

Article

Degradation of Micropollutants by UV–Chlorine Treatment in Reclaimed Water: pH Effects, Formation of Disinfectant Byproducts, and Toxicity Assay

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Abstract: The utilization of reclaimed water is a reliable and sustainable approach to enhance water supply in water-deficient cities. However, the presence of micro-organic pollutants (MPs) in reclaimed water has potential adverse effects on aquatic ecosystems and human health. In this study, we investigated the occurrence of 12 target MPs in the influent and reclaimed water collected from a local wastewater treatment plant, and the ultraviolet (UV)–chlorine process was applied to analyze its ability to remove MPs. The results showed that all 12 MPs were detected in both the influent and the reclaimed water, with the concentrations ranging from 25.5 to 238 ng/L and 8.6 to 42.5 ng/L, respectively. Over 52% of all the target MPs were readily degraded by the UV–chlorine process, and the removal efficiency was 7.7% to 64.2% higher than the corresponding removal efficiency by chlorination or UV irradiation only. The degradation efficiency increased with the increasing initial chlorine concentration. The pH value had a slight influence on the MP degradation and exhibited different trends for different MPs. The formation of known disinfectant byproducts (DBPs) during the UV–chlorine process was 33.8% to 68.4% of that in the chlorination process, but the DBPs' formation potentials were 1.3 to 2.2 times higher. The toxicity assay indicated that UV–chlorine can effectively reduce the toxicity of reclaimed water.

Keywords: MPs; UV–chlorine process; disinfectant byproducts; toxicity

1. Introduction

China, the largest developing country and one of the most important economic entities in the world, faces increasingly serious water scarcity and water pollution problems. In order to solve these problems, the State Council of China promulgated and implemented the Action Plan for Prevention and Treatment of Water Pollution in 2015. According to the plan, the utilization rate of reclaimed water, which has been proven as a reliable, safe, and sustainable approach to enhance water supply security [1] in water-deficient cities, should reach above 20% by 2020. Reclaimed water is encouraged to be used for landscaping, industrial purposes, agricultural irrigation, and even as a source to replenish groundwater in China, depending on the level of treatment [2–5]. According to the annual statistical yearbook for urban construction, 4.92×10^{10} m³ wastewater was discharged, more than 94.5% of the wastewater was treated by wastewater treatment plants (WWTPs), and 22.8% of the treated wastewater was used to yield reclaimed water in 2017 [6].

In past decades, the widespread occurrence of micro-organic pollutants (MPs) has been documented in the aquatic environment, such as endocrine disrupting compounds (EDCs) and pharmaceutical and personal care products (PPCPs) [7–11]. The presence of EDCs and PPCPs in the aquatic environment has received great attention because of their potential adverse effects on aquatic ecosystems and human health [12,13]. Various engineering techniques, such as bioprocesses, coagulation, filtration, and disinfection, are often applied to produce reclaimed water and have been reported to be inefficient for the removal of EDCs and PPCPs [4,12,14]. A study of 9 PPCPs and 5 EDCs from 12 cities in northern China showed that all the PPCPs and EDCs were found in reclaimed water, with a maximum concentration of 470.8 ng/L [15].

The ultraviolet (UV-based advanced oxidation processes (AOPs), including UV/H₂O₂, UV/O₃, and UV–chlorine, have gained recognition as promising approaches towards removing organic contaminants in aqueous solution through the formation of strong oxidation hydroxyl radicals (HO·). Among these AOPs, the UV/H₂O₂ process has been applied in full-scale water treatment plants, but excessive H₂O₂ is needed to reach the target efficiency because of the low molar absorption coefficient of H₂O₂ [16]. The UV–chlorine process has been considered as an emerging alternative to the UV/H₂O₂ process [17,18], because except for the HO·, reactive chlorine species (RSC) such as Cl·, Cl₂·[−] and ClO· are also generated by the UV–chlorine process. Several studies have proven the effectiveness of the UV–chlorine process in removal of organic contaminants, such as pesticides [19], ronidazole [20], chloramphenicol [21], benzophenone [22], as well as humic acid [23]. However, most of these studies have been conducted in simulated water and do not reflect the real efficiency in real water.

So far, there is a lack of information about the application of the UV–chlorine process for removal of MPs from reclaimed water. In this study, therefore, we collected reclaimed water samples from local WWTPs and investigated the occurrence of 12 target MPs in the reclaimed water. After that, the UV–chlorine process was applied to analyze its ability to remove the target MPs. The effects of chlorine concentration and initial pH on the degradation process were investigated. The formation of disinfectant byproducts, the cytotoxicity and genotoxicity of the reclaimed water before and after UV–chlorine treatment were also evaluated.

2. Materials and Methods

2.1. Materials

Estrogen (E1), 17 α -estradiol (17 α -E2), 17 β -estradiol (17 β -E2), ethinylestradiol (EE2), estriol (E3), carbamazepine (CBZ), naproxen (NAP), clarithromycin (CLA), diclofenac (DCF), ibuprofen (IBP), bisphenol A (BPA), and indomethacin (Indo) were purchased from Sigma-Aldrich (USA). Sodium hypochlorite (NaOCl) solution containing 10% free chlorine, methanol, methyl-tert-butyl ether (MTBE), and sodium thiosulfate (Na₂S₂O₃) were obtained from Aladdin (Shanghai, China). Sodium hydroxyl (NaOH) and sulfuric acid (H₂SO₄) were supplied by Fuchen Chemical Reagent Factory (Tianjin, China). Standards of trichloromethane (TCM), dichloroacetic acid (DCAA), and trichloroacetic acid (TCAA) were purchased from Supelco (Bellefonte, PA, USA). All reagents were of at least analytical grade and were used as received. The stock solutions were prepared in Milli-Q water.

2.2. Sample Collection

Triple water samples were collected from a local wastewater treatment plant (WWTP) from 24 June 2018, to 22 July 2018. The biotreatment process for the WWTP was anaerobic–anoxic–oxic (A/A/O). Coagulation, sedimentation, and sand filtration were employed to produce reclaimed water. The collected samples were filtered through 0.45 μ m membrane filters and stored at 4 °C before use. The water quality parameters are listed in Table 1.

Table 1. The water parameters of the local WWTP.

Parameters	Influent	Reclaimed Water
pH	7.2 ± 0.2 *	7.1 ± 0.2
UV ₂₅₄ (cm ⁻¹) **	0.26 ± 0.04	0.06 ± 0.01
NH ₃ -N (mg/L)	25.2 ± 3.6	2.6 ± 0.2
Total phosphorus (mg/L)	2.8 ± 0.2	0.4 ± 0.1
COD (mg/L)	240 ± 16	40 ± 5

* Standard deviation, ** the UV absorbance at 254 nm.

2.3. Experimental Procedures

UV photolysis and UV–chlorine advanced oxidation experiments were conducted in a cylindrical glass reactor, the inner diameter of which was 6.0 cm, and the effective height was 30.0 cm. A low-pressure mercury UV lamp (15 W, 60 mW/cm², Ruipu, Yangzhou, China) with an outer diameter of 3.0 cm and a height of 23.0 cm was fixed at the center of the reactor with a collimated tube. A 500 mL water sample was added into the reactor and a given volume of NaOCl solution was spiked into the sample to obtain a given initial chlorine concentration. The magnetic stirrer was used to keep the samples well mixed. The temperature was kept at 22 ± 1 °C during the experiment. After reaching a given time, the UV lamp turned off, 5 mL of the sample was used to determine the residual-free chlorine, and the other sample was quenched by the addition of Na₂S₂O₃ and concentrated by solid-phase extraction (SPE) for analysis of MP concentration.

The chlorination was conducted in an amber glass bottle. It was simulated by adding a given volume of NaClO solution to a 500 mL sample to obtain a given initial chlorine concentration. After reaching a given time, 5 mL of the sample was used to determine the residual-free chlorine, and the other sample was quenched with the addition of Na₂S₂O₃ and concentrated by SPE for analysis of MP concentration.

All the experiments were conducted in triplicate and the standard deviations were shown.

2.4. Solid-Phase Extraction Procedure

The SPE procedure was carried out for MP analysis by an Aqua Trace 899 automated SPE machine (GL Science, Tokyo, Japan). A 500 mL of sample was extracted by a C18 SPE cartridge (6 mL, 500 mg). The cartridge was preconditioned consecutively with 2 mL Milli-Q water, 2 mL of acetonitrile, and 2 mL of methylene dichloride. The samples passed through the cartridge at a flow rate of 10 mL/min. Then, the cartridge was rinsed with 5 mL Milli-Q water and 5 mL of hexyl hydride. The analytes absorbed on the cartridge were eluted with 4 mL of hexyl hydride at a flow rate of 3 mL/min and then dried with N₂. After that, 1 mL of acetonitrile was added, vortex oscillation was used to resolve the dried analytes, and the resolved analytes were stored at 4 °C and analyzed using liquid chromatography-tandem mass spectrometry (LC-MS/MS) within a week.

2.5. Formation Potential of Disinfectant Byproducts

The formation potential of disinfectant byproducts was assessed as in our previous work [24]. Briefly, 100 mL water was adjusted to pH 7.0 ± 0.2 with 0.1 M NaOH or H₂SO₄. 20 mg/L NaOCl was added, and then incubated at 25 °C for 24 h in the dark. The residual-free chlorine was kept over 2 mg Cl₂/L. Chlorine was analyzed by N, N-diethyl-p-phenylenediamine (DPD) method at 515 nm via T6 spectrophotometer (Pgeneral, China). The reactions were halted by the addition of sodium thiosulfate solution and samples were collected for gas chromatography (GC) analysis.

2.6. Analytical Methods

In this study, a high performance liquid chromatography (HPLC) system (HPLC-10AVP, Shimazu, Tokyo, Japan) consisting of a Waters Symmetry C18 column (50 mm × 2.1 mm, 3.5 µm particle size) was used for MP separation. The mobile phase was composed of ultrapure water (eluent A) and

acetonitrile (eluent B). The following gradient was used: 0–4 min, 45% A; 4–4.2 min, 45% A to 55% A; 4.2–5.0 min, 55% A to 10% A; 5.0–7.0 min, re-equilibrate with 45% A. The flow rate of the mobile phase was 0.25 mL/min for all stages and the sample injection volume was 20 μ L. Analyses were performed using Qtrap 5500 tandem mass spectrometry (Applied Biosystems Sciex, Vaughan, ON, Canada) equipped with a turbo ion spray source. Data acquisition was performed in the negative ion mode, and the optimized parameters were as follows: source temperature, 120 $^{\circ}$ C; desolvation temperature, 380 $^{\circ}$ C; capillary voltage, 3.2 kV; desolvation gas flow, 700 L/h; cone gas flow, 80 L/h. Argon (99.999%) was used as the collision gas. Quantitative analysis was performed in the multiple reaction monitoring (MRM) mode.

The overall method recoveries for the target analytes were between 78.3% and 116.1%, with a relative standard deviation of less than 13.4%. The limits of quantification of the target analytes were between 1 μ g/L and 5 μ g/L.

A gas chromatograph (PerkinElmer Clarus 680, Waltham, MA, USA) equipped with an electron capture detector and a DB-5 capillary column (30 m \times 0.25 mm \times 0.25 μ m) was used to analyze the concentration of TCM, DCAA, and TCAA following United States Environmental Protection Agency (USEPA) methods 551.1 and 552.3, with minor modifications.

2.7. Cytotoxicity Test

For cytotoxicity assay, water samples were pretreated following the method described by Pan et al. [25], with minor modifications. Overdosed Na_2SO_4 was added to a 500 mL water sample and acidified to pH 0.5 with concentrated sulfuric acid, while 100 mL MtBE was used to extract the water samples. The collected organic phase was concentrated to 1 mL with rotary evaporation and then mixed with 5 mL of ethyl acetate. The mixture was then dried under a high purity nitrogen stream and the organics were solvent transferred to 20 μ L of DMSO.

3-(4,5)-dimethylthiazolium(-z-y1)-3,5-di-phenyltetrazoliumromide (MTT) assay and lactate dehydrogenase (LDH) assay were conducted to evaluate the cytotoxicity of treated water samples. Both assays were performed on human hepatoma cell line (HepG2) cells, which were provided by the school of life science. The MTT assay was conducted following the description of our previous work [26]. As for LDH assay, the HepG2 cells were seeded and incubated in 96-well plates at 37 $^{\circ}$ C for 24 h, then exposed to the DMSO-dissolved samples for 24 h. The LDH content in the supernatants was measured using the LDH Cytotoxicity Assay Kit (KeyGEN BioTECH, Nanjing, China), according to the manufacturer's protocol. LDH activity was determined by spectrophotometric absorbance at 490 nm.

2.8. Statistical Analysis

T-test was performed for significance analysis by using the SPSS software package (IBM SPSS statistic 23.0), and the significance was determined at the 95% confidence limit ($p < 0.05$)

3. Results and Discussion

3.1. Occurrence of Micropollutants in Reclaimed Water

Firstly, the occurrence of the target MPs, consisting of 6 EDCs (E1, 17 α -E2, 17 β -E2, EE2, E3, and BPA) and 6 PPCPs (CBZ, CLA, DCF, IBP, Indo, NAP), in a local water treatment plant was investigated. As can be seen from Figure 1, all the target MPs were detected not only in the influent but also in the reclaimed water. The concentrations of MPs in the influent ranged from 25.5 to 238 ng/L, and CLA, BPA, and Indo were the most abundant MPs, with relatively high concentrations (>180 ng/L). The concentrations of MPs in the influent of current work were comparable with previous studies in China [27,28], revealing a national wide usage and release of these MPs.

All the target MPs with concentrations between 8.6 and 42.5 ng/L were detected from the reclaimed water, and even the wastewater was treated by the biotreatment process followed by tertiary treatment processes (coagulation, sedimentation, and sand filtration). The removal efficiencies for the target MPs varied largely from -7% to 92.6% ($p < 0.05$) with secondary and tertiary treatment processes, and

the results were consistent with previous work [28]. It is noted that EE2 showed negative removal efficiency ($p < 0.05$), probably due to the transformation from the conjugated form to the free form [29]. Except for EE2, only 27.8% of the removal efficiency was found for CBZ, which may be due to its persistence in conventional wastewater treatment processes.

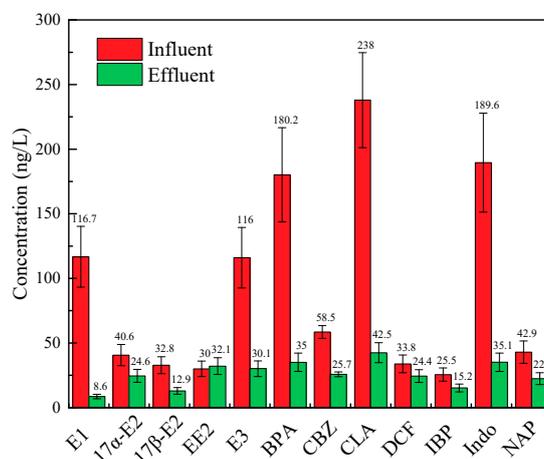


Figure 1. The concentrations of micro-organic pollutants (MPs) in the influent and reclaimed water of the local wastewater treatment plant (WWTP).

3.2. Degradation of Micropollutants

Figure 2 shows the comparison of the target MPs degradation from chlorine oxidation, UV photolysis, and UV–chlorine advanced oxidation process at pH 7.0 and 10 mg/L chlorine in reclaimed water in 5 min.

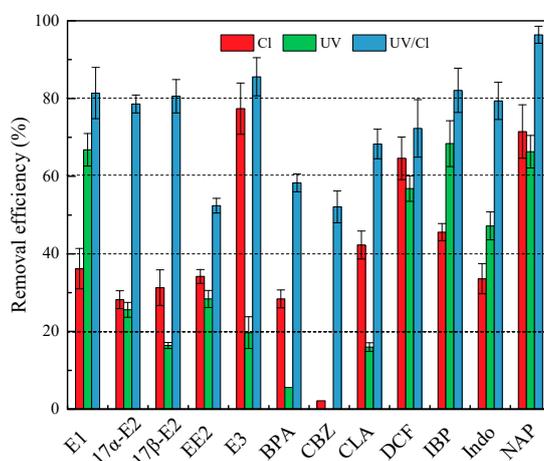


Figure 2. The micro-organic pollutant (MP) removal efficiency under different treatments.

Chlorine is highly selective, and its reactivity was proven to be related to the chemical structure (functional group and dissociation) of organic materials [30]. Only 2.2% CBZ was degraded by chlorination under 10 mg/L chlorine after 5 min in the present work, and the negligible chlorination efficiency of CBZ is in accordance with the results reported in different water matrices [31–33]. The other target MPs exhibited specific degradation efficiency values ranging from 28.2% to 77.4%, and E3 was most sensitive to chlorine.

Direct UV photolysis for MPs was ascribed to the molar absorption coefficient and quantum yield [34]. Among the target MPs, IBP exhibited the highest degradation percentage of 68.4% by UV photolysis. 5 MPs, including 17β-E2, E3, BPA, CBZ, and CLA, showed degradation percentage of lower than 20%, and negligible photolysis efficiency was found for CBZ.

Over 52% of all the 12 target MPs were readily degraded when UV–chlorine advanced oxidation process was used, and the removal efficiency was 7.7%–64.2% higher than the corresponding removal efficiency by chlorination or UV irradiation only. Especially, the degradation of CBZ, which was resistant to both chlorination and UV irradiation, was enhanced to 52.1%, which was 50.1% higher than the corresponding combined removal efficiency by chlorination and UV irradiation. As mentioned above, both chlorination and UV irradiation are selective, and the reactivity relates to the properties (chemical structure, molar absorption coefficient, and quantum yield) of organic materials, which result in low degradation efficiency for some MPs. Potent nonselective oxidizing agents, including $\text{OH}\cdot$ and $\text{Cl}\cdot$, can be generated during the UV–chlorine process [31], which can react with MPs and result in the significant enhancement of removal efficiency. Based on the above results, it is suggested that the UV–chlorine treatment has potential practical application in removal of MPs from real reclaimed water.

3.3. Effect of Initial Chlorine Concentration

Figure 3 shows the degradation efficiency of MPs from UV–chlorine processes at pH 7.0 in reclaimed water after 5 min with different initial concentrations of chlorine. Overall, the degradation efficiency for all the MPs increased with the increasing initial chlorine concentration. This is because chlorine is the primary source of the production of radicals, such as $\text{OH}\cdot$ and $\text{Cl}\cdot$, which accounts for MP degradation. On the other hand, as mentioned above, chlorine itself could oxidize MPs to some extent. Hence, the higher initial concentration of chlorine resulted in higher MP degradation efficiency.

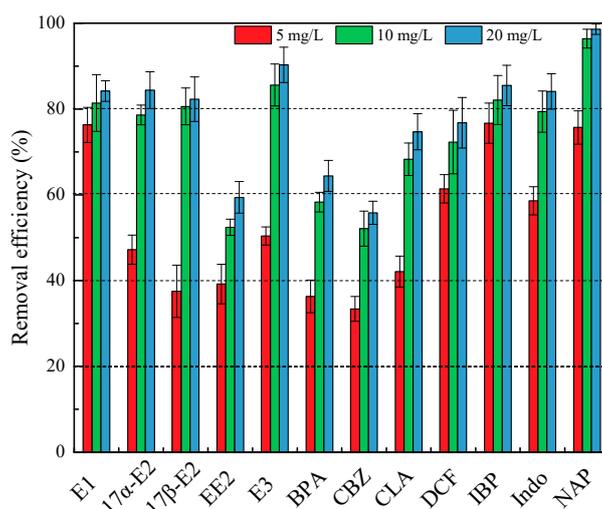


Figure 3. Effect of initial concentrations of chlorine on the degradation efficiency of MPs from UV–chlorine processes.

It should be noted that remarkably increased degradation efficiencies (5.1%–43.1%) were found when the initial concentration of chlorine increased from 5 to 10 mg/L, and the degradation efficiencies increased only 1.7%–6.4% when the initial concentration of chlorine increased from 10 to 20 mg/L. This trend is consistent with previous works when the UV–chlorine process was applied to degrade chloramphenicol [21] and six typical pesticides [19]. This phenomenon is presumably because when the chlorine concentration was lower than an optimal value, increasing the chlorine concentration promoted the production of $\text{OH}\cdot$. However, when the initial chlorine concentration was higher than an optimal value, excessive chlorine could act as a radical scavenger and UV filter [21]. This result is also supported by the mathematical model calculation, which predicts a 30% increase in net $\text{OH}\cdot$ production at pH 6.5 and no increase at pH 8.0 when the chlorine dose increases from 5 mg/L to 10 mg/L [35]. Therefore, there was a limited increase in MP degradation efficiencies when the initial concentration of chlorine increased from 5 to 10 mg/L.

3.4. Effect of pH

According to the local WWTP's regular monitoring data, the pH value of the reclaimed water was 7.0 ± 0.7 . As an essential environmental factor, the pH can affect the formation of free radicals and the ionization of organic pollutants. Thus, in the present work, the effects of pH on MP degradation by UV–chlorine were conducted at pH 6.0, 7.0, and 8.0, with 10 mg/L chlorine in reclaimed water over 5 min. The results are shown in Figure 4. Generally, the pH had a slight influence on the MP degradation, and with increasing pH from 6.0 to 8.0, the degradation of 7 MPs decreased, including 6 estrogens and CBZ, while 4 MPs increased, including CLA, DCF, IBP, and Indo. The pH had a negligible influence on the degradation of NAP. Previous studies demonstrated that lower concentrations of $\text{OH}\cdot$ and $\text{Cl}\cdot$ but a higher concentration of $\text{ClO}\cdot$ formed at higher pH levels [21,31,33]. With increasing pH, the decreasing concentrations of $\text{OH}\cdot$ and $\text{Cl}\cdot$ could be responsible for the decreased removal efficiencies of the 7 MPs, while the enhancement of $\text{ClO}\cdot$ could contribute to the accelerated degradation of MPs, such as CLA, DCF, IBP, and Indo.

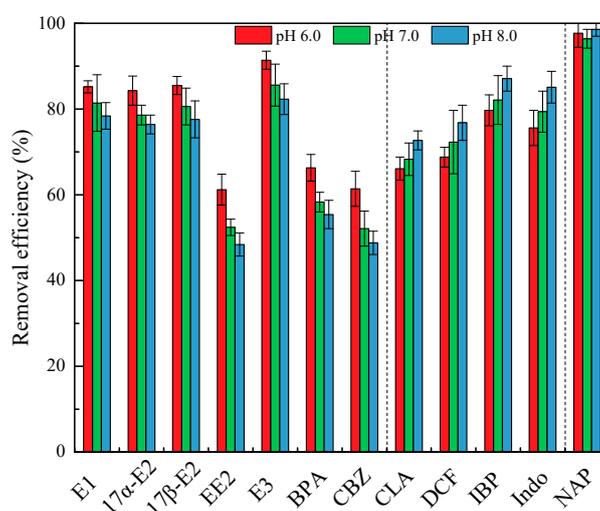


Figure 4. Effect of pH on the degradation efficiency of MPs from UV–chlorine processes.

3.5. DBP Formation

The formation of chlorinated DBPs, such as trihalomethanes (THMs) and haloacetic acids (HAAs), is of concern in the water treatment process when chlorine is applied. The known DBPs' yields in the chlorine oxidation and UV–chlorine process were evaluated.

Previous works reported that the UV–chlorine process could significantly increase the formation of DBPs, including THMs and HAAs, not only in commercial organic matter samples [36] but also in river water samples [37]. Different results were found in our work. After reacting at an initial chlorine concentration of 10 mg/L during the UV–chlorine process for 5 min, the formation amounts of TCM, TCAA, and DCAA were 7.6, 6.5, and 3.2 $\mu\text{g/L}$, respectively, which were 33.8%–68.4% of those formed during chlorination alone. The lower DBPs yields during the UV–chlorine process may contribute to the faster chlorine consumption by UV photolysis, which leads to the reduction of free chlorine available for the reactions with DBP precursors in reclaimed water. The residual chlorine values were 4.26 and 1.06 mg/L for chlorination and UV–chlorine process. On the other hand, the formation of $\text{HO}\cdot$ in the UV–chlorine process can inhibit the reaction of chlorine with DBP precursors because of the nonselectivity of $\text{HO}\cdot$ oxidation, leading to lower DBP formation.

Though the yields of DBPs in the UV–chlorine process were much lower than in the chlorine oxidation process, the DBP formation potential showed a reverse trend. The formation potentials of TCM, TCAA, and DCAA were 75.2, 46.8, and 27.4 $\mu\text{g/L}$ with UV–chlorine pretreatment, which were 1.3 to 2.2 times higher than those with only chlorine pretreatment following post-chlorination. This phenomenon can be explained by the formation of $\text{HO}\cdot$ during the UV–chlorine process, and $\text{HO}\cdot$ is known to readily react with DBP precursors in water through either hydrogen abstraction from the

C-H bond or addition to the C=C bond and C=O bond, which are conjugated with aromatic rings [38]. After HO· exposure, precursors that carry electron-donating groups generated products that were much more reactive toward electrophilic halogenation [39], leading to more DBP formation.

3.6. Cytotoxicity

Figure 5 shows the HepG2 cell death percentage according to MTT assay. One can readily see that the cell death percentage for the control incubation was about 15.1%, and the cell death percentage increased to 20.1% ($p < 0.03$, p value means significant difference between “target” and “normal”) when the cells were exposed to the extract of the reclaimed water, which means the reclaimed water produced from the WWTP water exhibited toxicity. The chlorine oxidation, UV photolysis, and UV–chlorine advanced oxidation processes can effectively reduce the toxicity of reclaimed water to a comparable level of the control incubation. From the perspective of LDH release, as can be seen from Figure 6, the extract of the water samples can significantly induce the LDH release, which means the water samples exhibited toxicity. The LDH release increased to 145.5% ($p < 0.04$, p is the significant difference in comparison with the control group) of the control cells when the cells were exposed to the reclaimed water extract. However, when the chlorine oxidation and UV–chlorine oxidation processes were applied, the LDH release levels decreased to 135.4% and 120.9% ($p < 0.05$, p is the significant difference in comparison with the control group) of the control cells, respectively. The results indicate that although the reclaimed water exhibits toxicity, the UV–chlorine can effectively reduce the toxicity.

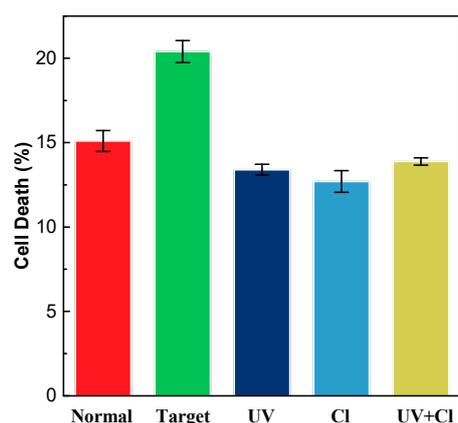


Figure 5. The human hepatoma cell line (HepG2) cell death percentage for the extract of different water samples (raw = reclaimed water; UV = reclaimed water treated by UV photolysis; chlorine = reclaimed water treated by chlorine oxidation; UV–chlorine = reclaimed water treated by UV–chlorine oxidation).

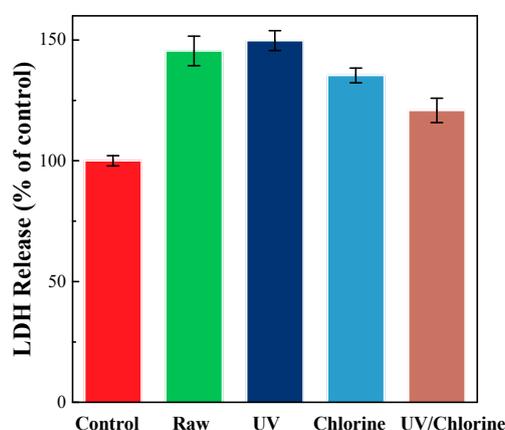


Figure 6. The lactate dehydrogenase (LDH) release for the extract of different water samples (raw = reclaimed water; UV = reclaimed water treated by UV photolysis; chlorine = reclaimed water treated by chlorine oxidation; UV–chlorine = reclaimed water treated by UV–chlorine oxidation.).

4. Conclusions

In summary, dozens to hundreds of ng/L of the 12 target MPs were detected from the influent of the local water treatment plant. Even after being treated by the combination of bio- and tertiary treatment processes, 8.6 to 42.5 ng/L of the 12 MPs were detected in the reclaimed water. Due to the formation of nonselective oxidizing radicals, the MPs removal efficiency was significantly enhanced by the UV–chlorine process. The higher initial concentration of chlorine resulted in higher MP degradation efficiency. With increasing pH from 6.0 to 8.0, the degradation of 7 MPs decreased, while 4 MPs increased. The pH had a negligible influence on the degradation of NAP. Lower amounts of known DBPs formed during the UV–chlorine process than in the chlorination process, however, the DBP formation potentials for the UV–chlorine process were 1.3 to 2.2 times higher than in the chlorination process. The UV–chlorine process can effectively reduce the toxicity of reclaimed water.

Author Contributions: C.W. and Z.Y. conceived and designed the experiments. C.W. and M.M. performed the experiments. C.W., W.Y., and M.H. analyzed the data. W.Y. contributed analysis tools. C.W. and W.Y. wrote the paper.

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Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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