

Article

Kinetics Modeling for Degradation of Geosmin and 2-Methylisoborneol by Photo-Electrogenerated Radicals

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Abstract: With increasingly severe cyanobacterial blooms, the overflow of off-flavor compounds represented by geosmin (GSM) and 2-methylisoborneol (2-MIB) is becoming a global water quality issue. The UV photo-electrochemical process is considered an environmentally friendly technology for GSM and 2-MIB degradation. In this study, a kinetics model using the pseudo-first-rate constants for the elimination of GSM and 2-MIB was developed in the UV photo-electrochemical process. The model can be applied successfully to predict the degradation of GSM and 2-MIB under different electrolyte concentrations, initial pH values of the solutions, and current densities. The GSM and 2-MIB degradation rates improved with increases in the electrolyte concentration. With an increase in the pH value from 5 to 11, the rate constants for the degradation of GSM and 2-MIB were reduced by 52.9% and 69.5%, respectively. The degradation of GSM and 2-MIB showed positive correlations with the current density in the kinetic model. Furthermore, the significant roles of HO• and Cl• were evaluated by scavenging experiments and kinetics modeling. HO• was the dominant radical for GSM degradation, and Cl• played a crucial role in 2-MIB elimination. The results demonstrate that the UV photo-electrochemical process could be an efficient way for the mineralization of off-flavor compounds.



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1. Introduction

The occurrence of off-flavor compounds in water environments has always been a serious concern in water quality control due to increasing eutrophication. As algae-derived secondary metabolites, geosmin (GSM) and 2-methylisoborneol (2-MIB) are the most well-known compounds that can migrate readily from the water and accumulate in the flesh and fat tissue of aquaculture products, then leading to the earthy and musty flavor of the cultured species in aquaculture [1]. Despite no risk to human health, GSM and 2-MIB have been considered important constraint indexes in drinking water quality standards by many countries [2–4]. The aqueous concentrations of GSM and 2-MIB are usually at an extremely low level at around ng/L; however, their association with an unpleasant taste profile can be easily perceived by human senses. The odor threshold concentrations for GSM and 2-MIB have been reported to be less than 7 ng/L and 6 ng/L, respectively [5].

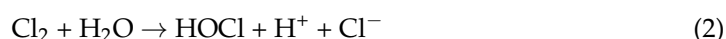
With the increasing requirements for water quality, great efforts have been devoted to removing GSM and 2-MIB from water environments. Several biochemical and physico-

ochemical techniques have been exploited and applied for the degradation of GSM and 2-MIB, including biodegradation [6], nanobubble fractionation [7], air stripping [8], activated carbon adsorption [9], chemical oxidation [10], and photocatalysis [11]. However, GSM and 2-MIB are not easily biodegradable [12] and are extremely resistant to commonly used oxidants, such as ozone and hydrogen peroxide [13], due to the presence of a tertiary alcohol structure. Therefore, the conventional treatment processes for water purification have limitations and poor efficiency in removing GSM and 2-MIB. Advanced oxidation processes (AOPs) have been demonstrated to be highly efficient and accepted approaches to control the two compounds [14,15]. AOPs can be broadly defined as oxidation methods involving the intermediate formation of highly reactive species such as the non-selective hydroxyl radical ($\text{HO}\bullet$) that can damage the majority of organic pollutants even at trace levels.

Ultraviolet (UV)-based AOPs based on $\text{HO}\bullet$ (2.8 V), chlorine radicals ($\text{Cl}\bullet$, 2.4 V), or some other reactive species have been under extensive research for eliminating GSM and 2-MIB. As one of the most common UV-AOPs for $\text{HO}\bullet$ generation, UV and hydrogen peroxide (H_2O_2) have been successfully employed to control both GSM and 2-MIB. Jo et al. [16] reported that 90% of GSM and 65% of 2-MIB were degraded by hydroxyl radicals resulting from the photolysis of 6 mg/L H_2O_2 with a UV dose of 1200 mJ/cm². The kinetic model based on the steady-state concentration of $\text{HO}\bullet$ can accurately predict the destruction of GSM and 2-MIB at low H_2O_2 concentrations [17]. The UV/chlorine process is considered an emerging alternative to the UV/ H_2O_2 process because more reactive species such as $\text{HO}\bullet$ and $\text{Cl}\bullet$ can be generated by the photolysis of free chlorine under UV radiation. As a selective oxidant, $\text{Cl}\bullet$, which has high reactivity with electron-rich moieties compared with $\text{HO}\bullet$, can react rapidly with compounds containing double bonds and aromatic rings. It has been suggested that UV/chlorine showed higher efficiency for GSM and 2-MIB removal at pH 6.5 than UV/ H_2O_2 at pilot and full-scale levels [18]. Springer et al. [19] concluded that 40–60% reductions in GSM and 2-MIB could be achieved with ambient water quality conditions in the medium-pressure UV/chlorine process. A dynamic model based on the hypothesis that $\text{HO}\bullet$ and $\text{Cl}\bullet$ are the predominant reactive species in the UV/chlorine process can be used to successfully predict the degradation of GSM and 2-MIB in a UV photoreactor when adding 0.1 mM hypochlorous acid (HOCl) [20]. For these frequently used UV-AOPs, there is one thing in common: strong oxidants such as H_2O_2 and chlorine need to be added in the processes to generate free radicals for pollutant degradation. This can result in an ensuing challenge regarding the storage management of hazardous chemicals and the chemical residual handling of UV-AOPs, which may increase the complexity and costs of the usage of UV-AOPs.

With the obvious difference from the UV/chlorine process by adding HClO or sodium hypochlorite (NaClO), free chlorine can be generated by anodic oxidation during the electrolysis process of chloride-containing solutions in practice (Equations (1)–(3)) [21]. The electro-oxidation mediated by active chlorine, including chlorine (Cl_2), hypochlorite ion (ClO^-), and HOCl , applied in water and wastewater treatment is considered a promising alternative technology as it does not require adding extra oxidants. In the electrochemical oxidation processes, highly reactive oxidizing species can be generated in situ directly or indirectly through redox reactions. The combined use of UV irradiation and chlorine production by electrochemical oxidation is an attractive approach to generating active radicals compared with UV/chlorine. $\text{HO}\bullet$ and $\text{Cl}\bullet$ will be photo-electrogenerated through the photolysis of active chlorine formed by the electrode reaction in the presence of chloride accompanied by UV radiation with wavelengths of 200–400 nm (Equations (4)–(6)) [22]. It has been reported that $\text{HO}\bullet$ and $\text{Cl}\bullet$ generated in the UV-assisted photo-electrochemical process played an important role in the degradation of GSM and 2-MIB by scavenging

experiments [23]. However, there are still some controversial perspectives concerning the contributions of HO• and Cl• to degrading GSM and 2-MIB. It was speculated that the degradation mechanism of GSM and 2-MIB was mainly attributed to the HO• produced by HOCl with UV, while the role of Cl• was to react with water and generate more HO• [2]. It was suggested that although HO• played a dominant part in removing GSM and 2-MIB, the contribution of Cl• was also considerable in the UV/chlorine process [24]. Therefore, the contributions of different free radicals to the degradation of GSM and 2-MIB require further clarification, especially in the UV photo-electrochemical process given the limited research about off-flavor compound elimination and kinetics modeling.



The main objective of the present study was to investigate kinetics modeling for the degradation of GSM and 2-MIB in the UV photo-electrochemical process. The degradation kinetics of GSM and 2-MIB under different electrolyte concentrations, current densities, and initial pH values of the solutions were explored to evaluate the applicability of kinetics modeling. The roles and contributions of different free radicals to the synergistic removal of GSM and 2-MIB were further elucidated by combining radical species-quenching experiments and model calculation. This work is expected to provide new insight into this alternative technology for eliminating off-flavor compounds compared with the commonly used UV-AOPs.

2. Materials and Methods

2.1. Chemicals

All the chemicals used in this study were of reagent grade or higher without further purification. Geosmin (GSM, purity >99.9%) and 2-methylisoborneol (2-MIB, purity >99.9%) were purchased from Sigma-Aldrich Co., Ltd. (St. Louis, MO, USA). Hydrochloric acid (HCl, 37% w/w), sodium hydroxide (NaOH), sodium chloride (NaCl), and nitrobenzene (NB) were acquired from China National Medicines Co., Ltd. (Shanghai, China). Tertiary butanol (TBA) and sodium sulfite (Na₂S₂O₃) were obtained from Macklin Biochemical Co., Ltd. (Shanghai, China). Acetonitrile (ACN, purity >99.9%) and methanol (MeOH, purity >99.9%) of HPLC grade were supplied by Tianjin Shield Specialty Chemical Co., Ltd. (Tianjin, China). Chemical solutions were prepared with reagent-grade deionized (DI) water (resistivity = 18.2 mΩ/cm) from a Millipore Milli-Q system (Billerica, MA, USA).

2.2. Experimental Procedures

In order to investigate the oxidation of GSM and 2-MIB by different reactive species in the photo-electrochemical process, synthetic solutions with a total volume of 300 mL

containing 1 µg/L GSM, 1 µg/L 2-MIB, and sodium chloride were regulated to a certain pH value and transferred into a quartz cell (Figure S1). Batch experiments for the degradation of GSM and 2-MIB were performed with different influencing factors, including initial chloride concentrations, initial pH values, and current densities. Specifically, different dosages of NaCl solutions with a concentration of 1.5 mol/L were added to 1.5 mL of a GSM and 2-MIB solution, both with concentrations of 200 µg/L, and then the solution was diluted to 300 mL using DI water to make synthetic solutions (pH 7) including 1 µg/L GSM, 1 µg/L 2-MIB, and initial chloride concentrations of 20, 40, 60, and 80 mmol/L. To study the factor of initial pH values, a 200 µg/L GSM and 2-MIB solution with a volume of 1.5 mL was mixed with 12 mL of NaCl solutions of 1.5 mol/L and DI water to obtain a 300 mL synthetic solution containing 1 µg/L GSM, 1 µg/L 2-MIB, and an initial chloride concentration of 60 mmol/L with an initial pH value of 7. Additionally, synthetic solutions with pH values of 5, 9, and 11 were made by spiking trace amounts of 1 mol/L HCl or 1 mol/L NaOH on the basis of synthetic solutions at pH 7. Different current densities of 5, 10, 15, and 20 mA/cm² were applied by adjusting the programmable power supply. To further elucidate the contributions of free radical species to GSM and 2-MIB oxidation in the photo-electrochemical process, radical species-quenching experiments were implemented at different concentrations of TBA or NB at initial pH values of 7 and a current density of 15 mA/cm² under initial chloride concentrations of 60 mmol/L. All the experiments were carried out at room temperature. Samples were collected and spiked immediately with 0.1 mL Na₂S₂O₃ with a concentration of 0.5 mol/L to quench the residual oxidants at different time intervals for the measurements. All tests were conducted at least thrice. The relative standard deviations (RSDs) for different experiments were regularly less than 10%.

2.3. Analytical Methods

The concentrations of GSM and 2-MIB were determined using solid-phase micro-extraction (SPME) coupled with GC/MS (7890B/5975A, Agilent, Santa Clara, CA, USA) equipped with an HP-5 MS column (30 m × 0.25 mm × 0.25 mm, Agilent, USA). GSM and 2-MIB were extracted by SPME fiber assembly (50/30 µm, DVB/CAR/PDMS, Supelco, Bellefonte, PA, USA) from the liquid samples. Triplicate samples with a volume of 5 mL supplemented with 1.5 g of dry NaCl were added into a screw-type SPME vial. The extraction of GSM and 2-MIB was carried out at 60 °C for 40 min on an autosampler. Then, the SPME fiber was placed in the injector of the GC (7890B, Agilent, Santa Clara, CA, USA), which was connected to the MS (5975A, Agilent, Santa Clara, CA, USA). The injector temperature was set to 250 °C, and the SPME fiber was thermally desorbed for 5 min at 250 °C. Helium with a high purity was used as a carrier gas at a constant flow rate of 1 mL min⁻¹. Sample injection was set under splitless mode with the temperature controlled at 250 °C. The oven temperature was held at 60 °C for 2.5 min after injection, followed by an increase to 250 °C at a rate of 8 °C min⁻¹, and finally kept at 250 °C for 5 min. Chlorine concentrations were measured following the N,N-diethylpphenylenediamine (DPD) colorimetric method. The pH values were determined by a pH meter (FiveGo F2, Mettler Toledo, Zurich, Switzerland).

2.4. Model Equations

Our previous study demonstrated that the pseudo-first kinetics can be used as the degradation model of GSM and 2-MIB in the photo-electrochemical process, during which hydroxyl radicals (HO•) and chlorine radicals (Cl•) played a dominant role [23]. Therefore, the kinetic model was established based on the hypothesis that the degradation of GSM and 2-MIB was attributed to HO• and Cl• in the photo-electrochemical process, while the contribution of other radicals such as ClO• can be neglected. The possible reactions and

corresponding rate constants involved in the photo-electrochemical process for GSM and 2-MIB degradation are summarized in Table S1 of the Supplementary Materials. Combined with the reactions, the kinetic expressions of HO• and Cl• in the photo-electrochemical process can be described by Equations (7) and (8).

$$\begin{aligned} \frac{d[\text{OH}\bullet]}{dt} = & r_{\text{OH}\bullet} + k_6[\text{ClOH}\bullet^-] + k_{17}[\text{O}^-\bullet][\text{H}_2\text{O}] - k_{10}[\text{OH}\bullet][\text{HOCl}] \\ & - k_{11}[\text{OH}\bullet][\text{OCl}^-] - k_5[\text{OH}\bullet][\text{Cl}^-] - k_{18}[\text{OH}\bullet][\text{OH}^-] \\ & - k_{1,c}[\text{OH}\bullet][c] - \sum_i k_{1,i}[\text{OH}\bullet][\text{S}_i] \end{aligned} \quad (7)$$

$$\begin{aligned} \frac{d[\text{Cl}\bullet]}{dt} = & r_{\text{Cl}\bullet} + k_4[\text{Cl}_2\bullet^-] + k_7[\text{ClOH}^-\bullet] + k_8[\text{ClOH}^-\bullet][\text{H}^+] \\ & - k_3[\text{Cl}\bullet][\text{Cl}^-] - k_{13}[\text{Cl}\bullet][\text{HOCl}] - k_{14}[\text{Cl}\bullet][\text{OCl}^-] \\ & - k_{15}[\text{Cl}\bullet][\text{OH}^-] - k_{2,c}[\text{Cl}\bullet][c] - \sum_i k_{2,i}[\text{Cl}\bullet][\text{S}_i] \end{aligned} \quad (8)$$

where $r_{\text{OH}\bullet}$ and $r_{\text{Cl}\bullet}$ are the generation rates of HO• and Cl• in the photo-electrochemical process, S_i is the concentration of radical scavengers in solution, $k_{1,c}$ and $k_{2,c}$ are the rate constants of HO• and Cl• reacting with specific pollutants, and $k_{1,i}$ and $k_{2,i}$ are the rate constants of HO• and Cl• reacting with corresponding scavengers.

Based on the free radical steady-state assumption, the generation rates of free radicals are equal to the consumption rates upon the reaction system reaching equilibrium. The modeling steady-state concentrations of HO• ($[\text{OH}\bullet]_{\text{ss}}$) and Cl• ($[\text{Cl}\bullet]_{\text{ss}}$) can be expressed by Equations (9) and (10).

$$[\text{OH}\bullet]_{\text{ss}} = \frac{r_{\text{OH}\bullet} + k_6[\text{ClOH}\bullet^-]_{\text{ss}} + k_{17}[\text{O}^-\bullet]_{\text{ss}}[\text{H}_2\text{O}]}{k_5[\text{Cl}^-] + k_{10} \frac{[\text{Chlorine}] 10^{\text{pK}_a - \text{pH}}}{10^{\text{pK}_a - \text{pH}} + 1} + k_{11} \frac{[\text{Chlorine}]}{10^{\text{pK}_a - \text{pH}} + 1} + k_{18}[\text{OH}^-] + k_{1,c}[c] + \sum_i k_{1,i}[\text{S}_i]} \quad (9)$$

$$[\text{Cl}\bullet]_{\text{ss}} = \frac{r_{\text{Cl}\bullet} + k_4[\text{Cl}_2\bullet^-]_{\text{ss}} + k_7[\text{ClOH}^-\bullet]_{\text{ss}} + k_8[\text{H}^+][\text{ClOH}^-\bullet]_{\text{ss}}}{k_3[\text{Cl}^-] + k_{13} \frac{[\text{Chlorine}] 10^{\text{pK}_a - \text{pH}}}{10^{\text{pK}_a - \text{pH}} + 1} + k_{12} \frac{[\text{Chlorine}]}{10^{\text{pK}_a - \text{pH}} + 1} + k_{15}[\text{OH}^-] + k_{2,c}[c] + \sum_i k_{2,i}[\text{S}_i]} \quad (10)$$

The generation rates of HO• and Cl• in the photo-electrochemical process can be expressed as follows.

$$r_{\text{OH}\bullet} = \frac{\Phi_{\text{HClO}} I_0 f_{\text{HClO}} (1 - 10^{-A}) L}{V} \quad (11)$$

$$r_{\text{Cl}\bullet} = \frac{(\Phi_{\text{HClO}} f_{\text{HClO}} + \Phi_{\text{ClO}^-} f_{\text{ClO}^-}) I_0 (1 - 10^{-A}) L}{V} \quad (12)$$

$$A = (\epsilon_{\text{HOCl}} C_{\text{HOCl}} + \epsilon_{\text{OCl}^-} C_{\text{OCl}^-} + \epsilon_{\text{S}_i} C_{\text{S}_i} + \dots) L \quad (13)$$

$$f = \frac{\epsilon C L}{A} \quad (14)$$

where Φ is the quantum yield, V is the reaction volume, L is the effective optical path, and ϵ is the molar absorption coefficient.

According to the steady-state assumption of free radicals, the degradation rate of GSM and 2-MIB in the photo-electrochemical process can be expressed as shown in (15).

$$\frac{d[C]}{dt} = [C](k_{1,c}[\text{Cl}\bullet]_{\text{ss}} + k_{2,c}[\text{OH}\bullet]_{\text{ss}}) = [C](k_{0,\text{Cl}\bullet} + k_{0,\text{OH}\bullet}) = [C]k_0 \quad (15)$$

where $k_{0,\text{OH}\bullet}$ and $k_{0,\text{Cl}\bullet}$ are the apparent rate constants of pollutant degradation reacting with HO• and Cl• in the photo-electrochemical process, respectively, and k_0 is the overall apparent rate constant of pollutant degradation. The contributions of HO• and Cl• to

pollutant degradation in the photo-electrochemical process can be represented by $k_{0,\text{OH}\bullet}$ and $k_{0,\text{Cl}\bullet}$, which can be described as shown in Equations (16) and (17).

$$k_{0,\text{OH}\bullet} = \frac{r_{\text{OH}\bullet} + k_6[\text{ClOH}\bullet^-]_{\text{ss}} + k_{17}[\text{O}^-\bullet]_{\text{ss}}[\text{H}_2\text{O}]}{k_5[\text{Cl}^-] + k_{10} \frac{[\text{Chlorine}]10^{\text{pK}_a - \text{pH}}}{10^{\text{pK}_a - \text{pH}} + 1} + k_{11} \frac{[\text{Chlorine}]}{10^{\text{pK}_a - \text{pH}} + 1} + k_{18}[\text{OH}^-] + k_{1,c}[\text{c}] + \sum_i k_{1,i}[\text{S}_i]} \quad (16)$$

$$k_{0,\text{Cl}\bullet} = \frac{r_{\text{Cl}\bullet} + k_4[\text{Cl}_2\bullet^-]_{\text{ss}} + k_7[\text{ClOH}^-\bullet]_{\text{ss}} + k_8[\text{H}^+][\text{ClOH}^-\bullet]_{\text{ss}}}{k_3[\text{Cl}^-] + k_{13} \frac{[\text{Chlorine}]10^{\text{pK}_a - \text{pH}}}{10^{\text{pK}_a - \text{pH}} + 1} + k_{12} \frac{[\text{Chlorine}]}{10^{\text{pK}_a - \text{pH}} + 1} + k_{15}[\text{OH}^-] + k_{2,c}[\text{c}] + \sum_i k_{2,i}[\text{S}_i]} \quad (17)$$

Kinetic modeling was carried out to study the degradation of GSM and 2-MIB in the photo-electrochemical process by using MATLAB (R2020b, MathWorks, Natick, MA, USA). The models are objective functions of different species, including the concentrations of free radicals and pollutants. The main contributions of different free radicals can be clarified by calculating the steady-state concentrations of free radicals and the rate constants.

3. Results and Discussion

3.1. The Kinetics of Chlorine Generation in the Electrochemical Reaction

Considering that $\text{HO}\bullet$ and $\text{Cl}\bullet$ mainly derive from the photodegradation of HOCl and OCl^- in the photo-electrochemical process, the kinetics of active chlorine production under different chloride concentrations (0.02–0.08 mol/L) and current densities (5–20 mA/cm^2) in the electrochemical reaction matched expectations.

As shown in Figure 1, the increase in chloride concentrations was conducive to generating active chlorine. It can be concluded that the rate constant of active chlorine production follows mathematical model (18) with chloride concentrations of 0.02–0.08 mol/L.

$$10^6 k(\text{Cl}^-) = -2.87 + 4.8e^{30.76 [\text{Cl}^-]} \quad (18)$$

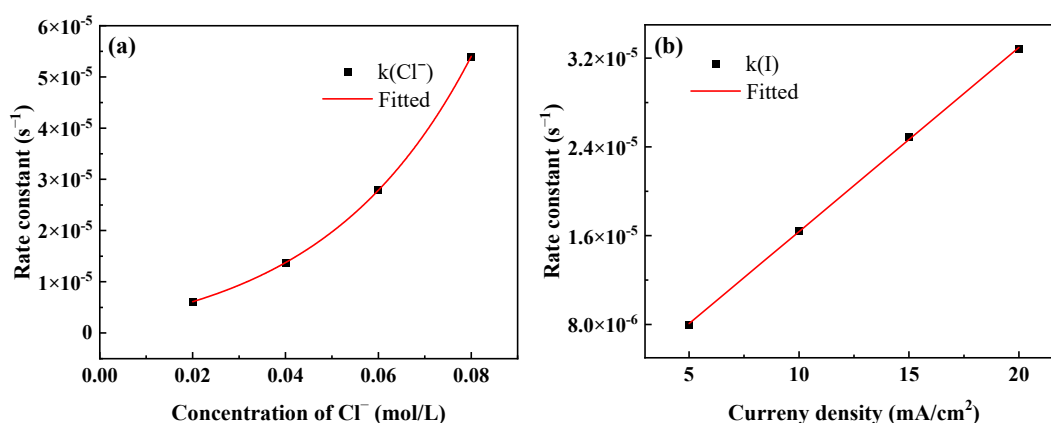


Figure 1. Active chlorine production in the electrochemical reaction under different (a) electrolyte concentrations and (b) current densities.

Meanwhile, the concentrations of active chlorine increased proportionally with the current densities. The generation rate constant of active chlorine follows model (19) with current densities of 5–20 mA/cm^2 .

$$10^6 k(\text{I}) = -0.22 + 1.66 \text{ I} \quad (19)$$

Zhang et al. [25] also confirmed the positive linear correlation between current densities of 1–5 mA/cm² and active chlorine evolution. Even with the current density reaching 30 mA/cm², the rate of active chlorine production correlated linearly with the current density [26]. It was also reported that the rate of active chlorine generation was mainly governed by the chloride ion concentration and current density [27]. Therefore, the rate constants of active chlorine production were used in the kinetic equations for GSM and 2-MIB degradation.

3.2. Degradation Kinetics of GSM and 2-MIB at Different Electrolyte Dosages

The rate constants of GSM and 2-MIB degradation in the UV-assisted electrochemical process at different electrolyte dosages are illustrated in Figure 2. As the chloride concentration increased from 20 mmol/L to 80 mmol/L, the experimental values of the rate constants for GSM and 2-MIB degradation increased from 0.0759 min^{−1} and 0.041 min^{−1} to 0.151 min^{−1} and 0.126 min^{−1}, respectively. It can be concluded that the degradation rate of GSM and 2-MIB improved with the increasing electrolyte concentration. Additionally, the experimental and predicted values of the pseudo-first-order rate constants for GSM and 2-MIB degradation were in good agreement, which shows the applicability of the kinetics model. It was obvious that HO• and Cl• radicals played a crucial role in removing the GSM and 2-MIB, during which the HO• radical made a greater contribution to the degradation of GSM and 2-MIB than the Cl• radical. This result has been proven by previous work indicating that the contribution of HO• for the degradation of GSM and 2-MIB was more than 90% at a pH of 6 compared with those of reactive chlorine species such as Cl• [28]. As listed in Table S1 (Equations (6) and (8)), the presence of chloride ions has a quenching effect on the HO• and Cl• radicals generated in the UV-assisted electrochemical process. However, Figure 2 shows that the increase in the chloride ion concentration is conducive to the degradation of GSM and 2-MIB. This discrepancy can be explained because chloride ions can react with HO• and Cl• radicals to generate ClOH•[−] and Cl₂•[−], which will decay and finally transform back into HO• and Cl• [29–31]. Therefore, the presence of chloride ions in the electrolyte did not diminish but instead promoted the rate constants of GSM and 2-MIB degradation in the photo-electrochemical process.

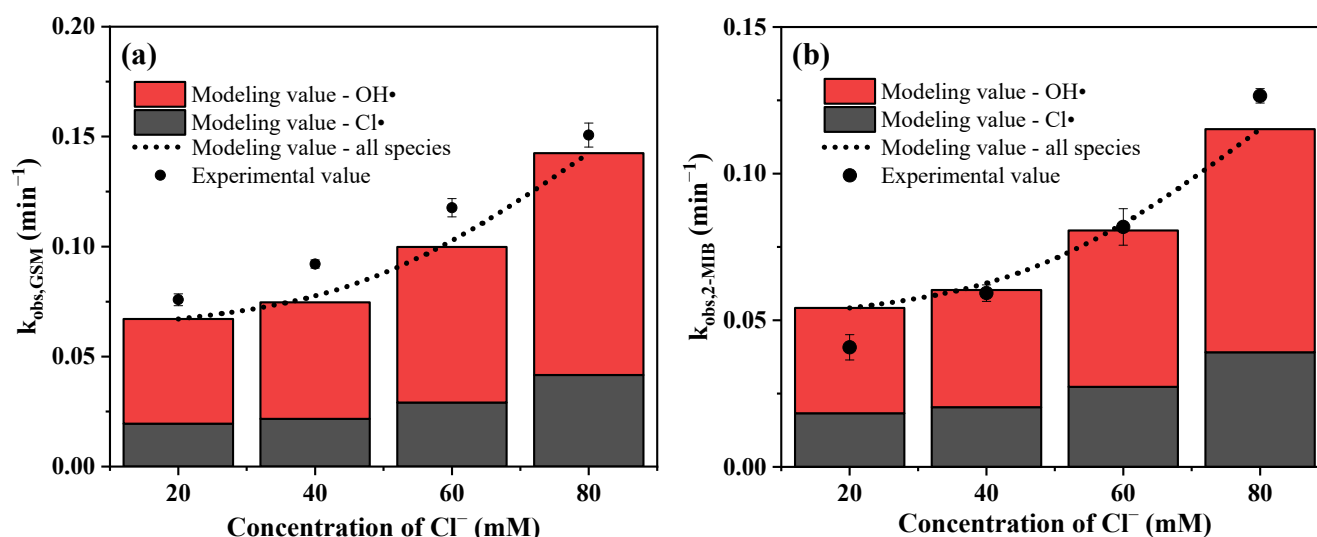


Figure 2. The individual and overall pseudo-first-order rate constants of (a) GSM and (b) 2-MIB degradation by HO• and Cl• under different electrolyte dosages in the photo-electrochemical process (initial pH: 7, current density: 15 mA/cm²).

3.3. Degradation Kinetics of GSM and 2-MIB at Different pH Values

The solution pH that is directly associated with the existing forms of active species has been recognized as a vital factor in the UV-assisted photo-electrochemical process [32]. The contributions of $\text{HO}\bullet$ and $\text{Cl}\bullet$ radicals to the degradation of GSM and 2-MIB at different pH values in the photo-electrochemical process are shown in Figure 3. A similar tendency of the apparent rate constants was observed among the experimental and predicted values. With increases in the pH value from 5 to 11, the rate constants for the degradation of GSM and 2-MIB decreased from 0.132 min^{-1} and 0.099 min^{-1} to 0.0622 min^{-1} and 0.0302 min^{-1} , thus decreasing by 52.9% and 69.5%, respectively. It has been reported that the formation of different radicals was significantly influenced by the solution pH. The concentrations of $\text{HO}\bullet$ and $\text{Cl}\bullet$ declined markedly when the pH increased from 7 to 10, especially for $\text{HO}\bullet$ [33]. Additionally, $\text{HO}\bullet$ has a lower oxidation potential at higher pH values [34]. It can be obtained from the modeling that the relative contributions of $\text{HO}\bullet$ to the degradation of GSM and 2-MIB were 61.08% and 55.8% at pH 5 but decreased to 0.11% and 0.09% at pH 11, respectively. The presence of $\text{Cl}\bullet$ played a more important role in GSM and 2-MIB degradation at pH 9 and 11 in the photo-electrochemical process. Liu et al. [35] also suggested that the degradation of sulfapyridine caused by $\text{HO}\bullet$ and $\text{Cl}\bullet$ showed significant differences at different pH values. When the pH increased from 4 to 10, the removal of sulfapyridine through $\text{HO}\bullet$ and $\text{Cl}\bullet$ was distinctly inhibited.

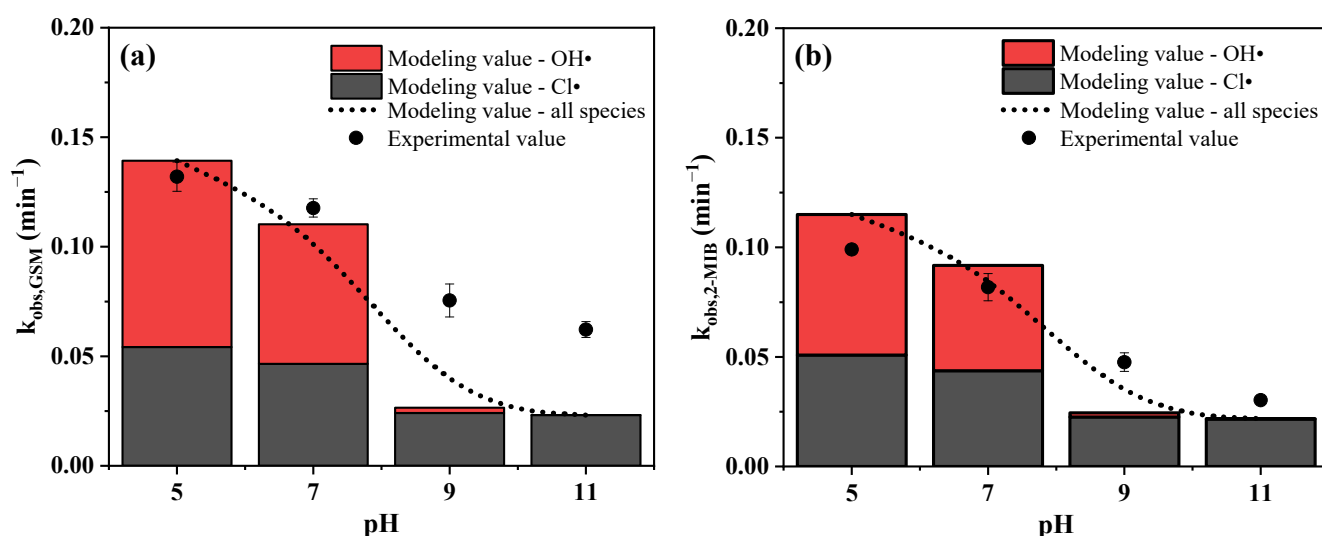


Figure 3. The individual and overall pseudo-first-order rate constants of (a) GSM and (b) 2-MIB degradation by $\text{HO}\bullet$ and $\text{Cl}\bullet$ under different pH values in the photo-electrochemical process (chloride concentration: 60 mmol/L, current density: 15 mA/cm²).

It is known that active chlorine presents a dissociation equilibrium associated with Cl_2 , HOCl , and OCl^- in an aqueous solution [36,37]. The primary species of active chlorine can convert into each other depending on the solution pH: <3 for Cl_2 , HClO in the ranges of 3–8, and >8 for ClO^- , where HOCl and ClO^- could generate $\text{HO}\bullet$ and $\text{Cl}\bullet$ radicals simultaneously after absorbing UV photons with a wavelength of 200–400 nm [22,38]. The predominant active chlorine species will transform from HClO into ClO^- with an increase in the pH from 5 to 11. The quantum yields of ClO^- were much lower than those of HClO at ambient temperature in the presence of 254 nm UV irradiation [31,39]. Therefore, the yield of $\text{HO}\bullet$ and $\text{Cl}\bullet$ will be reduced with an increase in the pH. Moreover, $\text{HO}\bullet$ and $\text{Cl}\bullet$ can be quenched by HOCl and ClO^- , with ClO^- showing higher quench rates with $\text{HO}\bullet$ and $\text{Cl}\bullet$ [40]. Generally, $\text{HO}\bullet$ and $\text{Cl}\bullet$ not only were weakened for generation but also accelerated for consumption in the presence of a large amount of ClO^- , which will result

in a decrease in the rate constants for GSM and 2-MIB degradation in an aqueous alkaline medium during the photo-electrochemical process.

3.4. Degradation Kinetics of GSM and 2-MIB at Different Current Densities

Current density is of great importance for the generation of active species in the UV-assisted photo-electrochemical process [21,41]. The process of photo-electrochemical degradation for GSM and 2-MIB at different current densities is depicted in Figure 4. With the current density increasing from 5 mA/cm² to 10 mA/cm², the rate constants of GSM and 2-MIB degradation were increased from 0.0970 min^{−1} and 0.0668 min^{−1} to 0.1233 min^{−1} and 0.1106 min^{−1}, respectively. An increasing current density will lead to an increase in the charge intensity on the two electrodes, which can cause the accumulation of active chlorine and further improve the yield of HO• and Cl• in the solution under UV radiation. As the current density increased to 15 mA/cm² and 20 mA/cm², the degradation rates of GSM and 2-MIB were not significantly promoted. This phenomenon could be mainly attributed to side reactions, such as oxygen gas evolution, which were promoted with the increase in current density [42,43]. A current efficiency decrease that can weaken the generation of active chlorine will follow. Additionally, the simulated rate constants and the respective contributions of HO• and Cl• to GSM and 2-MIB degradation in the kinetic model showed positive correlations with the current density in the range of 5–20 mA/cm². The fitting results showed some differences from the experimental rate constants, which could be due to the simplification of the kinetic model by using the generation rate of active chlorine for GSM and 2-MIB degradation. To further optimize the fitted model, more factors should also be taken into consideration, such as polarization effects in the electrochemical process, the synergistic effects of UV radiation and chlorine production, and the equilibria between different free radicals. Wang et al. [44] also reported that the discrepancy between the predicted model values and experimental values of the rate constants for carbamazepine degradation by UV/chlorine resulted from the fact that the relative amount of HOCl and OCl[−] was regarded as the only aspect used in the predicted model.

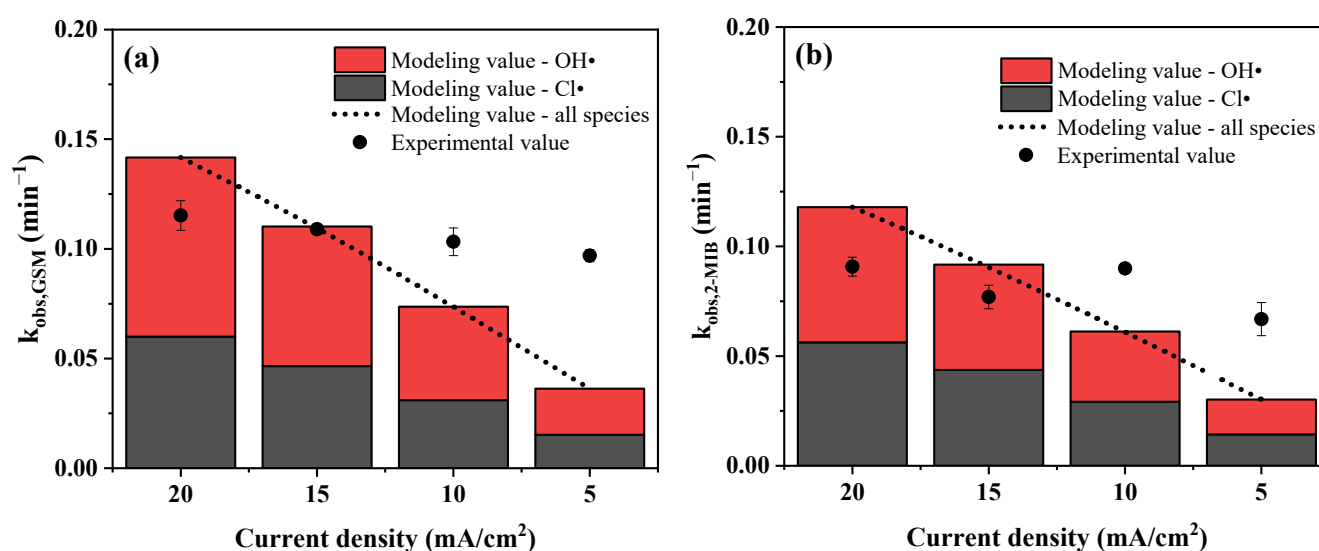


Figure 4. The individual and overall pseudo-first-order rate constants of (a) GSM and (b) 2-MIB degradation by HO• and Cl• under different current densities in the photo-electrochemical process (chloride concentration: 60 mmol/L, initial pH: 7).

3.5. Degradation Kinetics of GSM and 2-MIB in Existence of Free Radical Scavengers

In real aquatic environments, many complicated pollutants (e.g., natural organic matter), regarded as free radical scavengers, are widely distributed in the water matrices [45,46]. It is necessary to evaluate the feasibility of the kinetic models of GSM and 2-MIB degradation in the presence of organic matter. As a commonly used HO• radical scavenger, NB can react with HO• at a second-order rate constant of $3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, and its reactions with Cl• are negligible [39,47]. Considering that TBA could react with both HO• and Cl• actively with second-order rate constants of $6.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $3.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, respectively [48,49], it was applied to scavenge HO• and Cl• species. Therefore, TBA and NB are frequently used to distinguish the contributions of HO• and Cl• to pollutant degradation in advanced oxidation processes.

Different concentrations of NB or TBA were spiked in the electrolyte solution with a chloride concentration of 60 mmol/L at pH 7 to study the contributions of HO• and Cl• to GSM and 2-MIB degradation in the UV-assisted photo-electrochemical process. As shown in Figures 5 and 6, the calculated results of the apparent rate constants for GSM and 2-MIB degradation from the kinetic models were approximately consistent with the experimental values in the presence of the free radical scavengers NB or TBA. The pseudo-first-order kinetic constants of GSM and 2-MIB degradation in the UV-assisted photo-electrochemical process decreased with increasing concentrations of NB or TBA. The reactivities of the radicals with GSM and 2-MIB showed some differences, with GSM being more prone to oxidation degradation by the radicals than 2-MIB [2]. With the quenching effect of HO• in the presence of NB, the decrease in the pseudo-first-order kinetic constants for 2-MIB degradation was higher than that for GSM, meaning that Cl• played a crucial role in 2-MIB degradation. The modeling results indicated that with increasing concentrations of NB, the contributions of HO• to GSM and 2-MIB degradation declined, while the removal of GSM and 2-MIB by Cl• remained stable. In the presence of TBA, the pseudo-first-order kinetic constants of GSM and 2-MIB degradation decreased due to the absence of HO• and Cl• by the scavenging effect. Compared with the results of GSM degradation by Cl• in the presence of NB, the pseudo first-order kinetic constants of GSM degradation declined considerably at a TBA concentration of $1.0 \times 10^{-3} \text{ mol/L}$. Therefore, it could be concluded that HO• played a more important role than Cl• in GSM degradation in the photo-electrochemical process, which was in good agreement with the modeling calculation results. Bai et al. [50] reported that GSM can be mineralized by HO• through the opening reactions of the hexatomic ring. For 2-MIB degradation in the presence of TBA, the decrease in the pseudo-first-order kinetic constants approached that achieved by Cl• in the presence of NB. This result suggested that Cl• made more contributions to removing 2-MIB than HO•, which was also confirmed by the modeling values. It was reported that the degradation of off-flavor compounds by reactive chlorine species such as Cl• was found to be structurally selective, and that the reactive chlorine species contributed more to the degradation of 2-MIB than GSM [28]. Moreover, the degradation of GSM and 2-MIB was not completely suppressed even in the presence of TBA, implying that some other reactive species contributed to the removal of GSM and 2-MIB in the photo-electrochemical process.

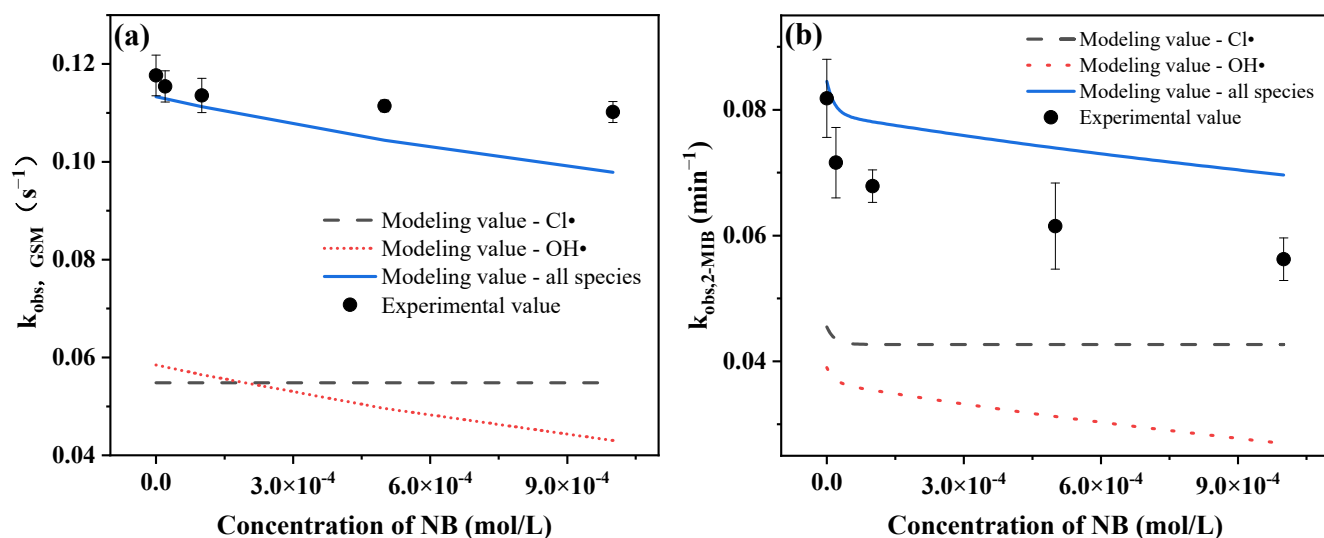


Figure 5. Contributions of reactive species to the degradation of (a) GSM and (b) 2-MIB in the presence of the scavenger NB in the photo-electrochemical process (chloride concentration: 60 mmol/L, initial pH: 7, current density: 15 mA/cm²).

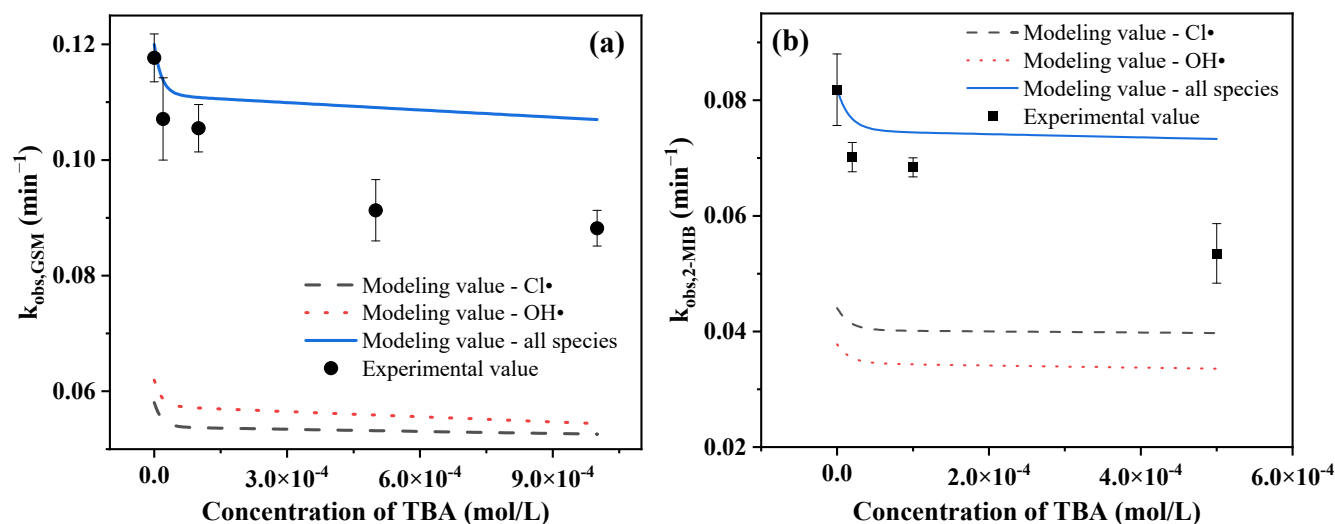


Figure 6. Contributions of reactive species to the degradation of (a) GSM and (b) 2-MIB in the presence of the scavenger TBA in the photo-electrochemical process (chloride concentration: 60 mmol/L, initial pH: 7, current density: 15 mA/cm²).

4. Conclusions

The degradation kinetics of GSM and 2-MIB in AOPs based on UV radiation and electro-oxidation mediated by active chlorine were investigated in this study. Dynamic models were established by applying the rate constants of GSM and 2-MIB with HO• and Cl• to simulate the elimination of GSM and 2-MIB in the UV photo-electrochemical process. The models were employed to evaluate the effects of water quality parameters (electrolyte concentrations and initial pH values of the solutions) and operation parameters (current densities) on the degradation of GSM and 2-MIB, during which the models presented a good prediction effect. Increases in the chloride ion concentration contributed to the degradation of GSM and 2-MIB in both modeling and experimental values. The rate constants for the degradation of GSM and 2-MIB decreased from 0.132 min⁻¹ and 0.099 min⁻¹ to 0.0622 min⁻¹ and 0.0302 min⁻¹ as the pH increased from 5 to 11. With increases in the current density from 5 to 10 mA/cm², the rate constants of GSM and 2-MIB degradation were increased by 21.33% and 39.60%, respectively. The contributions

of HO• and Cl• to the removal of GSM and 2-MIB were elucidated by kinetics modeling and scavenging experiments, which indicated that HO• played a crucial role in GSM degradation, and that Cl• was the dominant radical for 2-MIB elimination. These findings complemented some new viewpoints for the promising alternative UV-AOPs based on generating free radicals in situ to degrade off-flavor compounds.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/w17010057/s1>, Text S1: Experimental system for GSM and 2-MIB degradation; Text S2: Chemical reaction process for the kinetic modeling; Figure S1: Schematic diagram of the experimental apparatus; Table S1: The main reactions and rate constants involved in the kinetic model. References [2,20,39,51–55] are cited in Supplementary Materials.

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