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Role of trace TEMPO as electron shuttle in enhancing chloroquine phosphate elimination in UV-LED-driven persulfate activation process

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A B S T R A C T

Chloroquine Phosphate (CP) is an antiviral drug used for treatment of COVID-19. It is released into wastewater and eventually contaminates natural water. This study reports an effective homogeneous catalysis way for CP degradation by the 2,2,6,6-Tetramethylpiperidine-N-oxyl (TEMPO) enhanced persulfate (PDS) activation under UV-B-LEDs irradiation at 305 nm. TEMPO at a low concentration (0.1 \textmu M) enhanced CP degradation in UV$_{305}$/PDS process in deionized water at different pHs, in different anions and different molecular weight dissolved organic matter solutions and in real surface water. The enhancement was verified to be attributed to the electron shuttle role of TEMPO, which promoted the yield of SO$_4^-$ by enhancing electron donating capacity of the reacting system. The degradation products of CP and their acute toxicities suggested that UV$_{305}$/PDS/TEMPO process has better performance on CP detoxification than UV$_{305}$/PDS process. This study provides a new way to tackle the challenge of pharmaceutical pollutions in homogeneous photocatalysis process for natural water and sewage restoration.

1. Introduction

Chloroquine Phosphate (CP, structure shown in Fig. S1) is an antiviral drug that is recommended by the World Health Organization (WHO) for the treatment of Corona Virus Disease 2019 (COVID-19) [1–3]. It was inevitably released from municipal and hospital wastewater to surface water and bioaccumulated in aquatic organisms, which poses health threat to aquatic organisms and human beings [4,5]. This issue becomes even severer during the pandemic period, and methods to effectively reduce/eliminate CP in surface water are urgently needed.

Previous studies investigated the CP degradation by advanced oxidation process (AOPs) or photocatalytic processes, such as the electron-Fenton oxidation process and the metal-organic frameworks (MOFs) enhanced sulfate radical-based AOP [6,7]. UV/persulfate (UV/PDS) is an AOP that generates sulfate radicals (SO$_4^-$) and hydroxyl radicals (HO-) through cleavage of O-O bonds of persulfate molecule under UV irritation. SO$_4^-$ and HO- have redox potentials of 2.5 – 3.1 V and 1.8 – 2.7 V respectively, and can oxidize a wide spectrum of contaminants [8,9]. Attempts have been made to further improve the UV/PDS process in terms of radical yield in recent years [10]. One of the promising ways to achieve this target is via electron shuttle. In general, electron shuttle enhances AOP treatment efficiency via two main pathways: (1) electron shuttle can be transformed into ionic state upon the excitation of photon, which reacts with and destructs contaminants directly. (2) electron shuttle can store the electrons and pass them to the oxidant precursor (e.g., PDS), which enhances PDS activation and radical yield and contaminant degradation [7,11,12]. Series of redox mediators, such as 2,2′-azino-bis(3-ethylbenzothiazoline)-6-sulfonate (ABTS) and 1-hydroxybenzotriazole (HBT) has been used to enhance contaminants degradation in AOPs. Previous literatures reported that ABTS could enhance diclofenac abatement by promoting horseradish peroxidase (HRP) to decompose H$_2$O$_2$ in HRP/H$_2$O$_2$ process or accelerating Fe(III)/Fe(II) cycle in Fe(II)/peracetic acid (PAA) process [13,14]. Besides, ABTS could extremely accelerate Mn(VI) to degrade...
phenols in aqueous permanganate process [15]. These phenomena could be attributed to two aspects of mechanisms. On one aspect, the oxidation state of ABTS (ABTS⁺) directly oxidized pollutants; on the other aspect, the electron transfer process in ABTS/ATBS⁺ cycle accelerated the redox efficiency and enhanced the generation of radicals which promoted the degradation of pollutants. HBT had similar mechanism on Mn (VII) in aqueous permanganate process, which promoted electron transfer between Mn(VII) and pollutants to initiate bond cleavage, aromatic ring open and decarboxylation [15–17]. However, most of the electron shuttles were used in the heterogeneous systems, involving the solid-liquid electron transfers mechanisms. The roles of electron shuttles in homogeneous AOP systems are rarely known.

2,2,6,6-Tetramethylpiperidine-N-oxyl (TEMPO) was often used as a probe compound to demonstrate the existence of reactive oxygen species (ROS) by using the electron paramagnetic resonance spectroscopy (EPR) [18,19]. It was also reported to be oxidized to TEMPO oxoammonium cation (acetylaminio-2,2,6,6-tetra methyl-1-oxo-piperidinium tetrafluoroborate, TEMPO⁺) by the permanganate, which was then converted to hydroxyamine (TEMPOH) and transformed back into TEMPO [20]. In this cycle, TEMPO⁺ acted as an oxidant to degrade a number of contaminants. However, to our best knowledge, there is no research employing TEMPO in the UV/PDS process to examine the potential role of TEMPO as an electron shuttle for improving efficiency of the AOP.

The central hypothesis of this study was that TEMPO would enhance the yield of radicals through promoting electron transfer in the UV/PDS process, which in turn improved the degradation of CP. To verify this hypothesis, the concentration-dependent effect of TEMPO on the radical generation and CP degradation were explored, and the second-order rate constants of different of radicals towards CP were determined. In addition, the kinetics of CP degradation in the UV305/PDS and UV305/PDS/TEMPO process with different pHs were investigated and compared, and the enhancement effect of TEMPO on CP degradation the UV305/PDS process was also demonstrated in anions and three molecular weight DOM (< 1 kDa, 1 – 3 kDa and 3 – 5 kDa) deionized water solutions as well as in two real surface water. Specially, the effect of high concentration chloride ion on CP degradation in UV305/PDS/TEMPO process was investigated. Finally, the degradation pathways of CP in UV305/PDS/TEMPO process were proposed, and the toxicity of CP and its degradation products were assessed using ECOSAR method.

2. Material and methods

2.1. Chemicals

The details of the chemicals and materials used in this study are provided in Text S1 in Supplementary Information (SI).

2.2. Experimental procedures

The UV radiation was provided by a UV-LED setup emitting light at a wavelength of 305 nm (UVB range, hereafter referred to UV305). The UV-LED at this wavelength was selected because 1) UV-LEDs at UVB range photolysis experiments. A quartz plate was used to cover the reactor to prevent the evaporation of the chemicals from the reaction solution. Gentle mixing was provided throughout the reaction by using a magnetic stirrer. The reaction was maintained at 25 °C using a water bath. 1 mL of the reaction solution was taken at predetermined time intervals and transferred into an amber vial pre-filled with 0.5 mL of 50 mM ascorbic acid to quench the residual oxidants or radicals [24]. Samples were then subjected to the analyses of the residual concentrations of CP. Meanwhile, 1 mL of the reaction solution was taken at predetermined time intervals and immediately transferred into an amber vial without any scavenger to analyze the residual concentration of persulfate [25].

To investigate the role of TEMPO on the degradation of CP by the UV305/PDS process, experiments were conducted in the similar manner except that aliquot of TEMPO stock solution was additionally added into the reaction solution before UV305 irradiation, to give an initial TEMPO concentration of 0.05, 0.1, 0.2 μM, respectively. Control group of experiments for CP degradation by UV305 alone, PDS alone, TEMPO alone, UV305/TEMPO and PDS/TEMPO combination were conducted in the similar manner in the absence of oxidants or UV305 light. To verify the role of TEMPO⁺ on the degradation of CP in UV305/PDS process, experiments were conducted in the similar manner except that aliquot of TEMPO⁺ stock solution was spiked into the reaction solution before UV305 irradiation, to give an initial TEMPO⁺ concentration of 0.1 μM.

To determine the steady state concentrations of hydroxyl radical (HO·), sulfate radical (SO₄²⁻), chlorine radical (Cl·), tests were conducted in a similar manner, except that several probe compounds were additionally spiked into the reaction solution. The details of this approach were described in Text S2.

To evaluate the effect of pH on the degradation of CP by the UV305/PDS process, experiments were conducted in the similar manner except that predetermined quantities of phosphate buffer solutions were added into the reaction solution before UV irradiation, to give the solution pH at 5.0, 6.0, 7.0, 8.0 and 9.0, respectively.

To evaluate the effects of series of anions (HCO₃⁻, NO₃⁻, SO₄²⁻, Cl⁻) and three molecular weights of DOM on the degradation of CP by the UV305/PDS process, experiments were conducted in the similar manner except that predetermined quantities of NaHCO₃, NaNO₃, Na₂SO₄, NaCl and three solutions of per-ultrafiltrated SRDOM with different molecular weight and original SRDOM solutions were added into the reaction solution before UV irradiation, to give the solution HCO₃ at 1.0, 3.0, 5.0 mM; NO₃ at 0.1, 0.3, 0.5 mM; SO₄²⁻ at 1.0, 3.0, 5.0 mM; Cl⁻ at 50 mM, 100 mM, 200 mM, 400 mM as well as SRDOM (< 1 kDa, 1 – 3 kDa, 3 – 5 kDa and original) at 1 mgC L⁻¹.

To reveal the effect of water matrix components in real surface water on the degradation of CP by the UV305/PDS process in the presence of TEMPO, similar experiments were conducted except that two types of real surface water collected locally were used as alternative to DI water. The geographical sampling sites and the water quality of the two surface waters were shown in Fig. S3 and Table S4, respectively.

The oxoammonium cation of TEMPO was determined by EPR with Magnettech ESR5000 spectrometer at room temperature. Considering that TEMPO appeared signal on EPR spectrum, the attenuation and recovery of the TEMPO signal on EPR spectrum was used to indicate the generation and transformation of TEMPO⁺. The concentration of TEMPO was chosen as 10 μM in EPR detection to amplify the signal of TEMPO. In the first experimental group, TEMPO was dissolved in DI water and subjected to UV305 or dark treatments to explore the stability of TEMPO⁺ cycle (TEMPO⁺ can be auto-oxidized (cytosine, guanine and uracil deamination), and the transformation time from TEMPO to TEMPO⁺ under sole UV305 irradiation. In the second experimental group, TEMPO was dissolved in PDS solution and subjected to UV305 or dark treatments to investigate the acceleration of transformation from TEMPO to TEMPO⁺ by UV305/PDS process. The results were compared to reveal the promotion of TEMPO/TEMPO⁺ cycle to UV305/PDS process.

All of the above experiments were conducted in triplicate, and the relative standard deviation of the three replicates was below 5% in all
the experiments.

2.3. Analytical and computational methods

The emission spectrum of the UV-LED lamp was measured using a spectrophotometer (Ocean optics, USB-4000). The absorption spectra of CP and TEMPO (Fig. S2) were measured using a UV–vis spectrophotometer (Shimadzu UV-1750). The second-order rate constants of CP towards radicals were determined using competition kinetics and the details were shown in Text S3. The analytical methods to determine the concentrations of CP, its products, probe compounds, and PDS, the methods to determine the electron donation capacity (EDC), water quality parameters and EPR were described in Text S4.

The DFT calculation of CP transformation products was conducted using Gaussian 09 software and its DFT module. The geometry optimization and energy estimation of CP molecule was conducted by B3LYP method with 6–31G basis set [26]. The Gibbs free energy change (ΔG, kJ·mol⁻¹) was calculated according to Eq. (1), and the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) was calculated on the basis of 6–31G basis set and SMD solvent (water) module [27].

\[
\Delta G = \sum_{i=1}^{m} G_{\text{Product}} - \sum_{j=1}^{n} G_{\text{React. i}}
\]  

(1)

where \(G_{\text{Product}}\) referred to Gibbs free energy of product (kJ·mol⁻¹); \(G_{\text{React. i}}\) referred to Gibbs free energy of reactant (kJ·mol⁻¹); \(i\) referred to the product; \(n\) referred to the sum number of products or reactants.

In addition, the fukui index of CP was calculated on the basis of the result of geometry optimization and Multifima software [28]. The toxicity of the CP and its degradation products were evaluated using the Ecological Structure Activity Relationship (ECOSAR), which was used to assess the acute toxicity and chronic toxicity of toxin to fish, daphnids and green algae on the basis of the molecule structure of the toxin [29, 30].

3. Results and discussion

3.1. Concentration-dependent effect of TEMPO on the degradation of CP in the UV₃₀₅/PDS process

Fig. 1 showed the effect of TEMPO on the degradation of CP by the UV₃₀₅/PDS process. As shown in Fig. 1(a), CP was not degraded by PDS alone, TEMPO alone, or the PDS/TEMPO combination under the experimental conditions. UV₃₀₅ alone slightly degraded CP. However, its degradation was enhanced significantly in the UV₃₀₅/PDS process, with a pseudo first order rate constant of \(7.60 \times 10^{-4}\) s⁻¹. The results suggested that CP was only degraded by the radicals generated from UV₃₀₅ photolysis of PDS. Interestingly, the degradation rate constant increased by 1.13 times from \(7.60 \times 10^{-4}\) to \(8.55 \times 10^{-4}\) s⁻¹ by adding 0.1 μM of TEMPO in the UV₃₀₅/PDS process. As mentioned above, TEMPO poses two potential roles in the UV₃₀₅/PDS process, i.e., the electron shuttle and the radical scavenger. The enhancement to CP degradation was hypothesized to be attributed to the electron shuttling effect of TEMPO, which increased the PDS activation and radical concentrations in the UV₃₀₅/PDS process. The hypothesis was verified, and the underlying mechanisms were discussed in the following sections.

To verify whether such “electron shuttling” worked at other TEMPO dosages, experiments were conducted at three different TEMPO dosages at 0.05, 0.1, and 0.2 μM, respectively. As shown in Fig. 1(b) and Fig. S4, the degradation rate constant of CP increased slightly from \(7.60 \times 10^{-4}\) s⁻¹ to \(7.71 \times 10^{-4}\) s⁻¹ by adding 0.05 μM of TEMPO into the UV₃₀₅/PDS process. The rate constant further increased from \(7.71 \times 10^{-4}\) s⁻¹ to \(8.55 \times 10^{-4}\) s⁻¹ by increasing the TEMPO dosage from 0.05 to 0.1 μM. However, further increasing the TEMPO dosage from 0.1 to 0.2 μM decreased the degradation rate constant from \(8.55 \times 10^{-4}\) s⁻¹ to \(7.22 \times 10^{-4}\) s⁻¹. The degradation rate constant in the presence of 0.2 μM of TEMPO was even lower than that in the absence of TEMPO. The results demonstrated that the effect of TEMPO was concentration dependent. Low concentration (0.05 – 0.1 μM) of TEMPO enhanced CP degradation but high concentration (0.2 μM) of TEMPO inhibited the degradation. The enhancement to CP degradation at low TEMPO dosages was hypothesized to be attributed to the “electron shuttling effect” of TEMPO which enhanced PDS activation and radical generation. While the inhibition to CP degradation at high TEMPO dosages was likely because the radical scavenging effect of TEMPO became significant and dominant.

To verify the above hypotheses, the electron donating capacity (EDC) of the reaction solution in the presence and absence of TEMPO was determined by quantitative photometric method. As shown in Fig. 2(a), the EDC of the reaction solution increased with increasing the TEMPO dosages from 0 to 0.2 mM. The results clearly demonstrated that TEMPO enhanced the electron transfer in the reaction solution. The enhanced electron transfer promoted the activation of PDS and radical generation,
which was supported by the enhanced consumption of PDS in the presence of 0.1 μM of TEMPO. As shown in Fig. 2 (b) and Fig. S5, the 10 min consumption of PDS increased from 0.0157 mM to 0.0175 mM when the treatment process changed from UV$_{305}$/PDS to UV$_{305}$/PDS/TEMPO, indicating that the electron transfer between TEMPO/TEMPO$^+$ accelerated the consumption of PDS, and promoted the generation of sulfate radical.

In order to further verify the response of EDC to low dosage TEMPO, the mediated electrochemical oxidation (MEO) method was employed to measure current variation after adding TEMPO in PDS solution (in Fig. 2 (c)). The transferred amount of electrons ($Q$) was then estimated by integrating the oxidation current peaks (oxidation current peaks area positively correlated with $Q$), and linear regression line of transferred amount of electrons vs. added mole of TEMPO was established which slope corresponds to the electron donating capacities (in mole of TEMPO or in Carbon) [31]. As seen in Fig. 2(d), $Q$ increased as the addition of TEMPO increased from 0.1 μmol to 0.8 μmol in PDS solution, and EDC was calculated by Equation (S13) as EDC$_{TEMPO}$ = 3.73 nmol e$^-$·(μmol TEMPO)$^{-1}$ or EDC = 0.0345 nmol e$^-$·(g Char)$^{-1}$. Thus, TEMPO was confirmed to increase electrons transferred amount in UV$_{305}$/PDS process which promote CP degradation.

The enhanced PDS activation and radical generation was also supported by the theoretical calculation. The change of the Gibbs free energy ($\Delta G$) between PDS and TEMPO under UV$_{305}$ irradiation was calculated to be $-12.72$ kJ·mol$^{-1}$ (see detailed calculation in Section 2.3), suggesting that the reaction of Eq. (2) was favored and the radical production was enhanced.

$$S_2O_8^{2-} + $TEMPO$$^+ \rightarrow h\nu $TEMPO$$ + SO_4^{2-} + SO_2^•$$ (2)

To further elucidate the mechanism and contribution of TEMPO$^+$ to CP degradation in UV$_{305}$/PDS/TEMPO process, TEMPO$^+$ was directly purchased and used in UV$_{305}$/PDS process [10]. As seen in Fig. 3(a) and (b), $k_{obs-CP}$ was $8.58 \times 10^{-4}$ s$^{-1}$ in UV$_{305}$/PDS/TEMPO$^+$ process, which was similar with that in UV$_{305}$/PDS/TEMPO process ($8.55 \times 10^{-4}$ s$^{-1}$), demonstrating that UV$_{305}$/PDS/TEMPO and UV$_{305}$/PDS/TEMPO$^+$ had similar performance on CP degradation. Meanwhile, the values of $k_{obs-CP}$ were approximately equal to zero in TEMPO$^+$ alone and UV$_{305}$/TEMPO$^+$ process, illustrating that TEMPO$^+$ could not directly contribute to the degradation of CP. Thus, the enhancement of TEMPO to CP degradation in UV$_{305}$/PDS process could be attributed to the acceleration of electron transfer by TEMPO/TEMPO$^+$ cycle, which then promoted the transformation from PDS to sulfate radical.

The EPR spectra variation of TEMPO under different treatment could prove this mechanism. As seen in Fig. 3(c), TEMPO had obvious signal on EPR spectra, which was significantly attenuated after 5 min UV$_{305}$ irradiation (Fig. 3(c). line (1) – (2)). Our previous study indicated that...
TEMPO would transform into TEMPO$^+$ which had not signal on EPR spectra. Thus, the attenuation of ERP signal could attribute to the transformation from TEMPO to TEMPO$^+$ [32]. Meanwhile, EPR signal had no change after TEMPO was added into PDS solution for 1 h without UV irradiation (Fig. 3(c), line (1) – (3)), demonstrating that TEMPO would not donate electron to PDS and the cycle of TEMPO/TEMPO$^+$ was not established without the irradiation of UV. Then, the signal of TEMPO on EPR spectra was remarkably attenuated when PDS solution with TEMPO was irradiated by UV light for 2 s (see Fig. 3(c). line (3) – (4)), and the signal completely disappeared when UV light keep on irradiating to the solution for 10 s (see Fig. 3(c). line (4) – (5)), suggesting that UV/PDS/TEMPO process would trigger the cycle of TEMPO/TEMPO$^+$ by generating sulfate radical, and also accelerate the electron transfer. This also demonstrated that UV irradiation was a necessary condition for TEMPO or TEMPO$^+$ to accelerate the transformation of PDS to free radicals. When the UV-irradiated PDS/TEMPO solution was placed in light free area for 2 h, the EPR signal of TEMPO recovered (see Fig. 3(c). line (5) – (6)), indicating that TEMPO was temporarily transformed into TEMPO$^+$, which would transform back to TEMPO in light free condition.

Thus, the enhancement of TEMPO to UV$_{305}$/PDS process for CP degradation was summarized in Fig. 3(d), where TEMPO could enhance CP degradation only in PDS solution with the excitation of UV light.

### 3.2. The concentrations of radicals in the absence and presence of TEMPO

To more directly demonstrate that TEMPO increased the radical concentrations in the UV$_{305}$/PDS process, experiments were conducted to quantify the radical concentrations in the absence and presence of TEMPO. The detailed procedures for radical quantification were described in Text S2 in SI. Table 1 shows the steady-state concentrations of reactive species in different degradation systems.

**Table 1**

| Degradation process | HO (M)      | SO$_4^-$ (M) | Cl (M)      |
|---------------------|-------------|--------------|-------------|
| UV$_{305}$/PDS      | N.D.        | 2.62 $\times$ 10$^{-14}$ | 5.43 $\times$ 10$^{-16}$ |
| UV$_{305}$/PDS/TEMPO| N.D.        | 3.55 $\times$ 10$^{-14}$ | 4.50 $\times$ 10$^{-15}$ |
Among the tested radicals, the second order rate constant of CP towards SO$_2$ was determined to be $2.34 \times 10^{10} \text{M}^{-1}\text{s}^{-1}$, which was high and close to the diffusion limit [33]. The results supported that the enhanced SO$_2$ generation increased the CP degradation in the UV$_{305}$/PDS process in the presence of TEMPO. The enhancement to Cl$^-$ was mainly attributed to promotion of the cleavage of the C-Cl bonds from CP molecule and the subsequent transformation of Cl$^-$ to CP by SO$_2$ [34-36].

The contributions of SO$_2$ and other radicals on CP degradation were estimated according to the method described in Text S2. As shown in Fig. 4 and Table S3, the contribution of SO$_2$ on CP degradation increased from 80.0% to 96.4% by adding TEMPO into the UV$_{305}$/PDS process. The results suggested that although the increase of SO$_2$ concentration was not as much as that of Cl$^-$, the contribution of SO$_2$ still increased significantly. The results confirmed that SO$_2$, instead of HO- or Cl$^-$, was the dominant species on CP degradation.

3.3. Effect of pH on CP degradation in the UV$_{305}$/PDS/TEMPO process

The effect of pH on CP degradation in the UV$_{305}$/PDS and the UV$_{305}$/PDS/TEMPO processes were investigated, and the results were illustrated in Fig. 5.

As seen in Fig. 5(a) and (b), $k_{\text{obs-cp}}$ increased from $7.60 \times 10^{-4}$ s$^{-1}$ to 10.0 $\times 10^{-4}$ s$^{-1}$ in UV$_{305}$/PDS process as pH decreased from 7.0 to 5.0. Meanwhile, $k_{\text{obs-cp}}$ increased from $7.60 \times 10^{-4}$ s$^{-1}$ to 2.46 $\times 10^{-3}$ s$^{-1}$ in UV$_{305}$/PDS/TEMPO process as pH increased from 7.0 to 9.0. Under the acidic conditions, high concentration of protons accelerated the transformation of PDS into H$_2$SO$_2$ [Eqs. (3) and (4)], which increased the generation of SO$_2$ and promoted the CP degradation [8]. Under alkaline conditions, PDS could be activated by hydroxyl ions to generate SO$_2$ (as Eq. (5)) and promote the abatement of CP [14,37]. Besides, the pKa of CP is 8.10, that means CP will be deprotonated in pH > 8.0 solution. Previous literatures mentioned that the deprotonation of –NH$_2$ group in the side chain of CP molecule would enhance the oxidation of radicals toward the ring structure of CP [7,37]. Thus, Fukui index of 4-Amino-7-chloroquinoline (ACQ, the toxic structure of CP molecule) before and after deprotonation were calculated by Gaussian 09 and multiwfn software, where a higher value of $f$ – for an atom indicated it was susceptible to be oxidized by radicals [7,32,38]. As seen in Fig. 6(a) and (b), the deprotonation of –NH$_2$ group in ACQ structure led to a sharply increase of visual isosurface of –f of N17 (in Fig. 6) and its surrounding atoms from 0.0991 to 0.268, indicating that deprotonation promoted the reaction of radicals with N17 and its surrounding structure which then resulted in the broken of amino side chain of CP and ring opening reaction. These results further confirmed the CP degradation improvement in alkaline condition.

Interestingly, the enhancement to CP degradation by adding TEMPO was observed at all the five tested pHs (Fig. 5(b)), which were 10.5 $\times 10^{-4}$ s$^{-1}$, 9.26 $\times 10^{-4}$ s$^{-1}$, 8.55 $\times 10^{-4}$ s$^{-1}$, 18.37 $\times 10^{-4}$ s$^{-1}$, 27.68 $\times 10^{-4}$ s$^{-1}$, respectively at pHs = 5.0, 6.0, 7.0, 8.0 and 9.0, suggesting that TEMPO had better enhancement on CP degradation in UV$_{305}$/PDS process under alkaline condition than under acidic condition. That was because large amount proton would probe electron in TEMPO/TEMPO$^+$ cycle under acidic condition, which then weakened the enhancement of TEMPO to UV$_{305}$/PDS process for CP degradation [29,32].

$$\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{HSO}_2^- \quad \text{(3)}$$

$$\text{H}_2\text{SO}_2 \rightarrow \text{SO}_2^- + \text{H}_2\text{O} \quad \text{(4)}$$

$$\text{SO}_2^- \rightarrow \text{SO}_4^{2-} + \text{H}^+ \quad \text{(5)}$$

3.4. Enhancement effect of TEMPO in anions and three molecular weight DOM deionized water solutions as well as in two real surface water

The HCO$_3^-$, NO$_3^-$, SO$_2^-$ as well as the molecular weight of DOM were the common water matrices and coexisting substances, and were added in deionized water to disclose the effect of anions and DOM on CP degradation in UV$_{305}$/PDS process and UV$_{305}$/PDS/TEMPO process. NO$_3^-$ was the main existing form of carbonate in neutral water and its concentration in real surface water was in the range of 0.3 – 5.0 mM [39]. As seen in Fig. 7(a), $k_{\text{obs-cp}}$ decreased from $7.60 \times 10^{-4}$ s$^{-1}$ to 6.58 $\times 10^{-4}$ s$^{-1}$ in UV$_{305}$/PDS process, and decreased from 8.55 $\times 10^{-4}$ s$^{-1}$ to 7.05 $\times 10^{-4}$ s$^{-1}$ in UV$_{305}$/PDS/TEMPO process as the concentration of HCO$_3^-$ increased from 0 mM to 5.0 mM. This inhibition could attribute to the reaction of HCO$_3^-$ to SO$_2^-$ to generate CO$_2^-$, which redox potential is $E_0 = 1.63$ V and had lower oxidation capacity than SO$_2^-$ (see the Eq. (6)) [25].

$$\text{SO}_2^- + \text{HCO}_3^- \rightarrow \text{CO}_2^- + \text{SO}_4^{2-} + \text{H}^+ \quad \text{(6)}$$

The concentration of NO$_3^-$ in real surface water was in the range of 0 – 0.5 mM [38]. As shown in Fig. 7(b), $k_{\text{obs-cp}}$ decreased from $7.60 \times 10^{-4}$ s$^{-1}$ to 5.93 $\times 10^{-4}$ s$^{-1}$ in UV$_{305}$/PDS process, and decreased from 8.55 $\times 10^{-4}$ s$^{-1}$ to 6.30 $\times 10^{-4}$ s$^{-1}$ in UV$_{305}$/PDS/TEMPO process as the concentration of NO$_3^-$ increased from 0 mM to 0.5 mM. This phenomenon could attribute to the reaction between SO$_2^-$ and NO$_3^-$, which would further transform into NO$_2^-$ ($E_0 = 2.30$ V) and NO$_2^-$ ($E_0 = 1.03$ V) through Eqs. (7) and (8). These two radicals had lower redox potentials than SO$_2^-$ ($E_0 = 2.5 – 3.1$ V), which therefore inhibited the degradation of CP [25,37].

$$\text{SO}_2^- + \text{NO}_3^- \rightarrow \text{SO}_4^{2-} + \text{NO}_3^- \quad \text{(7)}$$

$$\text{NO}_3^- + \text{H}_2\text{O} + e^- \rightarrow \text{NO}_2^- + 2\text{OH}^- \quad \text{(8)}$$

The concentration of SO$_4^{2-}$ in real surface water was in the range of 0 – 4.0 mM [40]. As shown in Fig. 7(c), $k_{\text{obs-cp}}$ slightly decreased from $7.60 \times 10^{-4}$ s$^{-1}$ to 7.25 $\times 10^{-4}$ s$^{-1}$ in UV$_{305}$/PDS process, and slightly decreased from 8.55 $\times 10^{-4}$ s$^{-1}$ to 8.18 $\times 10^{-4}$ s$^{-1}$ in UV$_{305}$/PDS/TEMPO process as the concentration of SO$_4^{2-}$ increased from 0 mM to 4.0 mM, indicating that there was rare effect of SO$_4^{2-}$ on CP degradation in these two processes. That was because SO$_4^{2-}$ could not increase or decrease the content of SO$_2^-$ or HO-through chemical reaction [41].

DOM is ubiquitous in real surface water, and different molecular weight DOM play different roles in AOPs [39,42]. Thus, DOM in three molecular weight ranges (< 1 kDa, 1 – 3 kDa and 3 – 5 kDa) were separated by ultrafiltration membrane (molecular weight cut-off), and were added in deionized water to reveal the effect of different molecular weight DOM on CP degradation in UV$_{305}$/PDS and UV$_{305}$/PDS/TEMPO processes. As depicted in Fig. 7(d), the concentration of three DOMs was diluted to 1.0 mgC-L$^{-1}$ in these two processes. In UV$_{305}$/PDS process, DOM in its molecular weight range of below 1 kDa presented the strongest
inhibition on CP degradation, and its $k_{obs-cp}$ decreased from $7.60 \times 10^{-4}$ s$^{-1}$ to $5.87 \times 10^{-4}$ s$^{-1}$ in 1 – 3 kDa DOM solution, and decreased from $7.60 \times 10^{-4}$ s$^{-1}$ to $6.17 \times 10^{-4}$ s$^{-1}$ in 1 – 3 kDa DOM solution. However, when TEMPO was added in UV$_{305}$/PDS process, $k_{obs-cp}$ increased to $6.28 \times 10^{-4}$ s$^{-1}$, $6.89 \times 10^{-4}$ s$^{-1}$ and $8.18 \times 10^{-4}$ s$^{-1}$ in < 1 kDa, 1 – 3 kDa and 3 – 5 kDa DOM solution respectively, indicated that the lowest molecular weight DOM had the highest inhibition on CP degradation whether in UV$_{305}$/PDS or UV$_{305}$/PDS/TEMPO process, and TEMPO attenuated this inhibitory effect. Lower molecular weight DOM had stronger light shielding effect than higher one, which led to lower molecular weight DOM competed with PDS for more photons. This diminished the generation of SO$_4\bullet$-, and finally inhibited the degradation of CP [43]. Besides, the TEMPO/TEMPO$^+$ cycle deeply relied on the excitation of UV light, and light shielding effect of DOM would slow down the rate of this cycle, which then weakened the promotion of

Fig. 5. Effect of pH on CP photodegradation in the UV$_{305}$/PDS process. (a) Time-dependent degradation of CP in different processes; (b) Effect of pH on the pseudo 1st order rate constants of CP. Conditions: [PDS]$_0 = 0.1$ mM, [CP]$_0 = 20 \mu$M, and [TEMPO]$_0 = 0.1$ mM.

Fig. 6. (a) Visualize isosurface of $f$ – and corresponding Fukui index of ACQ structure when amino is undeprotonated, (b) Visualize isosurface of $f$ – and corresponding Fukui index of ACQ structure after amino is deprotonated.
TEMPO to CP degradation in UV305/PDS process [32].

The effects of TEMPO on CP photodegradation in the UV305/PDS process in two real surface water samples were examined. A few interesting findings were obtained: (1) The enhancement to CP degradation was also observed in both the real surface water samples (Fig. 8(a)), i.e., the degradation rate constants increased by 1.24 and 1.10 times in the NW and EW, respectively, compared to the cases without TEMPO in the same water setting. The enhancement in NW was even more significant.

Fig. 7. Effect of three anions and DOM molecular weights on pseudo 1st order degradation rate constants of CP in UV305/PDS process, (a) HCO$_3^-$, (b) NO$_3^-$, (c) SO$_4^{2-}$, (d) DOM. Conditions: [PDS]$_0 = 0.1$ mM, [CP]$_0 = 20$ μM, [TEMPO]$_0 = 0.1$ μM, pH = 7.0.

Fig. 8. Effect of TEMPO on CP photodegradation in the UV305/PDS process in real surface waters. (a) Time-dependent degradation of CP in different processes; (b) Pseudo 1st order rate constants of CP in UV305/PDS process with or without TEMPO in DI water and in two different natural waters. Conditions: [PDS]$_0 = 0.1$ mM, [CP]$_0 = 20$ μM, [TEMPO]$_0 = 0.1$ μM. DIW referred to DI water, NW referred to natural water from Minjiang North Branch; EW referred to natural water from Tangfan reservoir.
than that in the DI water. (2) The degradation rate constants of CP were lower in the NW compared to that in DI water, no matter in the presence of absence of TEMPO. In contrast, the rate constants were even higher in the EW than those in the DI water, regardless in the presence of absence of TEMPO (Fig. 8(b)). The different effects of TEMPO in NW and EW were likely due to the differences in the contents of radical scavenging substances in the two water samples. The absorbance coefficient at the wavelength of 355 nm (α355) of EW was measured as 4.45, which was lower than that of NW, suggesting that the scavenging effect of DOM on SO₄⁻ was weaker in EW than NW. Besides, the spectral slope represents the molecular weight of DOM, which was inversely proportional to DOM molecular weight [43,44]. Previous studies demonstrated that lower molecular weight DOM has higher radical scavenging capacity [43,44]. As shown in Table S4, spectral slope (S) in EW is lower than that in NW, indicating that DOM in EW has a higher average molecular weight than that in NW. The results further supported that DOM in EW posed lower radical scavenging effect on CP degradation than that in NW.

3.5. Effect of high concentration Cl⁻ on CP degradation in the UV₃₀₅/PDS/TEMPO process

High concentration chloride ion could react with SO₄⁻ to yield Cl⁻, which would further transform into ClO₂⁻ as the Eqs. (9) and (10). Thus, SO₄⁻ could be scavenged by Cl⁻ [42,45]. As shown in Fig. 9, kₐbs-cp sharply decreased from 7.60 × 10⁻⁴ s⁻¹ to 1.90 × 10⁻⁴ s⁻¹ by 75.0% when 200 mM Cl⁻ was added in UV₃₀₅/PDS process, and kₐbs-cp maintained in a constant value when Cl⁻ concentration increased to 400 mM, suggesting SO₄⁻ was scavenged by Cl⁻. Meanwhile, pCBA (probe compound of SO₄⁻) was added in UV₃₀₅/PDS and UV₃₀₅/PDS/TEMPO process, and found its contents was stable (see Fig. S6 (d) and (e) in SI), which confirmed that SO₄⁻ was scavenged by Cl⁻. Cl⁻ had stronger inhibition to CP degradation in UV₃₀₅/PDS/TEMPO process than in UV₃₀₅/PDS process in which kₐbs-cp decreased from 8.55 × 10⁻⁴ s⁻¹ to 1.02 × 10⁻⁴ s⁻¹ by 88.1%. This is attributed to the catalytic mechanism of TEMPO is to promote the generation of SO₄⁻ through electron transfer in UV₃₀₅/PDS/TEMPO process. Therefore, the original contribution of SO₄⁻ to CP degradation is higher, and it is more affected by Cl⁻.

Moreover, the second order rate constant of Cl₂⁻ towards CP was determined by competition kinetic studies in Text S3, and its value is 7.60 × 10⁻⁷ M⁻¹ s⁻¹ which is far lower than the second order rate constant of SO₄⁻ towards CP (2.34 × 10⁻⁸ M⁻¹ s⁻¹). Thus, high concentration of Cl⁻ can inhibit the degradation of CP, and the inhibition is achieved by transforming the stronger oxidant (SO₄⁻) into weaker one (Cl₂⁻).

\[
\text{SO₄⁻} + \text{Cl}^- \rightarrow \text{SO₄²⁻} + \text{Cl}^- \quad (9)
\]

\[
\text{Cl}^- + \text{Cl}^- \rightarrow \text{Cl}_2^- \quad (10)
\]

3.6. Products and toxicity

DFT calculation was used to explore the degradation products of CP in the UV₃₀₅/PDS process in the absence and presence of TEMPO. The HOMO-LUMO of CP molecule was calculated by Gaussian 09 software, and its diagram was depicted in Fig. 10 (a) and (b). The chlorine substituent on the CP molecule diminished the electron cloud density of aromatic ring. Consequently, LUMO (electron acceptor) located around the aromatic ring and HOMO (electron donor) located on the amino side chain and the nitrogen atom of the quinoline. Thus, the nitrogen atom of CP molecule tended to react with SO₄⁻ and led to ring cleavage [7]. Besides, there was an electron transfer between HOMO and LUMO of TEMPO, and PDS likely promoted the electron and the generation of SO₄⁻ [46]. Thus, CP was attacked by SO₄⁻, leading to the cleavage of carbon-nitrogen bond and chlorine substituent. Based on the above calculation results, the intermediate products of CP in UV₃₀₅/PDS and UV₃₀₅/PDS/TEMPO were proposed in Fig. S11.

Fig. 11 proposed the CP degradation pathways in UV₃₀₅/PDS/TEMPO process according to the LC-MS-MS analysis (Figs. S12–S28). In UV₃₀₅/PDS/PDS process, the dechlorination and decarburization reaction firstly occurred at the chlorine substituent and the side chain of chloroquine (P1, m/z: 320.19). Then they were transformed by SO₄⁻ into series of primary products, such as P2 (m/z: 263.09), P3 (m/z: 292.16) and P4 (m/z: 286.24). The intermediate products including P5 (m/z: 163.13), P6 (m/z: 158.15), P7 (m/z: 179.04) and P8 (m/z: 158.15) were then generated via a further dechlorination and decarburization reaction. The residual side chain and chloroquine structure of intermediate products were oxidized by SO₄⁻ and PDS, leading to a further cleavage of side chain of CP molecule and a ring opening reaction, and transform into P9 (m/z: 102.97), P10 (m/z: 116.99), P11 (m/z: 118.07) and P12 (m/z: 102.13), which then further be oxidized into CO₂ and H₂O. In UV₃₀₅/PDS/TEMPO process, chloroquine was firstly transformed into P2, P3 and P4 through the same pathway with UV₃₀₅/PDS process. Afterword, these products were further degraded through the aromatic ring opening reaction and side chain hydroxylation, and transformed into small molecular weight intermediate products, e.g. P13 (m/z: 136.95) and P14 (m/z: 112.11), because TEMPO accelerate the transformation from PDS to SO₄⁻, leading to a higher concentration of SO₄⁻ in
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Fig. 10. (a) HOMO orbitals of CP molecule. (b) LUMO orbitals of CP molecule.

Fig. 11. The proposed degradation pathway of CP in UV_305/PDS and UV_305/PDS/TEMPO process Conditions: [PDS]_0 = 0.1 mM, [CP]_0 = 20 μM, [TEMPO]_0 = 0.1 μM, and pH = 7.0.

the reaction solution than UV_305/PDS process. Then, these intermediate products were further decomposed into low molecular weight carboxylic acid structural products, such as P15 (m/z: 88.95), P16 (m/z: 99.94) and P17 (m/z: 58.94), which then be mineralized into CO_2 and H_2O.

ECOSAR method was used to assess the ecological toxicity of CP and its products, and the results were summarized in Table 2 and Table 3. In the aspect of acute toxicity, LC_{50} of CP products for fish, green algae and daphnid is above that of CP, indicating that the toxicity of CP products are lower than that of CP. The product toxicity of CP gradually decreases with the transformation from primary products, intermediate products to end products. The results of chronic toxicity are similar with that of acute toxicity. Fig. 12 illustrated the fish acute toxicity assessment results of CP products generated from UV_305/PDS and UV_305/PDS/TEMPO process. In UV_305/PDS process, the fish acute toxicity of all products is lower than that of CP, and the acute toxicity of three end products (P9, P10 and P11) is far lower than that of CP. Although P12 is considered as a harmful product, its LC_{50} value (40.7 mg·L^{-1}) was four times higher than that of CP (10 mg·L^{-1}), suggesting that the acute toxicity of P12 is lower than that of CP. Nonetheless, all the fish acute toxicities of the products (P13 – 17) are far lower than that of CP in UV_305/PDS/TEMPO process, regardless of the intermediate products or end products, because of the oxidation enhancement of TEMPO to UV_305/PDS process resulting in CP being decomposed more thoroughly. The above results demonstrated that the UV_305/PDS/TEMPO process has a better performance on CP detoxification process than UV_305/PDS process in water.

### Table 2

| Acute Toxicity | Fish Toxicity | Daphnid Toxicity | Green algae Toxicity |
|---------------|--------------|-----------------|---------------------|
|               | 96-h LC_{50} | 48-h LC_{50}    | 96-h EC_{50}        |
| P1            | 1.41         | 0.224           | 0.104               |
| P2            | 14.3         | 1.88            | 1.28                |
| P3            | 3.71         | 0.585           | 0.298               |
| P4            | 3.33         | 0.492           | 0.265               |
| P5            | 26.4         | 16.1            | 16.2                |
| P6            | 70.9         | 7.92            | 7.43                |
| P7            | 23.4         | 2               | 5.34                |
| P8            | 67.4         | 7.56            | 7.04                |
| P9            | 2080         | 1140            | 715                 |
| P10           | 283          | 27.8            | 33.7                |
| P11           | 9410         | 4350            | 1390                |
| P12           | 40.7         | 4.58            | 4.23                |
| P13           | 1370         | 434             | 1010                |
| P14           | 2020         | 2020            | 2020                |
| P15           | 653000       | 247000          | 343000              |
| P16           | 3190         | 1700            | 988                 |
| P17           | 25800        | 12300           | 4400                |

\*Unit: mg·L^{-1}

\* LC_{50}, EC_{50} Half Lethal Concentration; EC_{50} Half Effective Concentration. ↓: Reduced toxicity.
Table 3
Estimated chronic toxicity for fish, daphnids and green algae of CP and its products by ECOSSAR.*

| Chronic toxicity | Fish toxicity change | Daphnids toxicity change | Green algae toxicity change |
|------------------|----------------------|--------------------------|-----------------------------|
| ChV**            | ChV**                | ChV**                    | ChV**                       |
| P1               | 0.034                | 0.024                    | 0.043                       |
| P2               | 0.618                | 0.169                    | 0.455                       |
| P3               | 0.114                | 0.055                    | 0.115                       |
| P4               | 0.101                | 0.05                     | 0.103                       |
| P5               | 2.81                 | 1.92                     | 4.99                        |
| P6               | 5.03                 | 0.61                     | 2.35                        |
| P7               | 0.248                | 0.024                    | 1.54                        |
| P8               | 4.74                 | 0.585                    | 2.24                        |
| P9               | 194                  | 98.9                     | 171                         |
| P10              | 29.9                 | 1.89                     | 9.72                        |
| P11              | 722                  | 240                      | 231                         |
| P12              | 2.82                 | 0.356                    | 1.35                        |
| P13              | 81.5                 | 22                       | 185                         |
| P14              | 189                  | 189                      | 189                         |
| P15              | 39500                | 7780                     | 3640                        |
| P16              | 290                  | 140                      | 226                         |
| P17              | 2050                 | 732                      | 778                         |

a Unit: mg L⁻¹
b Chronic Value: chronic toxicity. ChV: the geometric mean of the no observed effect concentration and the lowest observed effect concentration. ↓:Reduced toxicity

4. Conclusions

This study focused on the effect of TEMPO as an electron shuttle on CP photodegradation in UV/PDS process. The second-order rate constants of radicals vs. CP were estimated. Then, CP degradation kinetic with probe compounds experiments results indicated that the rate of CP degradation significantly increased by 1.13 times from UV/PDS to UV/PDS/TEMPO process, in which SO₄²⁻ play the dominant role. TEMPO always enhances CP abatement in UV/PDS process in pH range of 5.0 – 9.0, where TEMPO has better enhancement on CP degradation under alkaline condition than under acidic condition. That is because electron is consumed by proton under acidic condition, which prevents the electron transfer in TEMPO/TEMPO⁺ cycle. Deeply, TEMPO enhances CP degradation in this process by promoting electron transfer rather than the oxidation of TEMPO⁻. The coexisting HCO₃⁻, NO₃⁻, Cl⁻ and DOM strongly inhibited CP degradation in UV/PDS process, while SO₄²⁻ rarely affected this degradation. TEMPO enhanced this degradation in all the coexisting water matrix solutions. The promotion of TEMPO to CP abatement in UV/PDS process also occurred in natural surface waters with UV/PDS/TEMPO process, where the pseudo 1st order rate constant of CP degradation in UV/PDS/TEMPO process is higher in the lower DOM amount natural water than in natural water with a higher DOM amount. The products of CP and their LC₅₀ for aquatic organism illustrated that UV/PDS/TEMPO process has better performance on CP decomposition and detoxification than UV/PDS process.

This work provides a deep insight into the electron shuttle role of TEMPO in UV/PDS process to eliminate COVID-19 antiviral drug like CP. In our future work, some efforts should be put to accomplish trace amount new electron shuttle enhancing antiviral drug degradation in homogeneous photocatalysis process for natural water and sewage restoration.

CRediT authorship contribution statement

Qiyuan Sun: Research plan, Data processing, Investigation, Software, Writing original draft preparation, Funding acquisition; Yongjie Fan: Most of photodegradation experiment operation and software; Jing Yang: CP degradation products detection; Zhilei Lu, Zeping Xu, Xingteng Lai: Probe compounds detection; Yuyi Zheng: Spectrum, EDC detection and Toxicity assessment of CP products; Kaicong Cai: Data processing and software; Feifeng Wang: Validation, Writing review & editing.

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.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2022.108641.

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