The research on the control of chlorinated by-products by the combined process of three-dimensional electrode system and ultraviolet-photocatalytic oxidation

Li Wang, Hong Liang*, Kaibin Zhang, Hong Huang and Qingchun Wang
Southwest Petroleum University, 8 Xindu Ave., Xindu District, Chengdu, Sichuan, China
*Corresponding author. E-mail: lianghong70@126.com

ABSTRACT

Advanced oxidation technology is considered to be the most potential wastewater treatment technology. As one of the advanced oxidation technologies, the three-dimensional electrochemical system (3DES) is often used to treat industrial wastewater that is difficult to degrade. Sulphonated phenolic resin (SMP) was treated as a characteristic pollutant in sulfonated drilling wastewater. The separate effect of current, the dosage of particle electrodes, chloride ion concentration and initial pH on chlorinated by-products were analyzed by response surface methodology (RSM). Results showed that current is the most dominant factor, followed by the dosage of particle electrodes. The ultraviolet-electrolysis (UVEL) system was implemented by adding ultraviolet light under the optimal electrolysis (EL) system. The chemical oxygen demand (CODcr) and total organic carbon (TOC) removal rates of the UVEL system were respectively increased by 19% and 29.39% compared with the EL system, the concentration of chlorinated by-products was also reduced by 534.4 mg/L when the UV irradiance was 5.24 mW/cm². These results indicated that the UVEL system degrades SMP more thoroughly. The enhanced reaction mechanism of the UVEL system and the possible degradation pathway for SMP were proposed by controlling free radical quenching experiments and the product of EL and UVEL processes. The results showed that the high degradation efficiency of the UVEL system could be attributed to the synergistic degradation mechanism present in the UVEL system, where the photolysis of active chlorine species (ACl) promotes the increase of hydroxyl radical (·OH).

Key words: active chlorine species, chlorinated by-products, electrochemistry, photochemistry, three-dimensional electrode

HIGHLIGHTS

- Current is the most important factor affecting ACl change.
- ACl is the main active substance to degrade SMP in EL system.
- The synergism degradation mechanism existing in the UVEL can be attributed to the additional increase of OH.
- Less chlorinated by-products were produced in the UVEL degradation system.
INTRODUCTION

The prerequisite for successful drilling of deep or ultra-deep wells is a high-density sulphonated drilling mud. SMP is usually used as an additive to prevent the loss of filtrate from sulphonated drilling mud. Various chemical additives (such as chlorine-containing chemical additives, SMP, etc.) inevitably remain in the used sulphonated drilling mud system. Among them, the water-solubility of SMP is attributed to the hydrophilic group sulfonmethyl (-CH₂SO₃⁻). All in all, sulphonated drilling wastewater is a complex mixture with high chemical oxygen demand (COD), high chloride ion concentration and containing various drilling fluid components (Yang et al. 2002). Current technologies for the treatment of sulphonated drilling wastewater include air flotation, coagulation, activated carbon adsorption, bio/coagulation and secondary coagulation. However, the application of these methods is constrained by the high investment and poor treatment results (Wang et al. 2004). Therefore, higher requirements are put forward for the treatment of sulphonated drilling wastewater processes.

Within the last decade, ozone (O₃), hydrogen peroxide (H₂O₂), ultraviolet (UV), persulfate (S₂O₈²⁻), and electrochemical oxidation based-advanced oxidation processes (AOPs) have been studied for removing organic pollutants of sulphonated drilling wastewater. These studies without exception show that AOPs have excellent processing performances. However, the production of chlorinated organic as by-products of AOPs has been reported due to the co-existence presence of organic pollutants and ACI. Martinez-Huitle detected the presence of chlorinated by-products such as chloramine, chlorate and perchlorate during the electrochemical treatment of pharmaceutical wastewater (Bergmann & Koparal 2006). In short, how to effectively deal with these toxic and harmful chlorinated by-products has received substantial interest. Hou studied the formation of chlorinated by-products by S₂O₈²⁻ oxidation based-AOPs in the presence of natural organic matter (NOM), these results indicated that the chlorinated by-products existed in the form of SO₄²⁻ and ACI mediators, which were completely degraded with NOM (Hou et al. 2018). The combination of different AOPs has been tested by Pradip Saha and Kosar Hikmat Hama Aziz as an alternative method for the deep mineralization of chlorinated by-products (Aziz et al. 2017; Saha et al. 2021). Kosar Hikmat Hama Aziz found that the removal rate of chloroacetic acid (CAA) was only 2% after plain ozonation treatment, while the UV-O₃-Fenton combined process can deeply mineralize CAA due to the process and can promote the generation of additional OH (Aziz 2019), similar reports have also been reported in the study of the treatment of fluorinated wastewater by plasma based-AOPs (Aziz et al. 2021). Recently, the novel UV/E-Cl&H₂O₂ process was tested by Haoran Yin as an alternative to the UV/Cl and UV/H₂O₂ processes to treat medical wastewater. The results
showed that the chlorinated by-products in the novel process were reduced by 21.4%, which can be attributed to the synergistic effect of OH and ACl (Yin et al. 2021). Teng and colleagues also found that completely mineralization of the herbicide atrazine (ATZ) was achieved by 3DES of a homemade particle electrode from waste resource recovery (Teng et al. 2021).

From the short review above, key findings emerge: firstly, the combination of various oxidation process based-AOPs provides a broad and promising prospect for the treatment of chlorinated by-products. Secondly, 3DES and UV catalytic oxidation have attracted more and more attention due to their ease of control, chemical stability, availability and low cost (Aziz 2019). Thirdly, it is necessary to improve the removal performance of the combined processes by adding additional chemical additives, which increases the cost and generates undesirable by-products.

The control of chlorinated by-products in the treatment of sulfonated drilling wastewater was not reported in preceding research. So the combined process of 3DES and UV radiation to degrade SMP and chlorinated by-products is proposed in this paper. Four operational parameters were examined with RSM to optimize the concentration of chlorinated by-products in EL system, and further be mineralized in UVEL system. Last but not least, the synergistic degradation mechanism of the UVEL system was also proposed in this study.

MATERIALS AND METHODS

Reagents and instruments

DDS-11A conductivity meter, HH-WO 1 L-100 L type constant temperature water bath magnetic stirrer, CT-K stable voltage and steady current switching power supply (Shanghai Lei Magnetic Co. Ltd); HH-6 chemical oxygen consumption tester (Jiangsu Instrument Co. Ltd); DF-101T magnetic stirrer, PHS-3E pH meter, LS125 ultraviolet tester, LSS UV-visible spectrophotometer, UV-1800 dual-beam ultraviolet spectrophotometer, QP2010 Plus gas chromatography-mass spectrometry instrument (Shimadzu, Japan).

N,N-Diethy1-1,4-phenylenediamine sulphate, ethylenediaminetetraacetic acid disodium salt, graphite powder, potassium dichromate (K2Cr2O7), sulphuric acid (H2SO4), ammonium ferrous sulfate (Fe(NH4)2(SO4)2), sodium chloride (NaCl), sodium sulfate (Na2SO4), potassium iodide (KI), sodium hydroxide (NaOH), dibasic sodium phosphate (Na2HPO4), potassium phosphate monobasic (KH2PO4), silver nitrate (AgNO3) and sodium hypochlorite (NaClO) were purchased from Chengdu Kelon Company. Graphite plates were purchased from Zhejiang Leqing Company. SMP was obtained from Daqing Oilfield. Pyrolusite comes from South Africa.

Experimental setup

The self-made electrolytic cell is illustrated in Figure 1. The electrolytic cell is made of Plexiglas and its size was 10 cm × 10 cm × 10 cm. Both the anode plate and the cathode plate are made of graphite with a thickness of 5 mm, and the distance between the anode and cathode plates is 60 mm. The pyrolusite particle electrode is filled between the cathode and anode plates. Regulated DC power supply provides power to the electrolytic cell.

Here, 0.5 g of sulfonated phenolic resin was poured into 1 liter of pure water, and a certain amount of sodium chloride and sodium sulfate were added to make SMP simulated wastewater stock solution. The pyrolusite particle electrode was made by
mixing graphite powder, pyrolusite powder and polytetrafluoroethylene aqueous dispersion in a certain proportion. EL and UVEL experiments were conducted at room temperature (25 °C). The UV irradiance in the UVEL system was 0.75 mW/cm², 1.4 mW/cm², 2.24 mW/cm², 2.98 mW/cm², 3.74 mW/cm² and 5.24 mW/cm². The samples were processed for 60 minutes, and samples were taken every 10 minutes for COD (Ji et al. 1992) and TOC analyses.

Design of response surface
Based on the preliminary experiment and the previous research results, a group of response surface tests with four factors and five levels were designed. The current, the dosage of particle electrode, current, chloride ion concentration value and initial pH were taken as independent variables, and the chlorinated by-product production was taken as the response quantity, as shown in Table S1 in Supplementary Material. In total, 30 groups of experiments were obtained through the response surface design software, including 25 factorial experiments and five central error experiments. The specific experimental scheme and experimental results are shown in Table S2. In order to clarify the influence of different electrolytic factors on the change rule of chlorinated by-products, a quadratic polynomial response equation was introduced to correlate the response quantity with the variable:

\[ Y_i = b_0 + \sum b_i x_i + \sum b_i x_i^2 + \sum b_i x_i y_j \]  

where, \( Y_i \) is the response factor, \( b_0, b_i, b_{ij} \) represents the model coefficient, and \( x_i, y_j \) represents the independent variable.

Analytical methods
The ACI concentration was measured using a N,N-diethyl-1,4-phenylenediamine sulfate spectrophotometer (HJ 586-2010). The concentration of chloride ions was determined by silver nitrate titration (GB 11898-89). The intermediate products of SMP in EL and UVEL were determined by gas chromatography-mass spectrometry (GC-MS) and ultraviolet-visible (UV-vis) spectrometry. A solid-phase microextraction technology used to separate the samples. The GC column was kept at 40 °C for 3 minutes and then increased to 150 °C at a rate of 5 °C per minute for 2 minutes, then to 270 °C at 10 °C per minute. Other experimental conditions were as follows: injection volume 1 L, pressure 49.5 kPa, total flow rate 9.0 mL/min, column flow rate 1.00 mL/min, purge flow rate 3.0 mL/min.

RESULTS AND DISCUSSION
The influence of electrolysis factors on chlorinated by-products
Due to the complex types of chlorinated organics, it is difficult to effectively characterize them. Therefore, we selected the consumption of chloride ions as an indicator of the degree of chloride ion conversion, which indirectly indicated the generation of chlorinated by-products (Varanasi et al. 2018; Aziz 2019). The following equation was obtained by quadratic multinomial fitting of the experimental results of the central composite design using the response surface:

\[ R = 1,060.17 + 6.29 * A + 84.54 * B - 1.29 * C + 72.54 * D + 5.56 * A * B + 14.94 * A * C \\
+ 5.94 * A * D - 8.81 * B * C + 22.69 * B * D + 63.31 * C * D - 24.93 * A^2 - 42.80 * B^2 \\
- 6.68 * C^2 + 35.82 * D^2 \]

where \( A \) is the concentration of chloride ion, \( B \) is current, \( C \) is initial pH value, and \( D \) is dosage of particle electrode.

Figure 2(a) shows that the concentration of chlorinated by-products increased when the current is in the range 0.9A to 1.5A. Increasing the current can accelerate the direct oxidation process and the indirect oxidation process (Brillas et al. 2015; Shen et al. 2017). The direct oxidation of SMP occurs on the surface of the graphite plate and the indirect oxidation is completed by the active oxidizing substances generated by EL, such as \( \cdot \)OH and ACI. In addition, chloride ions can be oxidized by \( \cdot \)OH to chlorine-free radicals (Equation (2)). Therefore, the formation of chlorinated by-products is the result of the reaction of these chlorine-containing reactive radicals with SMP. Hu's research also confirmed this (Hu et al. 2012). It is worth noting that the concentration of chloride ions determines the amount of ACI, and once the ACI is consumed then the \( \cdot \)OH will play the major degradation role. This is the reason the concentration of chlorinated by-products remains almost unchanged when the...
currents in the range 1.5A to 1.9A:

$$\text{OH} + \text{Cl}^- \rightarrow \text{Cl}^- + \text{ClOH}^-$$

(2)

The experimental results show that the concentration of chlorinated by-products increases with the increase in particle electrode dosage (Figure 2(b)). A similar pattern of results was obtained in the report (Liang et al. 2017). The pyrolusite particle electrode can act as a catalyst to accelerate the amount of OH produced by EL, which is attributed to its multiple aromatic groups and functional groups. Regarding the limitations of the fixed-size reactors, it could be argued that the more particle electrodes means a smaller volume of wastewater can be treated. In addition, more particle electrodes may cause the particle electrodes to contact each other and increase the short circuit current of the cell.

Figure 2(c) illustrates that the concentration of chlorinated by-products with the increase in chloride ion concentration first increase and then decrease. As a supporting electrolyte, sodium chloride can not only increase the conductivity of the liquid phase, but also be the source of ACl. Increasing the concentration of chloride ions will reduce the chlorine evolution potential of the cathode. As a result, the oxygen evolution reaction is inhibited and the yield of ACl is accelerated (Wintrich et al. 2019). The decrease in the concentration of chlorinated by-products in the late stage of the reaction can be explained from two
On the one hand, according to the diffusion-control theory, high chloride concentration is not conducive to the migration of chloride ions to the plate, but also hinders the directional movement of electrons (Bergmann & Koparal 2006). On the other hand, OH in the liquid phase will oxidize chloride ions into chlorine-free radicals, which have a higher oxidation potential ($E = 2.4$ V) (Equations (3)–(5)). So SMP and its intermediate products were degraded to stable products by ACl, chlorine-free radicals and other active substances.

We found that the initial pH of the solution had little effect on the concentration of chlorinated by-products (Figure 2(d)). Acidic or neutral conditions had almost no significant effect on the concentration of chlorinated by-products. However, the concentration of chlorinated by-products under alkaline condition gradually decreased with the pH of the solution increases. This is mainly because the surface charge distribution of the electrode will be affected by the initial pH of the solution, which in turn affects the existing form of ACl and its oxidizing ability (Yañez-Rios et al. 2020). A popular explanation is that the main forms of ACl in acidic and neutral conditions are Cl$_2$ and HClO respectively, their oxidation potentials are very close, which is why the concentration of chlorinated by-products does not change significantly (Table 1). However, under alkaline conditions (pH >8), the concentration of chlorinated by-products decreases gradually with the increase of pH of the solution. These results show that the ACl under alkaline conditions mainly exists in the form of ClO$^-$, which oxidation potential is low, in addition, alkaline conditions strengthen the formation of OH (Deborde & Von Gunten 2008), Cl$_2$ and HClO were obtained by oxidizing ClO$^-$/ClO by OH. As a result, the chlorinated by-products are degraded more thoroughly:

\[
\begin{align*}
\text{OH} + \text{Cl}^- & \rightarrow \text{ClO}^- \\
\text{HClO}/\text{ClO}^- + \text{OH} & \rightarrow \text{ClO}^- + \text{H}_2\text{O}/\text{OH}^- \\
\text{Cl}^- /\text{OCl}^- & \rightarrow \text{Cl}_2^- + \text{ClO}^- + \text{Cl}^-
\end{align*}
\]

The main active substance in the EL system

Previous studies have shown that amines have low reactivity with other free radicals except for ACl, and they can react to form stable chloramines (Equation (6)) (Huang et al. 2017). In order to verify that the key role in the EL system is ACl, 30 mM/l NH$_4$ is added to the solution to quench the ACl. Experimental evidence shows that the CODcr removal rate dropped from 74.3% to 36.6% after ammonium ions is added (Figure 3). From the results, it is clear that the significant decrease in CODcr removal rate is caused by the reaction of amines and ACl to form more stable chloramines. Therefore, we conclude that ACl is the main active substance that degrades SMP:

\[
\text{NH}_4^+ + \text{ACl} (\text{Cl}_2, \text{HClO and ClO}^-) \rightarrow \text{NH}_2\text{Cl}, \text{NHCl}_2... \text{so on}
\]

Influence of UV irradiance on chlorinated by-products in the UVEL system

The influence of UV irradiance on chlorinated by-products in the UVEL system is analyzed by TOC removal rate and CODcr removal rate. The experimental results show that the CODcr removal rate and TOC removal rate in the EL system are far lower than those in the UVEL system (Figures 4 and 5). Furthermore, the removal rate of CODcr and TOC both show an increasing trend with the increase of UV irradiance. The oxidation ability of the UVEL system is further enhanced, compared to the EL system. We speculate that this is related to the photolysis of ACl by UV. Then, some active substances with stronger oxidation capacity are formed (Equations (7)–(9), Table S4) (Reddy et al. 2014). In addition, Iacute et al. demonstrated that the ability of ACl to utilize UV is stronger than H$_2$O$_2$ and S$_2$O$_8^{2-}$, which ensures the advantages of the UVEL process in the treatment of

| pH | Dominate form | Standard electrode potential |
|----|---------------|-----------------------------|
| <3 | Cl$_2$        | $E^0 = 1.36$ V vs SHE       |
| 3–8| HClO          | $E^0 = 1.49$ V vs SHE       |
| >8 | ClO$^-$       | $E^0 = 0.89$ V vs SHE       |
chlorinated by-products (García-Espinoza et al. 2018):

\[
\text{HOCl} + h\nu \rightarrow \cdot \text{OH} + \text{Cl} \quad \text{(7)}
\]

\[
\text{OCl}^- + h\nu \rightarrow \cdot \text{O}^- + \text{Cl} \quad \text{(8)}
\]

\[
\text{O}^- + \text{H}_2\text{O} \rightarrow \cdot \text{OH} + \text{OH}^- \quad \text{(9)}
\]

Figure 6 illustrates that the concentration of ACI decrease when the UV irradiance is in the range of 0 (EL system) to 2.98 mW/cm². This phenomenon demonstrated that enhanced UV irradiance is beneficial to the photolysis of ACI. A popular explanation is that increasing the irradiance can provide photons for the formation of electrons–holes on the surface of the pyrolusite particle electrodes. In addition, the pyrolusite particle electrodes contain more MnOx with semiconductor characteristics, so O₂ and H₂O in the system are converted into OH via the action of electrons (e⁻) and holes (h⁺) (Equation (10)).
Therefore, the oxidation ability of the UVEL system is further enhanced (Liu et al. 2001; Ma et al. 2009; Cao et al. 2015). In addition, Exner has shown that the concentration of dissolved oxygen in the UVEL system is lower than that in the EL system, which indicates that the side reaction of oxygen evolution in the UVEL system can provide part of the source for the generation of ·OH (Exner 2019). From these standpoint, the generation of chlorinated by-products can be considered as the results of these active radicals react with SMP (Jin et al. 2011; Yang et al. 2016). The concentration of ACl no longer changes significantly in the later period, which can be explained from two aspects (Figures 6 and 7). On the one hand, it is limited by objective factors such as the size of electrolytic cell and electrolytic conditions. On the other hand, the ability of pyrolusite particle electrodes to effectively utilize photon quanta is limited. Once the carrier separation and recombination reached dynamic equilibrium, the number of active potentials would not increase, which inhibited the

**Figure 5** | Removal rate of TOC under different UV irradiance.

**Figure 6** | The concentration of ACl under different UV irradiance.
electron–hole oxidation (Fang et al. 2016):

\[
O_2 + H_2O + h\nu \rightarrow e^- + h^+ \rightarrow 2 \cdot OH
\]

(10)

The synergistic mechanism for UVEL treatment of SMP

Both the chlorine-containing system (7,000 mg/L) and the chlorine-free system (conductivity is supplemented by sodium sulfate) are constructed to verify that the photolysis of ACl promoted the generation of additional OH in the UVEL system. Figure 8 shows that in the chlorine-free system, the effect of UVEL is significantly weaker than the sum of EL and UV effects. We speculate that this might be due to the simultaneous photochemical reaction and electrochemical reaction on the surface of the pyrolusite particle electrode in UVEL system, resulting in competition for the active potential. An opposite pattern of results was obtained in the chlorine-containing system (Figure 9). We speculate that this might be due to the synergistic effect between electrochemical oxidation and UV-photocatalytic oxidation in UVEL system. The result is consistent with the previous reports.

It is by now generally accepted that it is difficult to quantitatively analyze OH due to its short lifetime. HCO\textsubscript{3}\textsuperscript{-} and CO\textsubscript{3}\textsuperscript{2-} were used as popular and efficient OH scavengers due to their high reactivity (Carlsson et al. 2005). In order to further verify that the high efficiency of UVEL can be attributed to the role of OH, 100 mM/L CO\textsubscript{3}\textsuperscript{2-} was added to the solution to quench the OH. As can be seen from Figure 10, after the addition of CO\textsubscript{3}\textsuperscript{2-}, the TOC removal of UVEL system significantly decreased. This can be explained in that CO\textsubscript{3}\textsuperscript{2-} reacted with OH leading to a consumption of OH. Together, our results on synergistic degradation mechanisms are broadly consistent with others (Hien et al. 2019; Teng et al. 2021). Therefore, our results demonstrated that OH plays a major role in the degradation of SMP in UVEL system and that ·OH is the dominant active substance in the UVEL synergistic mechanism.

Analysis of intermediate products and degradation pathways of SMP

UV-vis is used to compare the effects of EL and UVEL degradation systems to clarify the mechanism of EL and UVEL degradation systems. The time evolution of the UV-vis spectra of SMP in the EL and UVEL degradation systems are shown in Figures S1 and S2. In the simulated wastewater, the characteristic absorption peak at about 283 nm can be attributed to the sulfonated structure. After 60 minutes of EL treatment, the absorption peak at the wavelength of 283 nm was significantly weakened, and disappeared completely after 120 minutes. However, after only 30 minutes of treatment for UVEL, the absorption peak at the wavelength of 283 nm almost completely disappeared. This phenomenon further confirms that the previous inference. As for the new absorption peak at the wavelength of 290 nm, it is attributed to the similar benzene ring structure and disappears after 120 minutes.
SMP is a complex polymer, which cannot be characterized effectively by conventional organic detection methods. Figures S3 and S4 show the gas chromatography-mass spectra of SMP degradation of EL and UVEL, respectively. It can be seen from Figures S3 and S4 that the high response peaks of the chlorinated by-products detected in the EL system are more than those of the UVEL system. Tables 2 and 3 display the measurement results of GC-MS, it can be seen that the content and types of chlorinated by-products in the UVEL system are significantly lower than those in the EL system. As previously analyzed, this performance can be attributed to the synergistic degradation mechanism of the UVEL, which strengthens the oxidizing ability of the system.

We propose possible pathways for SMP degradation. Firstly, SMP is oxidized and degraded by ACl and OH, destroying the benzene ring structure in SMP, which is decomposed into methyl benzenesulfonate and carboxylic acid. Secondly, the sulfomethyl structure and the remaining benzene ring are further decomposed by ACl, OH and chlorine-free radicals into small...
Table 2 | The product after 60 minutes of electrolysis

| Substance                                      | Peak area  |
|------------------------------------------------|------------|
| 1-Butene, 3-chloro-2-methyl-                   | 361,769    |
| Chloroacetamidine hydrochloride                | 104,210    |
| 1,1-Dimethyl-3-chloropropanol                  | 191,856    |
| Butane, 2,3-dichloro-2-methyl-                 | 127,492    |
| Triethyl phosphate                             | 128,468    |
| 2H-Benzotriazole, 2-(2-butoxy-5-methylphenyl)  | 54,283     |
| Fumaric acid, 3,5-difluorophenyl undecyl ester| 401,393    |
| Carbamic acid, N-(3-chloro-4-methoxyphenyl)-, nonyl ester | 80,464 |
| Dodecanoic acid                                | 84,071     |
| Pyridinium,1-(benzoylamino)-3,5-dimethyl-,hydroxide, inner salt | 52,733 |
| cis-9-Hexadecenal                              | 52,771     |
| 5.beta.,7.beta.H,10.alpha.-Eudesm-11-en-1.alpha.-ol | 50,039   |
| (2,3-Diphenylcyclopropyl)methylphenyl sulfoxide, trans- | 98,482   |

Figure 10 | Effect of CO$_3$$^2$- on the degradation of SMP in the UVEL system.

Table 3 | The product after 60 min ultraviolet electrolysis

| Substance                                      | Peak area  |
|------------------------------------------------|------------|
| 3-Methyl-3-chloro-1-butene                     | 354,508    |
| 1,4-Dioxaspiro[4.5]deca-6,9-diene-2,8-dione    | 71,349     |
| Dichloroacetic acid, tridecyl ester            | 10,053     |
| 1,1-Dimethyl-3-chloropropanol                  | 167,728    |
| Butane, 2,3-dichloro-2-methyl-                 | 129,225    |
| 2-Propanone, 1,1,3,3-tetrachloro-               | 13,124     |
| Triethyl phosphate                             | 62,662     |
| 2-Propen-1-one, 3-(4-nitrophenyl)-1-phenyl-     | 26,056     |
molecular substances such as chlorinated alkynes and chlorinated alcohols. Finally, these small molecules are completely mineralized into CO2 and H2O.

CONCLUSION
In general, the effects of current, pyrolusite particle electrode, chloride ion concentration and initial pH on the concentration of chlorinated by-products had been systematically analyzed by RSM. We concluded that current was the most influential factor affecting the chlorinated by-products, while all the other factors were also significant. Compared with the EL system, the chlorinated by-products of the UVEL system were reduced by 534.4 mg/L. The results confirmed a strong effect of the UVEL system. Furthermore, the quenching experiment results of ACI and OH showed that the synergistic effect of UVEL performance was due to the generation of additional OH. Finally, the possible degradation pathway of SMP was proposed by us. All in all, the combined process of 3DES and UV may have a wide application prospect in treating drilling wastewater. We believe that apart from looking for the control of chlorinated by-products, future research should look for the quantitative of chlorinated by-products and the energy consumption.

FUNDING
This work was supported by the major national R&D projects of China (grant no. 2016ZX05040003-004-002).

AVAILABILITY OF DATA AND MATERIALS
The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

CONSENT FOR PUBLICATION
Manuscript is approved by all authors for publication.

COMPETING INTERESTS
The authors declare that they have no competing interests.

DATA AVAILABILITY STATEMENT
All relevant data are included in the paper or its Supplementary Information.

ETHICS APPROVAL AND CONSENT TO PARTICIPATE
Not applicable.

REFERENCES
Aziz, K. H. H., Miessner, H., Mueller, S., Mahyar, A., Kalass, D., Moeller, D., Khorshid, I. & Rashid, M. A. M. 2017 Comparative study on 2,4-dichlorophenoxyacetic acid and 2,4-dichlorophenol removal from aqueous solutions via ozonation, photocatalysis and non-thermal plasma using a planar falling film reactor. Journal of Hazardous Materials 343, 107–115.
Aziz, K. H. H. 2019 Application of different advanced oxidation process for the removal of chloroacetic acids using a planar falling film reactor. Chemosphere 228, 337–383.
Aziz, K. H. H., Miessner, H., Mahyar, A., Mueller, S., Moeller, D., Mustafa, F. & Omer, K. M. 2021 Degradation of perfluorosurfactant in aqueous solution using non-thermal plasma generated by nano-second pulse corona discharge reactor. Arabian Journal of Chemistry 14 (10), 103366.
Bergmann, M. E. H. & Koparal, A. S. 2006 Studies on electrochemical disinfectant production using anodes containing RuO2. Journal of Applied Electrochemistry 35 (12), 1321–1329.
Brillas, E. & Martinez-Huitle, C. A. 2015 Decontamination of wastewater containing synthetic organic dyes by electrochemical methods. An updated review. Catalysis B: Environmental 166 (2015), 603–643.
Cao, S., Chen, C., Zhang, J., Zhang, C., Yu, W., Liang, B. & Tsang, Y. T. 2015 MnOx quantum dots decorated reduced graphene oxide/TiO2 nanohybrids for enhanced activity by a UV pre-catalytic microwave method. Applied Catalysis B-Environmental 176, 500–512.
Carlsson, M., Stenman, D., Merényi, G. & Reitberger, T. 2005 A comparative study on the degradation of cotton linters induced by carbonate and hydroxyl radicals generated from peroxynitrite. Holzforschung 59 (2), 132–142.
Deborde, M. & Von Gunten, U. 2008 Reactions of chlorine with inorganic and organic compounds during water treatment – kinetics and mechanisms: a critical review. *Water Research* 42 (1), 13–51.

Exner, K. S. 2019 Controlling stability and selectivity in the competing chlorine and oxygen evolution reaction over transition metal oxide electrodes. *ChemElectroChem* 6 (13), 3401–3409.

Fang, H. B., Li, N., Xue, Z. B., Zhang, Y. K., Zhang, Y. Z. & Tao, X. 2016 Efficient charge separation promoting visible-light-driven photocatalytic activity of MnOxdecorated WS2 hybrid nanosheets. *Electrochemistry Communications* 72, 118–121.

García-Espinoza, J. D., Mijaylova-Nacheva, P. & Avilés-Flores, M. 2018 Electrochemical carbamazepine degradation: effect of the generated active chlorine, transformation pathways and toxicity. *Chemosphere* 192, 142–151.

Hien, N. T., Nguyen, L. H., Van, H. T., Nguyen, T. D., Nguyen, T. H. V., Chu, T. H. H., Nguyen, T. V., Trinh, V. T., Vu, X. H. & Aziz, K. H. H. 2019 Heterogeneous catalyst ozonation of Direct Black 22 from aqueous solution in the presence of metal slags originating from industrial solid wastes. *Separation and Purification Technology* 233, 115961.

Hou, S., Ling, L., Dionysiou, D. D., Wang, Y., Huang, J., Guo, K., Li, X. & Fang, J. 2018 Chlorate formation mechanism in the presence of sulfate radical, Chloride, Bromide and Natural organic matter. *Environmental Science and Technology* 52 (11), 6317–6325.

Hu, C. Z., Liu, H. J. & Qu, J. H. 2012 Optimum conditions for the formation of Al13 polymer and active chlorine in electrolysis process with Ti/RuO2-TiO2 anodes. *Journal of Environmental Science* 24 (2), 297–302.

Huang, T., Chen, J., Wang, Z., Guo, X. & Crittenden, J. C. 2017 Excellent performance of cobalt-impregnated activated carbon in peroxymonosulfate activation for acid orange 7 oxidation. *Environmental Science & Pollution Research* 24 (10), 9651–9661.

Ji, C., Zhong, Y., Ying, F. & Songlin, F. 1992 Determination of COD in wastewater high in Cl– oil-gas fields. *Journal of Southwest Petroleum Institute* 14 (4), 94–101.

Jin, J., El-Din, M. G. & Bolton, J. R. 2011 Assessment of the UV/chlorine process as an advanced oxidation process. *Water Research* 45 (4), 1890–1896.

Liang, H., Ren, Y. M., Qiu, Y., Cui, M. X. & Lee, H. S. 2017 Research on the electrolytic active chlorine in the process of treating chlorine-containing wastewater by three-dimensional electrode method. *Industrial Water Treatment* 37 (9), 37–40.

Liu, Y., Luo, M. F., Wei, Z. B., Xin, Q., Ying, P. L. & Li, C. 2001 Catalytic oxidation of chlorobenzene on supported manganese oxide catalysts. *Applied Catalysis B: Environmental* 29 (1), 61–67.

Ma, C. M., Ku, Y., Y. Kuo, Y. L., Chou, Y. C. & Jeng, F. T. 2009 Effects of silver on the photocatalytic degradation of gaseous isopropanol. *Water, Air, and Soil Pollution* 197, 313–321.

Reddy, K. R., Gomes, V. G. & Hassan, M. 2014 Carbon functionalized TiO2 nanofibers for high efficiency photocatalysis. *Materials Research Express* 2014 (1), 1–15.

Saha, P., Wang, Y., Moradi, M., Brüninghoff, R., Moussavi, G., Mei, B. & Mul, G. 2021 Advanced oxidation processes for removal of organics from cooling tower blowdown: efficiencies and evaluation of chlorinated species. *Separation and Purification Technology* 278, 119537.

Shen, B., Wen, X. & Huang, X. 2017 Enhanced removal performance of estriol by a three-dimensional electrode reactor. *Chemical Engineering Journal* 327, 597–607.

Teng, X., Li, J., Wang, J., Liu, J., Ge, X. & Gu, T. 2021 Effective degradation of atrazine in wastewater by three-dimensional electrochemical system using fly ash-red mud particle electrode: mechanism and pathway. *Separation and Purification Technology* 267, 118661.

Varanasi, L., Ciscarelli, E., Khaksari, M., Mazzoleni, L. R. & Minakata, D. 2018 Transformations of dissolved organic matter induced by UV photolysis, hydroxyl radicals, chlorine radicals, and sulfate radicals in aqueous-phase UV-based advanced oxidation processes. *Water Research* 135, 22–30.

Wang, Y. M., Yang, M., Zhang, J. & Zhang, Y. 2004 Improvement of biodegradability of oil field drilling wastewater using ozone. *Ozone: Science & Engineering* 26 (3), 309–315.

Wintrich, D., Öhl, D., Barwe, S., Ganassini, A., Möller, S., Tarnev, T., Botz, A., Ruff, A., Clausmeyer, J., Masa, J. & Schuhmann, W. 2019 Enhancing the selectivity between oxygen and chlorine towards chlorine during the anodic chlorine evolution reaction on a dimensionally stable anode. *ChemElectroChem* 6 (12), 3108–3112.

Yañez-Ríos, A. E., Carrera-Crespo, E. J., Luna-Sanchez, M. R., Palma-Goyes, E. R. & Jorge, V. 2020 The influence of pH and current density on an UV254 photo-assisted electrochemical process generating active chlorine and radicals for efficient and rapid ciprofloxacin mineralization compared to individual techniques. *Journal of Environmental Chemical Engineering* 8 (5), 104357.

Yang, M., Wang, Y., Wang, D., Zhou, X. Y., Gao, Y. & Jia, W. 2002 Evaluation of contribution of drilling additives to the COD of drilling wastewater and their coagulation effects. *Guocheng Gongcheng Xuebao* 3, 283–288.

Yang, X., Sun, J. L., Fu, W. J., Shang, C., Li, Y., Chen, Y. W., Gan, W. H. & Fang, J. Y. 2016 PPCP degradation by UV/chlorine treatment and its impact on DBP formation potential in real waters. *Water Research* 98, 309–318.

Yin, H., Zhang, Q., Su, Y., Tang, Y. & Zhou, M. 2021 A novel UV based advanced oxidation process with electrochemical co-generation of chlorine and H2O2 for carbamazepine abatement: better performance, lower energy consumption and less DBPs formation. *Chemical Engineering Journal* 425, 151857.

First received 19 June 2021; accepted in revised form 22 October 2021. Available online 1 November 2021