

ORIGINAL RESEARCH ARTICLE

Removal of trace organic pollutants and generation of halogenated disinfection by-products in membrane UV/chlorine combined process

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ABSTRACT

In this study, the degradation kinetics and degradation mechanism of 23 trace organic pollutants (TrOCs) in the secondary effluent of sewage by the combined membrane-UV/chlorine process were investigated, and the halogenated disinfection by-products (X-DBPs) in the combined process were investigated and its generation potential (X-DBPsFP), and the cytotoxicity and genotoxicity of the treated water samples were also evaluated. The results showed that membrane pretreatment could effectively promote the degradation of TrOCs in UV/chlorine system, and nanofiltration (NF) was more effective than ultrafiltration (UF). Compared with UF, NF intercepts more dissolved organic matter (DOM), thus weakening the light shielding effect, chlorine consumption and radical quenching to a greater extent. It is found that the degradation mechanism of TrOCs can be divided into the following four categories: Ho^\cdot dominated, RHS dominated, chlorine and RHS jointly dominated and chlorine dominated. Membrane pretreatment can well reduce the formation of X-DBPs, among which UF and NF reduce the formation of haloacetamide (HAMs) and trihalomethanes (THMs) most significantly, while NF reduces the formation of X-DBPs and X-DBPsFP and the toxicity of water samples much stronger than UF. In addition, NF UV/chlorine can significantly remove the precursors of X-DBPs, so as to effectively control the enhancement of cytotoxicity and genotoxicity of water samples in the post chlorination process. The research results promote the development of advanced sewage treatment technology and provide theoretical guidance for related research.

Keywords: UV/Chlorine; Trace Organic Pollutants; Halogenated Disinfection By-Products; Membrane Pretreatment; Dissolved Organic Matter

ARTICLE INFO

Received: 1 February 2022
Accepted: 21 April 2022
Available online: 28 April 2022

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1. Introduction

In recent years, trace organic pollutants (TrOCs) such as drugs and personal care products (PPCPs) and endocrine disruptors (EDCs) have attracted much attention^[1,2]. With the wide application of PPCPs and EDCs in medicine, animal husbandry, agriculture, daily life and other fields and the progress of analysis and detection technology, these TrOCs are frequently detected in sewage, surface water, groundwater and other water bodies, with concentrations ranging from $\text{ng}\cdot\text{L}^{-1}$ to $\mu\text{g}\cdot\text{L}^{-1}$ varies^[3-5]. A large number of studies have shown that PPCPs and EDCs have strong environmental persistence and bioaccumulation, can enter high nutritional level organisms through food chain transmission and bioconcentration, and can induce the production of resistance genes, which will eventually affect ecological security and human health^[6,7]. Because traditional water/sewage treatment processes such as coagulation, sedimentation, filtration and biological treatment are difficult to remove TrOCs in water, advanced oxidation technology (AOPs)^[8] and membrane

filtration technology^[9] and other advanced water treatment processes continue to rise.

Among AOPs, UV/chlorine technology has more advantages than UV/H₂O₂ technology in degrading TrOCs. On the one hand, the molar absorption coefficient and photodissociation quantum yield ($\epsilon_{254(\text{HOCl}/\text{OCl}^-)} = 62/60 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$, $\Phi_{254(\text{HOCl}/\text{OCl}^-)} = 0.62/0.55 \text{ mol}\cdot\text{E}^{-1}$) of chlorine at 254 nm^[10] are higher than those of H₂O₂ ($\epsilon_{254(\text{H}_2\text{O}_2)} = 18.6 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$, $\Phi_{254(\text{H}_2\text{O}_2)} = 0.5 \text{ mol}\cdot\text{E}^{-1}$), UV/chlorine system can generate HO· more effectively ($E^0 = 1.9 - 2.7 \text{ V}$); on the other hand, the system can also produce Cl· ($E^0 = 2.55 \text{ V}$) and other reactive chlorine species (RCS), which have a higher reaction rate with organic compounds with electron rich groups than HO·^[12]. However, a large amount of dissolved organic matter (DOM) in the actual water body will inhibit the degradation effect of UV/chlorine on TrOCs through light shielding effect, chlorine consumption and radical quenching, and also produce Halogenated Disinfection by-products (X-DBPs, X = Cl⁻, Br⁻)^[13,14]. Toxicity tests and epidemiological studies have shown that X-DBPs can not only damage the nervous system of mice, but also have a certain association with carcinogenesis, mutagenicity and adverse pregnancy^[15-17]. It can be seen that how to effectively remove TrOCs in water and effectively control the generation of X-DBPs is a key problem to be solved in the field of advanced sewage treatment.

In view of the fact that membrane filtration technologies such as ultrafiltration (UF) and nanofiltration (NF) can effectively remove DOM through size exclusion, electrostatic repulsion and adsorption^[18], this paper explores the effect of membrane pretreatment on the degradation of TrOCs and the formation of X-DBPs in the membrane UV/chlorine advanced oxidation combined process. The main research contents include: (1) degradation kinetics of TrOCs in membrane UV/chlorine system; (2) degradation mechanism of TrOCs in membrane UV/chlorine system; (3) X-DBPs formation and X-DBPs formation potential (X-DBP_{sp}) of membrane UV/chlorine system; (4) cytotoxicity and genotoxicity analysis after membrane UV/chlorine treatment.

2. Materials and methods

2.1 Reagents and equipment

Diclofenac (DCF), naproxen (NAP), mefenamic acid (MA), sulfadiazine (SD), sulfadiazine (SDM), ciprofloxacin (CIP), ofloxacin (OFL), norfloxacin (NOR), bezafibrate (BZF), gemfibrozil (GEM), tetracycline (TTC), estrone (E1), triclosan (TCS), roxithromycin (Rox), tinidazole (TNZ), atrazine (ATZ), caffeine (TCS CAF), carbamazepine (CBZ), iodopropamine (IPM), metoprolol (MTP), primidone (PMD) Theophylline (TPL), trimethoprim (TMP), nitrobenzene, benzoic acid, 1,4-dimethoxybenzene, sodium dihydrogen phosphate dihydrate, disodium hydrogen phosphate dodecahydrate, sodium hypochlorite solution, sodium thiosulfate, ascorbic acid, anhydrous sodium sulfate, methyl tert butyl ether, 1,2-dibromopropane, sulfuric acid (sigma Aldrich in the United States and Merck in Germany, analytical purity); Methanol, acetonitrile, formic acid, acetic acid (Merck, Germany, HPLC grade); THMs mix (including chloroform (TCM), tribromomethane (TBM), dichlorodibromomethane (DBCM), dichloromonochloromethane (BDCM)), m-551b (including Trichloroacetonitrile (tcan), dichloroacetonitrile (DCan), bromochloroacetonitrile (bcan), dibromoacetonitrile (DBAN), chloral hydrate (CH), dichloroacetone (DCP), Trichloroacetone (TCP), trichloro nitromethane (tcnm)), dichloroacetaldehyde (DCAL), trichloroacetamide (TCAM), and dichloroacetylammmonium (DCAM), dibromoacetamide (DBAM) Bromochloroacetamide (bcan) (accustandard, USA, standard).

Ultra high performance liquid chromatography triple quadrupole mass spectrometer (Agilent1290-6430, Agilent Technologies Co. Ltd.), gas chromatograph (Agilent 7890A, Agilent Technologies Co. Ltd., USA), high performance liquid chromatograph (Ultimate 3000, Thermo Fisher Co. Ltd., USA), ion chromatograph (ICS-600, Thermo Fisher Co. Ltd., USA), laser flash photolysis spectrometer (LKS80, Applied photophysics Co. Ltd., UK), UV-vis spectrophotometer (UV-2700, Shimadzu Corporation of Japan), TOC detector (TOC-LCPH, Shimadzu Corporation of Japan), pH meter (S210, Mettler Toledo Co. Ltd., Switzerland).

2.2 Experimental method

2.2.1 Membrane pretreatment experiment

The water sample used in this study was taken from the secondary effluent of a sewage treatment plant in Guangzhou. The water samples were filtered through a 0.45 μm mixed cellulose ester (MCE) membrane and divided into 3 parts: one part is not treated as raw water, and the other two parts are UF and NF respectively by using constant pressure cross flow filter device (effective membrane filtration area of 16 cm) to obtain UF water and NF water. UF uses polyether sulfone (PES) membrane (UE050, Rising-Sun Membrane Technology Co., Ltd., China) with an average molecular weight of 50 kDa, with an operating pressure of 300 kPa and a gear pump speed of 1,500 $\text{r}\cdot\text{min}^{-1}$; NF adopts polyamide composite membrane (Synder NFW) with an average molecular weight of about 500 Da, the operating pressure is 700 kPa, the gear pump speed is 2,000 $\text{r}\cdot\text{min}^{-1}$, and the cooling water tank controls the operating temperature to 25 $^{\circ}\text{C}$.

2.2.2 Degradation test

During the experiment, the light source of the circulating UV/chlorine degradation experimental device is composed of three 10W low-pressure mercury lamps (maximum emission wavelength 253.7 nm) and two fans. The light source vertically irradiates the cylindrical quartz dish with a diameter of 7 cm below, and the reaction solution is kept uniform through a magnetic stirrer. Reaction conditions: $T = 25\text{ }^{\circ}\text{C}$, $V = 100\text{ ml}$, $[\text{TrOCS}]_0 = 1\text{ }\mu\text{g}\cdot\text{L}^{-1}$, [phosphate buffer] = 2 $\text{mmol}\cdot\text{L}^{-1}$, $[\text{chlorine}]_0 = 5\text{ mg}\cdot\text{L}^{-1}$, [light intensity] = 0.186 $\text{mW}\cdot\text{cm}^{-2}$, $\text{pH} = 7.0$. When the reaction time is 0, 0.5, 1, 3, 5, 7, 10, 20, 30 min, take 2 ml of reaction solution and quench the residual chlorine with excess $\text{Na}_2\text{S}_2\text{O}_3$. The obtained sample is used to determine the concentration of TrOCs. In the control group, no chlorine was added in the separate UV experiment, and the UV lamp was turned off in the separate chlorination experiment. Other conditions were the same.

2.2.3 Probe experiment

Nitrobenzene, benzoic acid and 1,4-dimethoxybenzene were used as probes to determine the

steady-state concentrations of $\text{HO}\cdot$, $\text{Cl}\cdot$ and $\text{ClO}\cdot$ in UV/chlorine system. Add 0.5 $\mu\text{mol}\cdot\text{L}^{-1}$ probe on the basis of UV/chlorine reaction conditions, when the reaction time is 0, 0.5, 1, 3, 5, 7, 10, 20, 30 min, take 1 ml of reaction solution, quench the remaining oxidant with excess $\text{Na}_2\text{S}_2\text{O}_3$, and determine the probe concentration by high performance liquid chromatography.

2.2.4 X-DBPs generation experiment

After the raw water, UF water and NF water are treated with UV/chlorine for 30 minutes, the residual chlorine is determined by N, N-diethyl-p-phenylenediamine (DPD) spectrophotometry^[19]. Take 30 mL of water sample, quench the residual chlorine with excess ascorbic acid, and determine the X-DBPs generated; continue to add sodium hypochlorite solution to the remaining water sample until the chlorine concentration in the system is 10 $\text{mg}\cdot\text{L}^{-1}$. After 24 hours of avoiding light reaction, take 30 ml of water sample and add excessive ascorbic acid to quench the residual chlorine, and determine the X-DBPs generated, namely X-DBPsFP.

2.3 Analysis and test methods

2.3.1 Determination of water quality parameters

pH meter, UV-vis spectrophotometer and TOC tester are used for pH, UVA_{254} and DOC of water samples, respectively. Anions, for example, Cl^- , Br^- , NO_3^- , and NO_2^- etc., are analyzed with Dionex IonPacTM AS19 analytical column (4 mm \times 250 mm) and Dionex IonPacTM AG protective post (4 mm \times 50 mm), the gradient procedure of KOH eluent is as follows: the initial concentration of KOH eluent is 10 $\text{mmol}\cdot\text{L}^{-1}$, which is maintained for 10 minutes, then rises to 20 $\text{mmol}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$ with 2 $\text{mmol}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$, which is maintained for 5 minutes, and the flow rate of eluent is 1 $\text{mL}\cdot\text{min}^{-1}$. Ammonia nitrogen was determined by Nessler reagent spectrophotometry.

2.3.2 TrOCs concentration measurement

The concentration of TrOCs was determined by online solid phase extraction (online-SPE) coupled with LC-MS/MS system. The injection volume of Online-SPE was 100 μL , and DVB cartridges were

used in positive and negative ion modes (SampleQ On-line SPE, 10 mm × 2 mm, Waters) and HLB cartridges (Oasis On-line SPE, 10 mm × 2 mm, Waters). The mobile phase of the liquid chromatography column consisted of 0.1% formic acid solution (A) and acetonitrile (B), the extracted samples were separated by a chromatographic column InfinityLab Poroshell 120 SB-C18 (2.1 mm × 50 mm, 2.7 μm, Agilent) and then entered into mass spectrometry analysis.

2.3.3 Determination of free radical concentration and second-order reaction rate constant

NB, BA, and DMOB concentrations were determined by HPLC equipped with a C18 reverse column (4.6 mm × 250 mm, 5 μm) using a mobile phase of 0.1% acetic acid and acetonitrile (40:60 ratio), the steady-state concentrations of HO·, Cl· and ClO· were calculated according to the degradation rates of the probes (Equations 1–3); other radical concentrations were determined using Kintecus kinetic models. Second-order reaction rate constants (*k* values) of radicals with TrOCs is determined by laser flash photolysis or predicted by quantitative structure–activity relationship (QSAR) model^[20].

$$[\text{HO}\cdot]_{\text{ss}} = \frac{k_{\text{obs(NB)}}}{k_{\text{HO}\cdot,\text{NB}}} \quad (1)$$

$$[\text{Cl}\cdot]_{\text{ss}} = \frac{k_{\text{obs(BA)}} - k_{\text{HO}\cdot,\text{BA}}[\text{HO}\cdot]_{\text{ss}}}{k_{\text{Cl}\cdot,\text{BA}}} \quad (2)$$

$$[\text{ClO}\cdot]_{\text{ss}} = \frac{k_{\text{obs(DMOB)}} - k_{\text{HO}\cdot,\text{DMOB}}[\text{HO}\cdot]_{\text{ss}} - k_{\text{Cl}\cdot,\text{DMOB}}[\text{Cl}\cdot]_{\text{ss}}}{k_{\text{ClO}\cdot,\text{DMOB}}} \quad (3)$$

2.3.4 X-DBPs concentration measurement

After the samples were extracted with methyl tert butyl ether containing internal standard (1,2-dibromopropane), the concentrations of trihalomethanes (THMs), haloacetonitrile (HANs), haloacetaldehyde (HALs), haloketones (HKs), haloacetamide (HAMs) and TCNM were determined by gas chromatography according to the standard method USEPA method 551.1^[21]. Among them, the determination of THMs, Hans, HALS and HKS adopts Agilent DB-5 (0.25 mm × 30 m) separation column, the

temperature of injection port is 120 °C, and the temperature of detector is 290 °C. The determination of hams adopts Agilent DB-1701 (0.25 mm × 30 m) separation column, the temperature of injection port is 200 °C, and the temperature of detector is 260 °C. The injection volume is 2 μL during measurement. The injection mode is non split, and the nitrogen flow rate is 1.0 mL·min⁻¹.

2.3.5 Calculation of water sample toxicity

Toxicity of water samples: the cytotoxicity and genotoxicity of Chinese hamster ovary (CHO) cells were evaluated by X-DBPs generated by the system^[22,23], and the calculation formula is as follows:

$$\begin{aligned} & \text{Total cytotoxicity of water sample} \\ &= \sum \frac{\text{A certain DBP concentration}}{\text{The LC}_{50} \text{ of the DBP on CHO cells}} \end{aligned} \quad (4)$$

$$\begin{aligned} & \text{Total genotoxicity of water sample} \\ &= \sum \frac{\text{A certain DBP concentration}}{\text{The EC}_{50} \text{ of the DBP on CHO cells}} \end{aligned} \quad (5)$$

3. Results and discussion

3.1 Degradation kinetics of TrOCs in membrane-UV/chlorine system

Figure 1 shows the effect of different membrane pretreatment on the degradation kinetics of 23 TrOCs in UV/chlorine system under the same oxidant dosage, light intensity and pH value.

The quasi first-order degradation rates (*k*_{obs}) of TrOCs in UV/chlorine, UF-UV/chlorine and NF UV/chlorine processes are 0.011–8.125 min⁻¹, 0.011–8.813 min⁻¹ and 0.016–9.542 min⁻¹, respectively, of which TNZ and ATZ degrade the slowest and SDM and MA degrade the fastest. UF and NF pretreatment increased the *k*_{obs} of TrOCs by 1%–86% (except TNZ) and 6%–3,132%, respectively, and promoted the degradation of TMP and NAP most significantly. The internal illustration in **Figure 1** compares the overall degradation characteristics of the target pollutants by the three processes. The solid line and dotted line of the box represent the mean and median degradation rates respectively. Compared with UV/chlorine, the average and median rates of UF-UV/chlorine system increased by 21% and 73%,

respectively, while NF-UV/chlorine system increased by 48% and 171% respectively. The above results show that membrane pretreatment can

effectively promote the degradation of TrOCs in UV/chlorine system, and the effect of NF is more significant than that of UF.

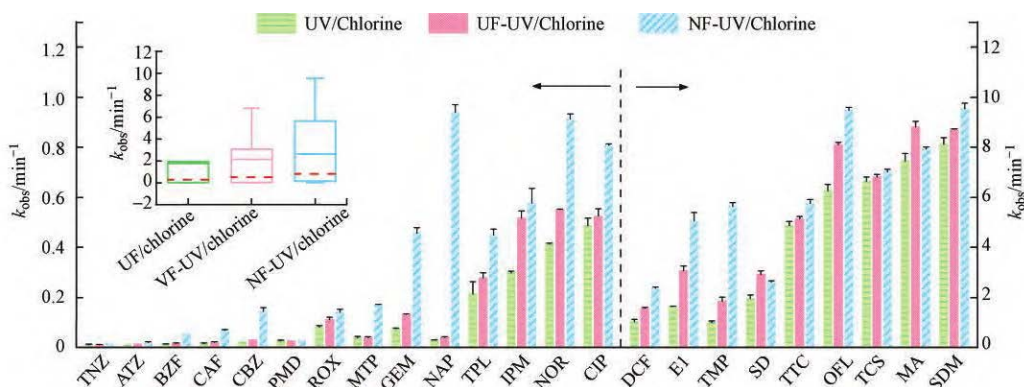


Figure 1. Comparison of the k_{obs} values of 23 TrOCs treated by individual UV/chlorine, UF-UV/chlorine or NF-UV/chlorine processes.

3.2 Degradation mechanism of TrOCs in membrane-UV/chlorine system

In order to explore the mechanism of degradation of TrOCs by membrane-UV/chlorine process, the TOC changes of raw water, UF water and NF water were measured, and it was found that the removal rates of TOC by UF and NF were 9% and 64% respectively. The degradation of TrOCs in three water samples by UVA₂₅₄, UV and chlorination was further determined. The results showed that UVA₂₅₄ of UF water and NF water decreased by 6% and 64%, respectively, compared with raw water, indicating that the removal of DOM by the membrane weakened its UV light shielding effect; the k_{obs} of TrOCs in UF-UV and NF-UV systems increased by 0.5%–8% and 5%–23% respectively compared with the single UV system, indicating that UF has little effect on UV photolysis of TrOCs, and NF has little effect on it; The k_{obs} of TrOCs in UF chlorination and NF chlorination systems increased by 8%–163% (except SDM and TTC) and 9%–181% (except MA) respectively compared with that in chlorination alone. Combined with the change of residual chlorine in the system after 30 minutes of reaction (2.80, 4.10, 2.28 mg·L⁻¹, respectively), it can be seen that the interception of DOM by the membrane reduced the consumption of chlorine by DOM in the oxidation stage ($k_{DOM,HClO} = 0.7\text{--}5 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$)^[24], which promoted the degradation of TrOCs by chlorine; because NF has a stronger interception effect on DOM than UF,

its promoting effect on the degradation of TrOCs is also more obvious.

Table 1 shows the steady-state concentrations of free radicals obtained from probe experiments and kinetic model. Compared with UV/chlorine, the concentration of free radicals in UF-UV/chlorine and NF-UV/chlorine systems increased by 4%–119% and 102%–1,688%, respectively, which may be because the removal of DOM by the membrane reduced its quenching of free radicals ($k_{DOM,HO\cdot} = 2.5 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, $k_{DOM,Cl\cdot} = 1.3 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, $k_{DOM,ClO\cdot} = 4.5 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, $k_{DOM,Cl_2\cdot} = 5.0 \times 10^2 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, $k_{DOM,Br\cdot} = 2.6 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, $k_{DOM,Br_2\cdot} = 3.0 \times 10^2 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, $k_{DOM,CO_3\cdot} \cdot CO_3^{2-} = 2.8 \times 10^2 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$)^[13,25–28]. To sum up, membrane pretreatment can reduce the competitive consumption of reactive oxidation species in UV/chlorine system by intercepting DOM, thus promoting the degradation of TrOCs.

Table 2 lists the k values of active free radicals and 23 TrOCs. It can be seen from **Table 2** that HO[·] has non selectivity and high reactivity, and the k value for TrOCs is generally high, ranging from $2.92 \times 10^9\text{--}2.60 \times 10^{10} \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$. Cl[·] and Br[·] are also highly reactive with TrOCs, with k values respectively ranging from $6.20 \times 10^9\text{--}4.08 \times 10^{10} \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ and $<1.00 \times 10^8\text{--}2.23 \times 10^{10} \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$. In contrast, the overall reaction activity of Cl₂^{·-}, ClO[·], CO₃^{·-} and Br₂^{·-} with TrOCs is low, and the rate constants are respectively $<5.00 \times 10^6\text{--}2.05 \times$

$10^8 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, $< 1.00 \times 10^6 - 4.46 \times 10^{10} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, $4.10 \times 10^6 - 3.07 \times 10^8 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ and $5.00 \times 10^5 - 6.26 \times 10^8 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. At the same time, it can be

found that these four free radicals also have strong selectivity in the reaction with TrOCs.

Table 1. The steady-state concentrations of reactive radicals in UV/chlorine, UF-UV/chlorine, NF-UV/chlorine processes

	OH [•]	Cl [•]	Cl ₂ ^{•-}	ClO [•]	CO ₃ ^{•-}	Br [•]	Br ₂ ^{•-}	ClBr ^{•-}
UV/chlorine	2.23×10^{-14}	2.76×10^{-15}	5.2×10^{-14}	1.74×10^{-13}	7.21×10^{-12}	1.07×10^{-14}	4.82×10^{-13}	7.85×10^{-14}
UF-UV/chlorine	2.45×10^{-14}	3.51×10^{-15}	5.43×10^{-14}	3.81×10^{-13}	7.95×10^{-12}	1.18×10^{-14}	5.20×10^{-13}	8.31×10^{-14}
NF-UV/chlorine	8.14×10^{-14}	6.92×10^{-15}	1.05×10^{-13}	3.11×10^{-12}	2.40×10^{-11}	4.13×10^{-14}	1.53×10^{-12}	2.42×10^{-13}

Note: The steady-state concentrations of OH[•], Cl[•] and Cl₂^{•-} were determined by probe experiments, others were obtained by Kintecus model.

Table 2. The second-order reaction rate constants (k) of free radicals towards 23 TrOCs ($\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$)

TrOCs	$k_{\text{HO} \cdot} (\times 10^9)$	$k_{\text{Cl} \cdot} (\times 10^{10})$	$k_{\text{Cl}_2 \cdot^-} (\times 10^8)$	$k_{\text{ClO} \cdot} (\times 10^8)$	$k_{\text{CO}_3 \cdot^-} (\times 10^7)$	$k_{\text{Br} \cdot} (\times 10^9)$	$k_{\text{Br}_2 \cdot^-} (\times 10^7)$
DCF	$8.38 \pm 1.24^{[29]}$	$3.77 \pm 0.65^{[20]}$	$11.54 \pm 0.52^{[20]}$	$3.54^{[11]}$	$7.80^{[30]}$	$22.3 \pm 0.3^{[31]}$	$27.9 \pm 3.7^{[31]}$
NAP	$8.61^{[29]}$	$2.01 \pm 0.15^{[20]}$	$6.57 \pm 0.43^{[20]}$	$< 23^{[11]}$	—	$13.2 \pm 1.9^{[31]}$	$17.2 \pm 1.6^{[31]}$
MA	11.4a	1.53a	9.02b	9.34b	30.7b	$18.6 \pm 2.1^{[31]}$	$24.8 \pm 3.3^{[31]}$
SD	$4.5 \pm 1.13^{[20]}$	$3.35 \pm 0.22^{[20]}$	$4.27 \pm 0.37^{[20]}$	0.413b	1.02b	$12.1 \pm 1.5^{[31]}$	$16.8 \pm 1.3^{[31]}$
SDM	9.1a	$4.08 \pm 0.24^{[20]}$	$4.46 \pm 0.50^{[20]}$	0.413b	1.02b	$14.6 \pm 1.4^{[31]}$	$15.2 \pm 1.9^{[31]}$
CIP	$5.94 \pm 1.72^{[29]}$	$1.39 \pm 0.35^{[20]}$	$2.19 \pm 0.08^{[20]}$	—	—	$11.0 \pm 0.8^{[31]}$	$8.17 \pm 1.10^{[31]}$
OFL	$4.2 \pm 0.5^{[32]}$	$1.54 \pm 0.25^{[20]}$	$3.48 \pm 0.39^{[20]}$	—	—	—	$0.72 \pm 0.1a$
NOR	$5^{[33]}$	1.14a	—	—	—	—	$15.7 \pm 1.2^{[31]}$
BZF	$8.00 \pm 0.22^{[34]}$	$1.04 \pm 0.09^{[20]}$	—	1.6b	$0.533^{[30]}$	$10.6 \pm 1.7^{[31]}$	$7.67 \pm 0.95^{[31]}$
GEM	$10.0 \pm 0.6^{[34]}$	$2.14 \pm 0.17^{[20]}$	$2.87 \pm 0.12^{[20]}$	$4.16^{[13]}$	$0.410^{[30]}$	$10.7 \pm 1.2^{[31]}$	$9.24 \pm 2.20^{[31]}$
TTC	$7.70^{[29]}$	$1.98 \pm 0.42^{[20]}$	$11.80 \pm 0.79^{[20]}$	—	—	$16.7 \pm 1.5^{[31]}$	$62.6 \pm 4.9^{[31]}$
EI	$26^{[35]}$	$2.06 \pm 0.21^{[20]}$	$3.66 \pm 0.24^{[20]}$	3.12b	9.2b	$9.9 \pm 1.2^{[31]}$	$8.83 \pm 0.97^{[31]}$
TCS	$4.43^{[35]}$	$2.76 \pm 0.44^{[20]}$	$2.48 \pm 0.14^{[20]}$	0.707b	1.83b	$8.99 \pm 0.69^{[31]}$	$2.79 \pm 0.56^{[31]}$
ROX	$5.4 \pm 0.3^{[36]}$	$0.72 \pm 0.07^{[20]}$	$< 0.05^{[20]}$	—	—	$6.66 \pm 0.77^{[31]}$	$1.42 \pm 0.27^{[31]}$
TNZ	$2.92 \pm 0.276^{[37]}$	—	—	$0.0137^{[11]}$	—	$0.41 \pm 0.10^{[31]}$	$0.09 \pm 0.02^{[31]}$
ATZ	$3.0^{[38]}$	$0.687^{[36]}$	$< 0.05a$	$< 0.01^{[38]}$	$0.939^{[30]}$	$< 0.1^{[31]}$	$0.05 \pm 0.02^{[31]}$
CAF	$6.4 \pm 0.71^{[29]}$	$3.87 \pm 0.35^{[20]}$	$9.28 \pm 0.52^{[20]}$	$1.31^{[11]}$	$0.609^{[30]}$	$7.19 \pm 0.69^{[31]}$	$7.58 \pm 0.44^{[31]}$
CBZ	$8.8 \pm 1.2^{[37]}$	$3.30 \pm 0.26^{[20]}$	$0.43 \pm 0.03^{[20]}$	$1.97^{[11]}$	$1.25^{[30]}$	$9.88 \pm 1.05^{[31]}$	—
IPM	$3.3^{[29]}$	$2.75 \pm 0.39^{[20]}$	$20.54 \pm 0.96^{[20]}$	—	—	—	$47.8 \pm 7.3^{[31]}$
MTP	$8.39 \pm 0.06^{[39]}$	$1.71 \pm 0.31^{[20]}$	$5.07 \pm 0.38^{[20]}$	$1.34^{[11]}$	$0.51^{[40]}$	$9.48 \pm 0.72^{[31]}$	$5.76 \pm 0.55^{[31]}$
PMD	$6.63^{[13]}$	$0.62 \pm 0.10^{[20]}$	$1.58 \pm 0.02^{[20]}$	$0.551^{[11]}$	—	—	—
TPL	$8.22 \pm 0.03^{[41]}$	$3.98 \pm 0.42^{[20]}$	$8.78 \pm 0.34^{[20]}$	—	—	$8.33 \pm 0.78^{[31]}$	$1.68 \pm 0.16^{[31]}$
TMP	$6.3 \pm 0.85^{[29]}$	$2.11 \pm 0.12^{[20]}$	$18.78 \pm 0.23^{[20]}$	$446^{[11]}$	$4.91^{[30]}$	$15.0 \pm 2.2^{[31]}$	$24.0 \pm 3.2^{[31]}$

Note: ^a determined by laser flash photolysis experiments; ^b obtained by QSAR models.

According to the steady-state concentration of free radicals in **Table 1** and the k value in **Table 2**, combined with the measured degradation rate of TrOCs in the process of single UV (k_{UV}) and single chlorination (k_{chlorine}), a simplified kinetic model (equation 6) is established, and the predicted degradation rate ($k_{\text{cal.}}$) of TrOCs in UV/chlorine, UF-UV/chlorine and NF-UV/chlorine systems is obtained. The relationship between the two is shown in **Figure 2** by comparing the measured value ($k_{\text{exp.}}$) in **Figure 1**. According to **Figure 2**, $k_{\text{cal.}}$ of 20 TrOCs in

UV/chlorine, UF UV/chlorine and NF-UV/chlorine systems fit well ($0.5 < k_{\text{cal.}}/k_{\text{exp.}} < 2.0$), especially the error values of MA, SDM, OFL, TCS and ROX in the three reaction systems are all within 15%. The $k_{\text{cal.}}$ of IPM, NOR and CIP is significantly lower than that of $k_{\text{exp.}}$, which may be caused by the lack of k value with free radicals such as ClO[•], CO₃^{•-}.

$$k_{\text{cal.}} = \sum k_{\text{radical,MP}} \times [\text{radical}]_{\text{ss}} + k_{\text{UV}} + k_{\text{chlorine}} \quad (6)$$

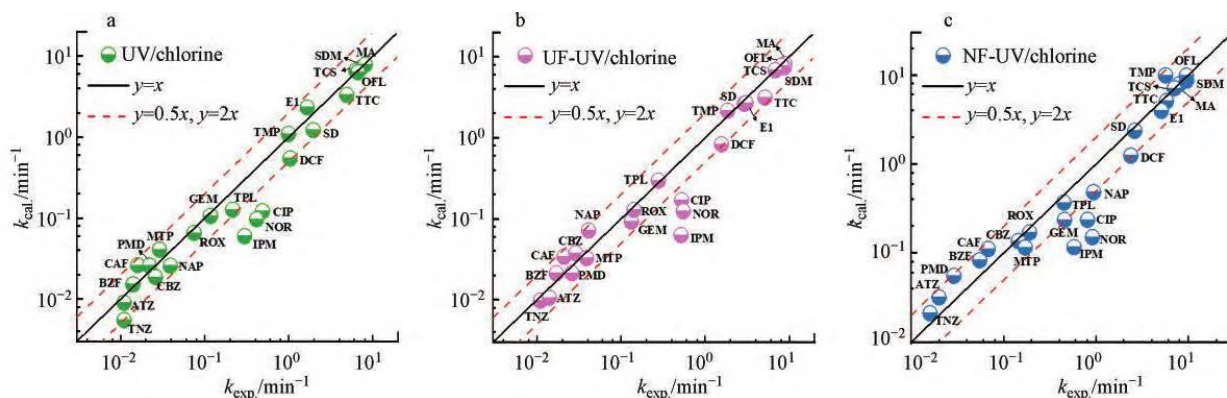


Figure 2. Relationships between $k_{cal.}$ and $k_{exp.}$ of 23 TrOCs in (a) UV/chlorine, (b) UF-UV/chlorine and (c) NF-UV/chlorine processes.

Based on the above results, the contributions of various active species in UV/chlorine, UF-UV/chlorine and NF-UV/chlorine systems to the degradation rate of TrOCs were obtained (**Figure 3**). It can be seen from **Figure 3** that the dominant active species that degrade different TrOCs are different, which can be divided into the following four categories: (1) Class I (G1): mainly degraded by HO^\cdot ($k_{HO^\cdot}/k_{RHS} > 1$), where RHS refers to RCS such as Cl^\cdot , $CO_3^{\cdot-}$ and ClO^\cdot , and active bromine species such as Br^\cdot and $Br_2^{\cdot-}$ (RBS). Such TrOCs include TNZ, ATZ and PMD. (2) Class II (G2): mainly degraded by RHS ($0.2 \leq k_{HO^\cdot}/k_{RHS} < 1$), including BZF, CAF, CBZ, IPM, MTP and NAP. (3) Class III (G3): mainly degraded by chlorine and RHS ($0.5 < k_{RHS}/k_{chlorine} < 2$), including GEM and TMP. (4) Class IV (G4): mainly degraded by chlorine ($k_{RHS}/k_{chlorine} < 0.2$, $k_{HO^\cdot}/k_{chlorine} < 0.2$), including ROX, TPL, NOR, CIP, DCF, E1, SD, TTC, OFL, TCS, MA and SDM. K_{obs} of different TrOCs generally conform to the following

rules: $G1 < G2 < G3 < G4$ (except NAP and TMP). Most substances in G4 contain electron rich groups such as aniline (such as SDM and MA), phenol (such as TCS and TTC), fused rings (such as OFL and TTC), resulting in rapid reaction of chlorine with them^[42]. RHS and HO^\cdot have good degradation effects on some TrOCs with strong chlorine resistance (such as NAP, MTP and PMD). Compared with HO^\cdot non selective degradation of target pollutants, RHS tends to selectively react with TrOCs containing electron donor groups. For example, RCS and RBS have high reactivity with compounds containing amine groups (such as IPM) and methoxy groups (such as NAP and GEM) on the aromatic ring^[13,31]. The contribution of UV and $CO_3^{\cdot-}$ to the degradation of pollutants k_{obs} is generally very small. UV only accounts for a large proportion in the degradation of PMD and IPM (42% and 33% respectively), while $CO_3^{\cdot-}$ only contributes significantly to the degradation of ATZ (26%).

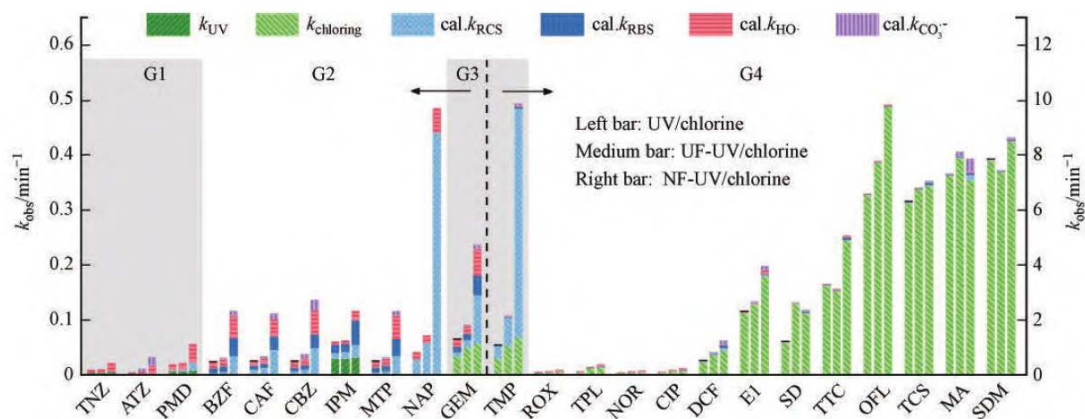


Figure 3. The contributions of reactive species to k_{obs} in UV/chlorine, UF-UV/chlorine and NF-UV/chlorine processes (the shadows represent grouped TrOCs).

3.3 X-DBPs formation and X-DBPsFP of membrane-UV/chlorine system

Figure 4 shows the formation of X-DBPs in raw water, UF water and NF water during separate UV, separate chlorination, UV/chlorine and post chlorination. In each treatment stage, the concentration of THMs is the highest, followed by HANs, and

the concentration of TCNM is the lowest ($<5 \mu\text{g}\cdot\text{L}^{-1}$). Compared with chlorination alone, the concentration of X-DBPs produced by raw water, UF water and NF water in UV/chlorine system increased by 1%–69%, 0.5%–88% and 1%–40%, respectively (except TCNM and TCAM), among which the concentration of THMs increased most significantly.

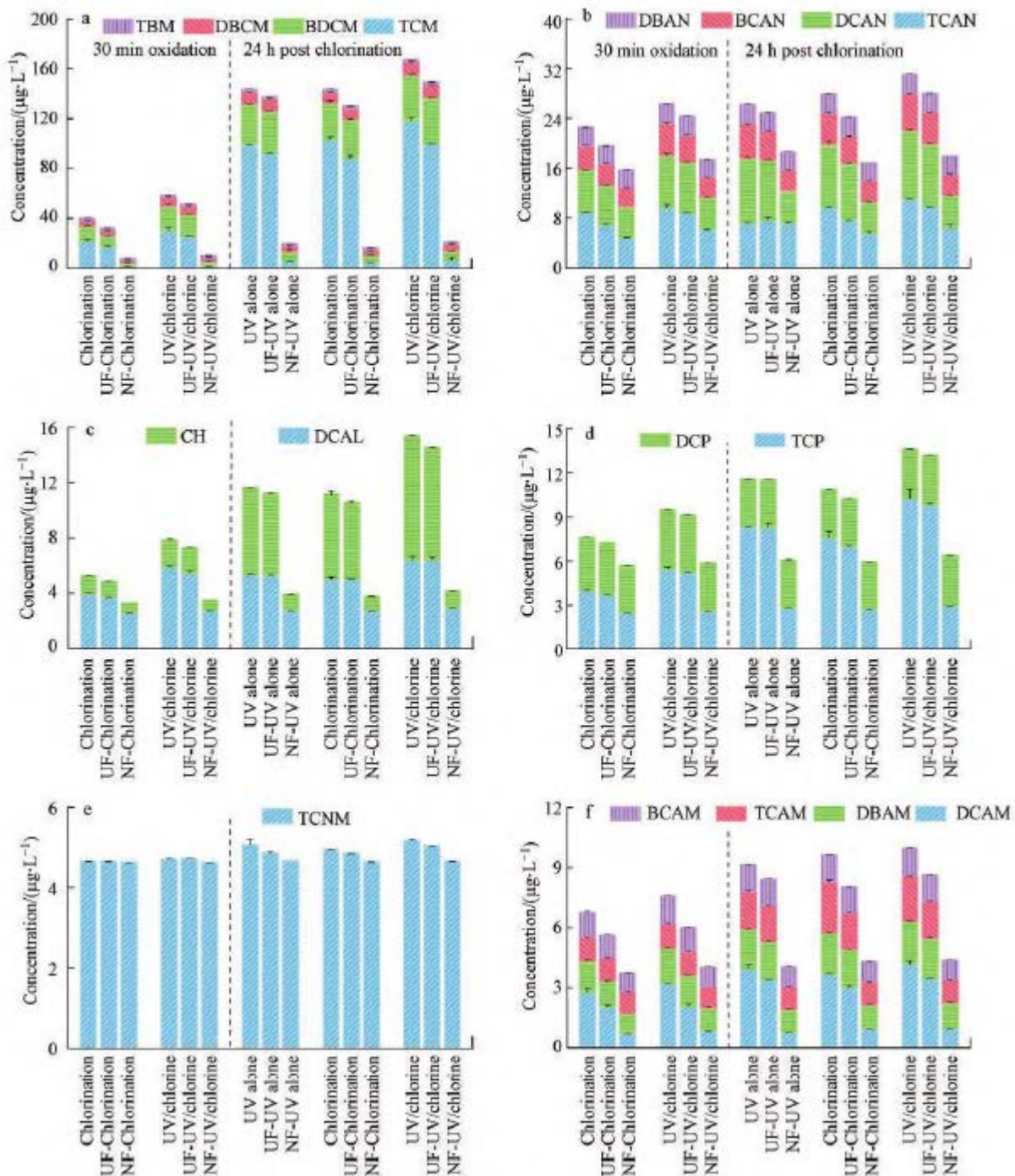


Figure 4. The formation of X-DBPs during individual UV photolysis, chlorination, UV/chlorine and post chlorination processes of wastewater with or without pretreatment of ultrafiltration and nanofiltration.

This may be due to the attack of active free radicals such as HO[·] and R_{HS} in the UV/chlorine system, which changes the properties of DOM, resulting in more X-DBPs precursors^[43], or the direct attack of RCS leads to the formation of X-DBPs^[25]. For example, Xiang *et al.*^[44] believed that the attack of free radicals on aromatic rings in UV/chlorine system would lead to the increase of THMs precursors. Lei *et al.*^[25] confirmed that Cl[·] can be directly added to form chlorinated by-products (CL-BPs) on DOM by using laser flash photolysis technology. Membrane pretreatment can reduce the generation of various X-DBPs in UV/chlorine system to varying degrees. The reduction degree of UF and NF to various X-DBPs is: HAMs (20%) > THMs (12%) > HANs (8%) > HALs (7%) > HKs (4%) > TCNM (<1%) and THMs (83%) > HALS (55%) > HAMs (47%) > HKs (38%) > HANs (34%) > TCNM (2%). It can be seen that UF and NF reduce the generation of hams and THMs most significantly. In general, UF and NF reduced the concentration of X-DBPs in UV/chlorine system by 1%–36% (except TCNM) and 2%–93%, respectively. It can be seen that the reduction of X-DBPs formation by NF is significantly stronger than that by UF.

The experimental results of X-DBPs formation potential showed that the X-DBPsFP of UV/chlorine, UF-UV/chlorine and NF UV/chlorine systems increased by 2%–47% (except TBM, TCAM and BCAM), 2%–47% (except TBM) and 2%–43% (except TCNM and BCAM) respectively than that of chlorination alone, UF chlorination and NF chlorination systems, which may be due to the attack of active free radicals on DOM, resulting in more X-DBPs precursors. For example, Xie *et al.*^[45] reported that HO[·] can convert part of organic matter into aldehydes, thereby promoting the formation of CH in the post chlorination process. In addition, comparing various X-DBPsFS of UV/chlorine, UF-UV/chlorine and NF-UV/chlorine systems, it can be found that UF and NF reduce the generation potential of THMs, HANs, HALs, HKs, TCNM and HAMs by 11%, 10%, 6%, 3%, 2%, 13% and 87%, 42%, 73%, 53%, 10% and 56%, respectively. It can be seen that UF reduces all kinds of X-DBPsfs very little (<15%), while the effect of NF is very obvious (see **Figure 2**).

Except TCNM). It is worth mentioning that the increase of X-DBPsfp in NF-UV/chlorine system in the post chlorination stage (0.5%–19%, THMs 107%) is much lower than that in UF-UV/chlorine system (7%–99%, THMs 189%) and UV/chlorine system (10%–96%, THMs 184%), which shows that NF-UV/chlorine process can effectively reduce the precursors of X-DBPs.

3.4 Cytotoxicity and genotoxicity analysis after membrane-UV/chlorine treatment

Cytotoxicity and genotoxicity are important indicators of biological risk in water, representing chronic toxicity of inhibiting cell growth and acute toxicity of damaging genetic DNA, respectively^[23]. Among all X-DBPs included in the calculation, the order of contribution to cytotoxicity and genotoxicity is HANs > HAMs > HALs > TCNM ≈ THMs and HANs > TCNM > HAMs > DCAL, respectively. **Figure 5** shows the cytotoxicity and genotoxicity of raw water, UF water and NF water after single UV, single chlorination and UV/chlorine and post chlorination treatment.

The results showed that the cytotoxicity and genotoxicity of raw water after UV/chlorine system reaction increased by 19% and 10%, respectively compared with chlorination alone, which was mainly due to the increase of the concentration of HANs and HAMs in UV/chlorine system respectively. However, after pretreatment with UF and NF, the cytotoxicity and genotoxicity of water samples were significantly reduced, and the weakening effect of NF on the two toxicity (29% and 19%, respectively) was stronger than that of UF (8% and 5%, respectively), which was consistent with the result of reduction of X-DBPs production by UF/NF in UV/chlorine system. It is worth noting that the enhancement of cytotoxicity and genotoxicity of NF-UV/chlorine system in the post chlorination stage (4% and 3%) is much lower than that of UF-UV/chlorine (14% and 10%) and UV/chlorine system (11% and 9%), indicating that NF UV/chlorine process can effectively control the enhancement of water toxicity, which is also consistent with the previous conclusion that it can effectively reduce the precursors of X-DBPs.

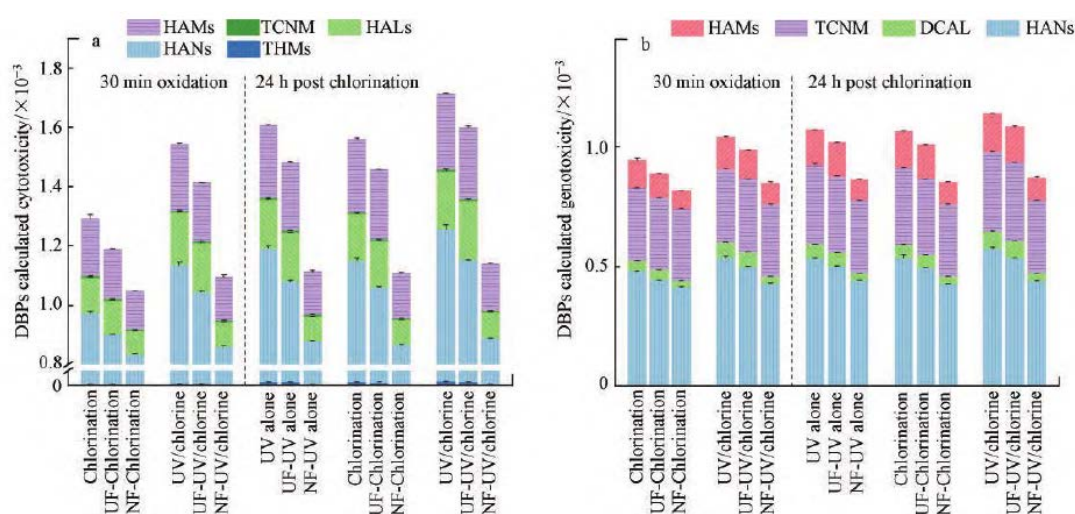


Figure 5. Calculated cytotoxicity (a) and genotoxicity (b) of the wastewater with or without pretreatment of ultrafiltration and nanofiltration after individual UV photolysis, chlorination, UV/chlorine treatment and post chlorination.

4. Conclusions

(1) Compared with UV/chlorine, the degradation rate of TrOCs in UF-UV/chlorine and NF-UV/chlorine systems increased by 1%–86% (except TNZ) and 6%–3,132%, respectively, indicating that membrane pretreatment can significantly promote the removal of TrOCs in UV/chlorine systems, and the effect of NF is stronger than that of UF.

(2) The membrane reduces the light shielding effect, chlorine consumption and radical quenching by intercepting DOM, thus promoting the degradation of TrOCs. The kinetic model established in this study can better predict the degradation rate of TrOCs, so it is further obtained that the degradation mechanism of TrOCs is: TNZ, ATZ and PMD are degraded by HO[•] while 6 TrOCs such as BZF, CAF and CBZ are degraded by RHS, GEM and TMP are degraded by chlorine and RHS, and 12 TrOCs such as ROX, TPL and nor are degraded by chlorine.

(3) Membrane pretreatment can effectively reduce X-DBPs and X-DBPsFP and weaken the toxicity of water samples. The reduction effect of NF on X-DBPs and X-DBPsFP (2%–93% and 10%–87%) was significantly stronger than that of UF (1%–36% and <15%); the weakening effect of UF and NF on cytotoxicity (8% and 29%) was stronger than that of genotoxicity (5% and 19%). In addition, NF UV/chlorine system can significantly reduce the precursor of X-DBPs, so as to control the increase of water toxicity in the post chlorination process.

Acknowledgement

This work was supported by the National Key Research and Development Program of China (2017YFE0133200).

Conflict of interest

The authors declared no conflict of interest.

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