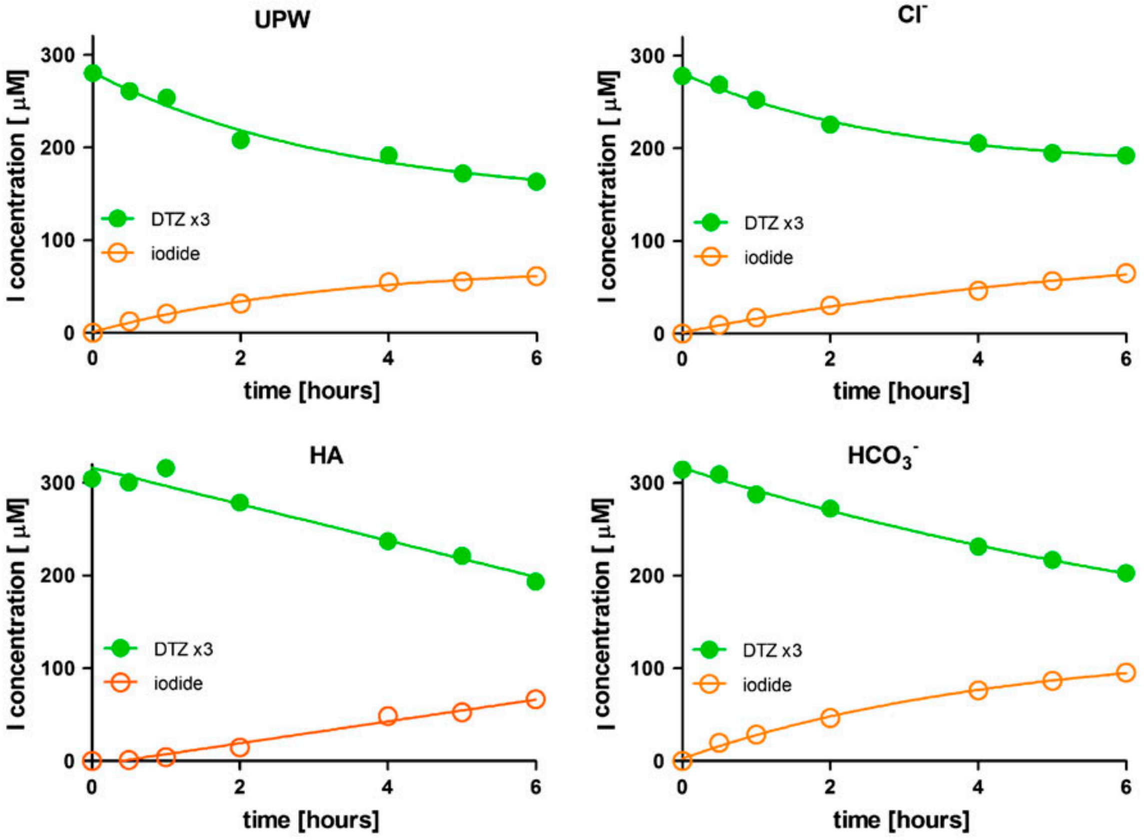


Fig. 5. Transformation and deiodination of DTZ during UVA-TiO_2 treatment of synthetic solutions. UPW: ultrapure water; Cl^-: chlorides solution; HA: fulvic acid solution; HCO_3^-: bicarbonate alkalinity solution. Symbols represent actual data. Lines represent fit to first-order kinetics.

rather complete mineralization that takes place within the time frame studied. These results are in line with previous data [11] that reported in NTP system a pseudo-first-order rate constant of $0.4\,s^{-1}$ for IOPr compared to $0.08\,s^{-1}$ for DTZ in the background of first-stage RO brines. In ozonation experiments at 15 mgL^{-1} as ozone dose, 91% IOPr transformation was reported against 14% for DTZ [25], whereas at 5 mgL^{-1} ozone, no significant removal of DTZ was found in comparison to 60% IOPr transformation [26]. Reaction rate constants measured during γ radiation were more than one order of magnitude higher for IOPr than that of DTZ [27]. The higher susceptibility of oxidation of IOPr regardless of the oxidation technique can be attributed most probably to the molecule structure, namely IOPr possess longer side chains in comparison to DTZ, presenting more sites to oxidant species attack. Indeed, our results regarding the transformation/deiodination ratio strongly suggest that initial transformation during UVA-TiO_2 oxidation, in DTZ presumably starts at the triiodinated moiety whereas in IOPr appears to start at the side chains, in line with results reported for NTP oxidation [11].

Water matrix components in RO brines play an important role in AOP efficiency. The low transformation and mineralization of model compounds found in RO brines are due to the quenching performed by the water matrix components [19]. Bicarbonates and carbonates have been cited in literature to react with hydroxyl radicals to form carbonate radicals as described in Eqs. (1) and (2) [28].

$$HCO_3^- + OH^\bullet \rightarrow CO_3^{-\bullet} + H_2O \quad k = 8.5 \times 10^6 M^{-1}s^{-1} \tag{1}$$

$$CO_3^{-2} + OH^\bullet \rightarrow CO_3^{-\bullet} + OH^- \quad k = 3.9 \times 10^8 M^{-1}s^{-1} \tag{2}$$

Carbonates radicals are less reactive than $OH^\bullet$, decreasing the transformation of model compounds.

It was reported that the rate reaction constant of fenuron with carbonate radicals is three orders of magnitudes lower than that of hydroxyl radicals [29].

The mechanism of radical scavenging by HA seems to be rather complex. UV light screening has been identified as the main mechanism responsible for the decrease of the removal rate of nitrobenzene in the presence of humic acids during ozonation and O_3/UV [30]. Hydroxyl radicals possess affinity to carbon–carbon double and triple bonds abundant in humic-fulvic acids/polyaromatic aromatic compounds [31,32], reacting preferably with HA and leaving less free radicals to react with the target compounds. Moreover, in systems catalyzed by particles such as TiO_2, further interactions between humic acid and TiO_2 were reported as surface deactivation and competition for active sites in the photocatalyst [33].

The quenching effect of chlorides, although very low, can be attributed also to competence for OH•.

The following reactions between chlorides and hydroxyl radicals were reported [34]:

$$OH^\bullet + Cl^- \leftrightarrow HOCl^{\bullet -} \quad k_{eq} = 0.70 \pm 0.13\,M^{-1} \tag{3}$$

$$HOCl^{\bullet -} + H^+ \leftrightarrow Cl^\bullet + H_2O \quad k_{eq} = 1.6 \times 10^7 M^{-1} \tag{4}$$

$$Cl^- + Cl^\bullet \leftrightarrow Cl_2^\bullet \quad k_{eq} = 1.9 \times 10^5 M^{-1} \tag{5}$$

Chlorides can react with hydroxyl radicals as in Eq. (3) due to its high forward constant $k_{forward} = 4.3 \pm 0.4 \times 10^9\,M^{-1}s^{-1}$. $HOCl^{\bullet -}$ initially formed can dissociate back to chloride and hydroxyl radical with $k_{back} = 6.1 \pm 0.8 \times 10^9\,M^{-1}s^{-1}$ or react with H^+ as in Eq. (4) $k_{forward} = 2.1 \pm 0.7 \times 10^{10}\,M^{-1}s^{-1}$. Additionally, $Cl^\bullet$ can associate back to hypochlorite radicals as in Eq. (4) with $k_{back} = 1.3 \times 10^3\,M^{-1}s^{-1}$ or react with chlorides as in Eq. (5) with $k_{forward} = 2.1 \times 10^{10}\,M^{-1}s^{-1}$.

5. Conclusions

The transformation of the ICM, IOPr and DTZ, during UVA/TiO_2 oxidation in the RO brines and UPW, was examined, and the influence of chorides, fulvic acid and bicarbonate alkalinity was evaluated. Although a pronounced decrease in transformation of both models compounds was observed in RO brines, IOPr displayed significantly lesser susceptibility to quenching and higher degree of transformation than that of DTZ, regardless of the water matrix applied. The HA and alkalinity decreased the transformation rates of both model compounds due to hydroxyl radicals scavenging, whereas chlorides had no effect. Low deiodination/transformation ratio for IOPr indicates that the initial transformation starts at the aliphatic side chains, whereas the high deiodination/transformation ratio in DTZ suggests that the initial transformation predominantly takes place in the triiodinated aromatic structure. Deiodination of IOPr and DTZ leads to iodide formation without accumulation of iodate. Further research focused on reducing quenching effect in brines should be done in order to improve feasibility of AOP systems for brines discharge.

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