

# Enhanced mineralization of hypersaline wastewater with $\text{Fe}^{2+}/\text{Cu}^{2+}$ catalyzed UV-Fenton process: process optimization and catalytic mechanism

Xiaofang Yang, Zhaoyi Yang, Zhen Liu, Weijun Zhang and Dongsheng Wang

## ABSTRACT

The efficiency of Fenton oxidation was inhibited by the high content of salt in the industrial wastewater. However, enhanced mineralization of hypersaline industrial wastewater is necessary for advanced treatment and subsequent wastewater salt recovery process. Therefore,  $\text{Fe}^{2+}$  and  $\text{Cu}^{2+}$  catalyzed UV-Fenton oxidation were carried out to improve the total organic carbon (TOC) removal efficiency for a hypersaline wastewater from resin manufacturing. The performance of UV-Fe/Cu-Fenton oxidation was comparatively investigated and optimized using response surface methodology (RSM) to develop a practical high-efficient mineralization treatment technique for hypersaline wastewater. More than 90% of TOC was removed under optimal conditions of UV- $\text{Fe}^{2+}$  and UV- $\text{Cu}^{2+}$ -Fenton oxidation, namely 9.6 mM  $\text{Fe}^{2+}$  and 176 mM  $\text{H}_2\text{O}_2$ , and 2.95 mM  $\text{Cu}^{2+}$  and 276 mM  $\text{H}_2\text{O}_2$ , respectively. The reactive oxygen radicals identified using electron spin resonance (ESR) spectroscopy revealed that hydroxyl radical was dominant oxidant in UV- $\text{Fe}^{2+}$ -Fenton process, while  $\text{HO}_2\cdot/\text{O}_2\cdot^-$  played a more important role in the UV-Cu-Fenton system. The  $\text{Cl}^-$  effect is also different for UV Fe and Cu Fenton. Moreover, no scaling and sludge problem makes UV-Cu-Fenton a promising alternative method for efficient mineralization of hypersaline industrial wastewater.

**Key words** | copper(II), hypersaline wastewater, mineralization, radicals, UV-Fenton

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## INTRODUCTION

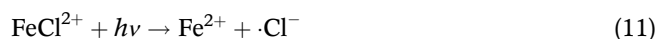
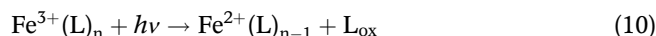
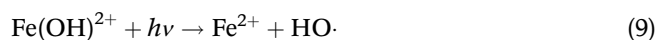
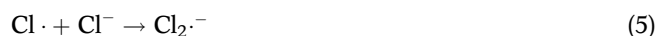
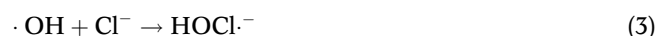
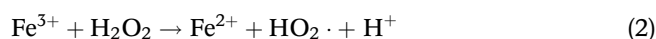
Industrial wastewater with high organic content and salinity is a big challenge for biological treatment systems without pre-treatment. For instance, the chemical oxygen demand (COD) of wastewater discharged from epoxy resin and epoxy chloropropane manufacturing is higher than 10,000 mg/L and the NaCl concentration is higher than 20% w/v. Using conventional pre-dilution and biodegradation processes for high saline wastewater treatment, not only consume large amount of fresh water and increase the discharge load of secondary waste water, but also lose valuable mineral salt resource. Accordingly, when salt recycling is of a major consideration, enhanced total organic carbon (TOC) removal is important in the wastewater treatment. That is because the currently used salt concentration techniques, such as multiple effect evaporation (MEE) or membrane electrolysis, require low organic content of the influent water. Therefore, advanced treatment and

enhanced mineralization of hypersaline industrial wastewater is very imperative and provide a possibility for salt resources recovery from the wastewater.

Fenton oxidation technique is one of the most commonly used advanced oxidation processes (AOPs) for mineralization treatment of hazardous and/or biorefractory wastewater (Teel *et al.* 2001; Pignatello *et al.* 2006; Wang & Xu 2012). It is well known that Fenton process is dependent on non-selective radicals- $\text{HO}\cdot$  which are formed as described by Equations (1) and (2), and the efficiency of conventional Fenton oxidation on organics removal is largely inhibited by inorganic ions such as chloride and sulfate ions (Lipczynskakochany *et al.* 1995; Pignatello *et al.* 2006). Chloride ions could act as the scavengers of  $\text{HO}\cdot$  and form chlorine radicals which are less reactive than  $\cdot\text{OH}$  (Pignatello 1992), as shown in Equations (3)–(5). Chloride ions are also able to form complexes with  $\text{Fe}^{2+}/\text{Fe}^{3+}$

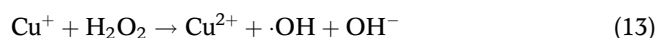
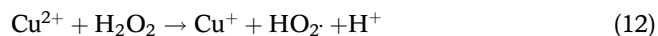
(Equations (6)–(8)), thus decreasing the reaction rate of Fe species with H<sub>2</sub>O<sub>2</sub> (De Laat *et al.* 2004).

Extensive studies have shown that addition of external photo energy could enhance the oxidative degradation and mineralization of pollutants by Fenton reaction (Pignatello 1992; Wei *et al.* 2011; Wang & Xu 2012; Wu *et al.* 2016). It has been reported that the effect of NaCl on the mineralization of synthetic phenol wastewater by UV-Fenton reaction was insignificant at low NaCl concentration, and the mineralization was only moderately inhibited at high NaCl concentration (>50 g/L) (Maciel *et al.* 2004). In UV assisted Fenton oxidation, the reduction of Fe(III) species to Fe(II) (Equations (9)–(11)) were accelerated (Pignatello *et al.* 2006; Giri & Golder 2014). Therefore, UV assisted Fenton oxidation could be used for the TOC removal of hypersaline resin processing wastewater which is colorless and relatively low turbidity. However, the reaction conditions and organics degradation performance need to be optimized for practical application in the treatment of high saline wastewater.



Besides Fe ions, Cu is also an active transition metal which shows hydrogen peroxide activation ability (Equations (12) and (13)) (Nieto-Juarez *et al.* 2010; Bokare & Choi 2014). Copper ions (Cu<sup>2+/+</sup>) have similar redox properties as iron ions (Fe<sup>3+/2+</sup>) but different solubility and complexation characteristics, resulting in a different behavior of Cu<sup>2+/+</sup> in Fenton-like reaction. Cu<sup>2+/+</sup> shows a faster H<sub>2</sub>O<sub>2</sub> reaction rate than Fe<sup>3+/2+</sup> species and could be carried out under more neutral conditions, since the cupric aqua species are more soluble at neutral pH

(Bokare & Choi 2014; Peng *et al.* 2016). However, copper was seldom used in homogeneous Fenton oxidation due to the instability of Cu<sup>+</sup> and the higher cost of copper salt and potential toxicity of residue copper ions in effluent. Nevertheless, it has been found that UV radiation could also enhance the Cu ions catalyzed Fenton-like oxidation (Nerud *et al.* 2001; Salazar *et al.* 2012). However, the performance of Cu-Fenton oxidation of saline wastewater and the catalytic mechanism were still not clearly understood.



Therefore, the purposes of this work were to: (a) comparatively evaluate the performance of UV assisted Fe-Fenton and Cu-Fenton for organic pollutants removal from hypersaline wastewater; (b) optimize the mineralization efficiency using response surface methodology (RSM) and develop a practical high-efficient mineralization treatment technique for actual hypersaline wastewater; (c) elucidate the catalytic mechanisms involved in the Fe<sup>2+</sup> and Cu<sup>2+</sup> catalyzed UV-Fenton process.

## MATERIALS AND METHODS

### Materials

The industrial wastewater samples were taken from an epoxy resin manufacturer in Jiangsu Province, China. The wastewater samples contain mainly glycerin, NaCl, bisphenol A diglycidyl ether and epoxy chloropropane. Raw wastewater and water samples after primary Fenton oxidation on site were taken. About 55% of COD and 8% TOC were removed by the primary Fenton oxidation, but the water quality was not good enough for further salt recovery using membrane electrolysis technique. The UV-visible spectra of the wastewater before and after primary Fenton oxidation are given in supporting information (Figure S1 in the Supplementary Material, available with the online version of this paper). The characteristics of the wastewater sample are given in Table S1 (available online). The present study was carried out using the pre-treated samples as advanced treatment in order to further enhance the TOC removal of the wastewater.

All chemicals used are analytical grade reagents. Hydrogen peroxide (30% w/w), ferrous sulfate (FeSO<sub>4</sub>·7H<sub>2</sub>O), Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, HCl and NaOH were purchased from Sinopharm Chemical Reagent Co. Ltd. 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) used in electron spin resonance (ESR) experiments

were supplied by J&K Scientific Ltd. Ultrapure water (Milli-Q) was used to prepare solutions.

## Experimental procedure

### UV-Fenton oxidation procedure

The Fenton reagents were added into the wastewater sample to start the reaction in a single dose or continuous dosing by peristaltic pump in an experimental setup as in Figure S2 (available online). In the optimization experiments of oxidation process conditions, lamps with various powers were used as described in the data. The pH and temperature of solution were measured during the reaction. At given time intervals, a small aliquot was sampled and added with excess of NaOH to quench the reaction. After immediate centrifugation, the supernatant was collected for analysis. All experimental runs were performed in duplicate at ambient temperature unless indicated otherwise.

### Analysis methods

TOC and UV absorbance of water sample was measured using TOC-Vcph analyzer (Shimadzu, Japan) and UV-Vis spectrophotometer (U-2910, Hitachi, Japan), respectively.  $\text{H}_2\text{O}_2$  concentration was measured using titanium sulfate method (Eisenberg 1943). The species of radicals in the filtrate of the reaction solution were identified using 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) as trapping agent by ESR spectroscopy (Bruker model ESP 300E). The ESR spectroscopy was operated at 3514 G center field and 9.85 GHz microwave frequency.

### Response surface methodology (RSM) experimental design

The process optimization was carried out using a Box-Behnken design with three factors and three coded levels experimental design (Design Expert 8.0). The dosages of  $\text{H}_2\text{O}_2$  ( $X_1$ ) and Fe(II) salt or Cu(II) salt ( $X_2$ ) and power of UV lamp ( $X_3$ ) were chosen as independent input variables. The TOC removal efficiency was used as the dependent output variable ( $y$ ). The response variable was fitted by a quadratic polynomial equation

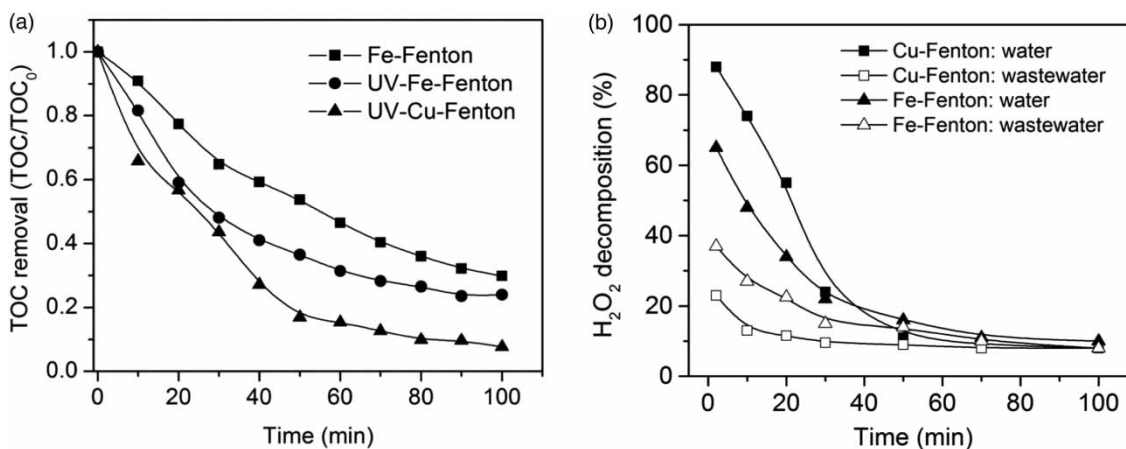
$$y = b_0 + \sum_{i=1}^3 b_i X_i + \sum_{i=1}^3 b_{ii} X_{ii}^2 + \sum_{i=1}^2 \sum_{j=i+1}^3 b_{ij} X_i X_j \quad (14)$$

where  $y$  represents the predicted TOC removal rate of wastewater sample after oxidation,  $b_0$ ,  $b_i$  and  $b_{ij}$  are the fitted coefficients,  $X_i$  and  $X_j$  are the code values of the independent variables. The experimental range and coded levels of the variables are listed in Table S1 in the supporting information.

## RESULTS AND DISCUSSION

### TOC removal and $\text{H}_2\text{O}_2$ decomposition in UV-Fe/Cu-Fenton oxidation

Figure 1(a) shows the TOC removal efficiency with time in different oxidation processes catalyzed by  $\text{Fe}^{2+}$  or  $\text{Cu}^{2+}$  ions. After 100 min reaction, the TOC was reduced to 85, 68 and 22 mg/L for Fe-Fenton, UV-Fe-Fenton and



**Figure 1** | (a) UV enhanced TOC removal ( $[\text{Fe}^{2+}]_0 = [\text{Cu}^{2+}]_0 = 0.0167 \text{ mol/L}$ ,  $[\text{H}_2\text{O}_2]_0 = 0.5 \text{ mol/L}$ ) and (b)  $\text{H}_2\text{O}_2$  decomposition ( $[\text{Fe}^{2+}]_0 = [\text{Cu}^{2+}]_0 = 0.01 \text{ mol/L}$ ,  $[\text{H}_2\text{O}_2]_0 = 0.3 \text{ mol/L}$ ) in UV Fe/Cu-Fenton oxidation processes.

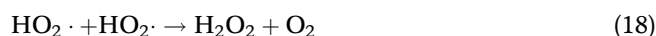
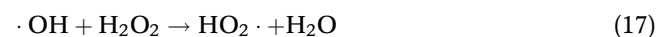
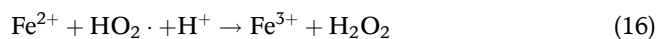
UV-Cu-Fenton systems, respectively. UV irradiation could significantly promote the Fenton oxidation rate and mineralization of pollutants as expected. In addition, UV assisted Cu-Fenton system shows a better TOC removal than Fe-Fenton system. This is partly due to the reactive radicals generation rates in the  $\text{Cu}^+/\text{Cu}^{2+}\text{-H}_2\text{O}_2$  reactions (Equations (12) and (13)) are several orders of magnitude higher than  $\text{Fe}^{2+}/\text{Fe}^{3+}$  catalyzed reactions (Equations (1) and (2)) (Moffett & Zika 1987; Bokare & Choi 2014). The kinetic rate constants for reaction in Equations (1), (2) and (12), (13) are  $40\text{--}80\text{ (mol/L)}^{-1}\cdot\text{s}^{-1}$ ,  $2 \times 10^{-3}\text{ (mol/L)}^{-1}\cdot\text{s}^{-1}$ , and  $4.6 \times 10^2\text{ (mol/L)}^{-1}\cdot\text{s}^{-1}$ ,  $1 \times 10^4\text{ (mol/L)}^{-1}\cdot\text{s}^{-1}$  (Moffett & Zika 1987; Salazar et al. 2012). The photo-induced reduction of  $\text{Fe}(\text{OH})^{2+}$  to  $\text{Fe}^{2+}$  and generation of  $\text{HO}\cdot$  (Equations (9)–(11)) contributed to the promoted TOC removal (Maciel et al. 2004; Machulek et al. 2007). With the presence of high concentration of  $\text{Cl}^-$  ions, the photolysis of  $\text{Fe}(\text{III})$ -complexes such as  $\text{FeCl}^{2+}$  to  $\text{Fe}^{2+}$  and  $\text{Cl}\cdot$  increased the reduction of  $\text{Fe}(\text{III})$  species to  $\text{Fe}(\text{II})$  compared to non-irradiated process (Nadtochenko & Kiwi 1998). Similarly, in the UV-Cu-Fenton reaction, the reduction of  $\text{Cu}(\text{II})$  species with  $\text{H}_2\text{O}_2$  was increased due to the photo-reactivity of the formed  $\text{Cu}(\text{II})\text{-Cl}$  and  $\text{Cu}$ -organic ligand complexes (Millero et al. 1992).

As shown in Figure 1(b),  $\text{H}_2\text{O}_2$  was decomposed rapidly in the first 30 min in all the systems. In pure water medium, the decomposition of  $\text{H}_2\text{O}_2$  by  $\text{Cu}$  ions was slower than by the  $\text{Fe}$  ions possibly due to the oxidation of  $\text{Cu}(\text{I})$  by oxygen (Gallard et al. 1999). With the presence of organic pollutants, the decomposition of  $\text{H}_2\text{O}_2$  increased significantly than in the pure water medium, especially for  $\text{Cu}^{2+}\text{-H}_2\text{O}_2$  system. More than 70% of  $\text{H}_2\text{O}_2$  was decomposed by  $\text{Cu}^{2+}$  in the first 1 min of reaction. The complexes of  $\text{Fe}$  with degradation intermediates are more stable and less reactive with  $\text{H}_2\text{O}_2$  than  $\text{Cu}$  complexes, leading to a lower TOC removal efficiency of UV-Fe-Fenton than UV-Cu-Fenton (Millero et al. 1992; Nerud et al. 2001; Lan et al. 2016). About 90% of  $\text{H}_2\text{O}_2$  was decomposed in the wastewater sample after 30 min of reaction for both  $\text{Cu}$  and  $\text{Fe}$  catalytic systems. However, the TOC unceasingly reduced about 30% in UV-Cu-Fenton oxidation and 20% in UV-Fe-Fenton oxidation after 30 min of reaction when most of the  $\text{H}_2\text{O}_2$  was consumed.

### Effects of reagent dosing manner and pH in UV-Fe-Fenton

The TOC removal efficiency varied with concentration of  $\text{Fe}^{2+}$  and reagent dosing manners (Figure S3 in

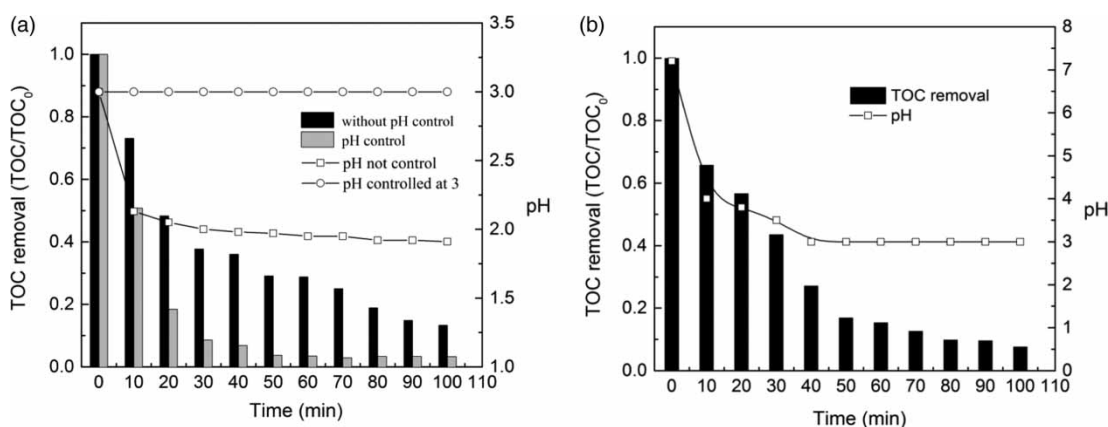
Supplementary Material, available with the online version of this paper). The TOC removal rate was increased with increased  $\text{Fe}^{2+}:\text{H}_2\text{O}_2$  molar ratio from 1:30 to 1:20, and reduced at 1:10 with fixed  $\text{H}_2\text{O}_2$  dosage. Excess amount of  $\text{Fe}^{2+}$  ions and  $\text{H}_2\text{O}_2$  both will consume the generated  $\text{HO}\cdot$  and  $\text{HO}_2\cdot/\text{O}_2\cdot^-$  (Equations (15)–(18)). In fact, it is the actual concentration, instead of the dosage, of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  determines the kinetics and affect the performance of Fenton reaction in the process.



Compared with single dose of reagent (Figure S3), the continuous dosing of Fenton's reagent was benefit for the reaction by lowering the instantaneous concentration of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  at the initial stage of the reaction and sustaining the generation of  $\text{HO}\cdot$ . Therefore, the continuous dosing manner was used for both  $\text{Fe}$  and  $\text{Cu}$ -Fenton system in order to obtain a better TOC removal efficiency.

pH is an important factor for Fenton reaction by determining the iron species distribution (Pignatello et al. 2006). Normally, pH between 3 and 4 is optimal for Fe-Fenton reaction (Tang & Huang 1996; Duesterberg & Waite 2006). It was noted that pH of reaction medium was always declined in wastewater treatment due to hydrolysis of ferric ions and formation of organic intermediates, such as formic acid and acetic acid. Results in Figure 2(a) reveal that keep the pH at 3 is beneficial for TOC removal, which is in accordance with literature (Tang & Huang 1996; Duesterberg & Waite 2006). Without pH control, the pH of the solution decreased to pH 2, and the corresponding TOC removal was about 86% after 100 min of reaction (Figure 2(a)). However, when the pH was maintained at 3, a maximum 96% TOC removal was achieved at 50 min (Figure 2(a)). Therefore, to get a better TOC removal using the  $\text{Fe}$  catalyzed Fenton, particular attention needs to be paid on continual control of pH throughout the process.

However, for the  $\text{Cu}$ -Fenton reaction, the final pH dropped to 3 without pH control and the TOC removal efficiency still reached 90% after 90 min (Figure 2(b)). The  $\text{Cu}$ -Fenton is less sensitive to pH and could be carried out in near neutral pH range due to the  $\text{Cu}^{2+}$  species are more soluble at higher pH than  $\text{Fe}^{3+}$  (Millero et al. 1992; Peng et al. 2016). Therefore, for UV-Cu-Fenton oxidation, pH control was less important compared with Fe-Fenton oxidation.



**Figure 2** | Effects of pH on TOC removal in (a) UV-Fe-Fenton and (b) UV-Cu-Fenton (no pH control). Columns, the TOC removal efficiency under different pH conditions; lines with scatters, the variation of pH during reaction;  $[\text{Fe}^{2+}]_0 = 0.025 \text{ mol/L}$ ,  $[\text{Cu}^{2+}]_0 = 0.017 \text{ mol/L}$ ,  $[\text{H}_2\text{O}_2]_0 = 0.5 \text{ mol/L}$ , the Fenton's reagent was dosed continuously.

### Optimization of reaction conditions of UV-Fe/Cu-Fenton oxidation using response surface methodology (RSM)

RSM was used to optimize the reaction conditions for UV-Fe-Fenton and UV-Cu-Fenton systems. A Box-Behnken design with three factors and three coded levels experimental design was used, and a total of 17 batch experiments were carried out for each system to develop the response surface model (Table S2, available online). Equations (19) and (20) show the fitted quadratic polynomial model in terms of coded variables for UV-Fe-Fenton and UV-Cu-Fenton system, respectively. The obtained TOC removal efficiencies varied between 26% to 96% for UV-Fe-Fenton system and 62% to 91% for UV-Cu-Fenton system, and the predicted values were in good agreement with the experimental observations.

$$y = 78.32 + 18.93X_1 - 3.35X_2 + 14.43X_3 + 7.69X_1X_2 - 5.67X_1X_3 + 6.91X_2X_3 - 15.93 \quad (19)$$

$$y = 74.60 + 8.84X_1 - 7.12X_2 + 1.53X_3 - 3.13X_1X_2 - 0.19X_1X_3 - 0.12X_2X_3 - 2.96X_1^2 + 1.98X_2^2 + 5.54X_3^2 \quad (20)$$

where  $y$  is the predicted TOC removal,  $X_1$  is the dosage of  $\text{H}_2\text{O}_2$  coded values,  $X_2$  is the concentration of ferrous sulfate or copper nitrate coded values,  $X_3$  is the power of UV lamp.

The analysis of variance (ANOVA) results for UV-Fe/Cu-Fenton systems are summarized in Table S3 in the Supplementary Material (available online). The quality of the fitting was expressed by the correlation coefficient  $R^2$ , which is 0.9767 for UV-Fe-Fenton and 0.9882 for UV-Cu-Fenton, suggesting that 97.67% and 98.83% of total variation

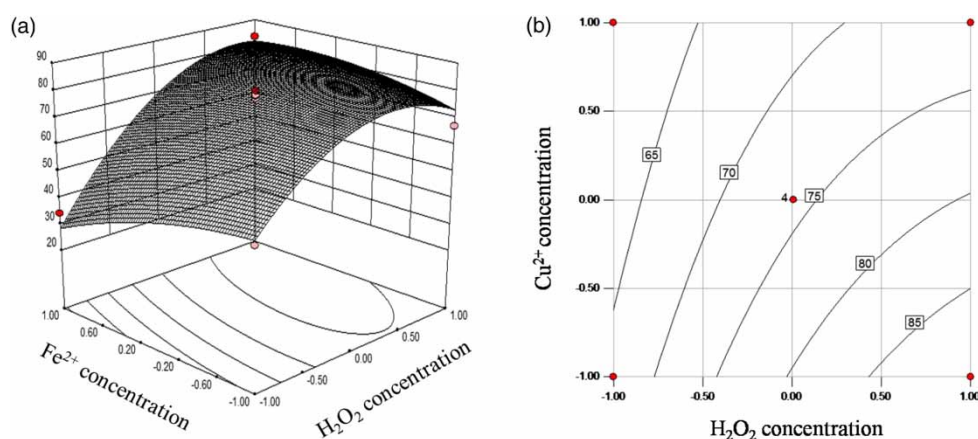
could be explained by the model, respectively. The model  $P$  value calculated from ANOVA analysis indicated that the derived regression model is significant for TOC removal in both Fe- and Cu-Fenton systems. Therefore, the derived model is adequate for prediction and optimization of the reaction conditions of the UV-Fenton reaction.

The significance of each independent variable was evaluated using the calculated  $P$  value, as denoted in Table S3. The results indicate that for the Fe-Fenton system, the TOC removal of the studied hypersaline wastewater is significantly affected by  $\text{H}_2\text{O}_2$  concentration and the intensity of UV irradiation and the Fe concentration has a relatively minor effect. For the UV-Cu-Fenton system, all the three variables are significant, and  $\text{Cu}^{2+}$  and  $\text{H}_2\text{O}_2$  concentration are more important factors for the TOC removal. The interactive relationships of independent variables and response value were presented in Figure 3 and Figures S4 and S5 (available online).

The maximum profile of surface response for UV-Fe-Fenton indicates that the TOC removal efficiency could be improved by increasing the intensity of UV irradiation when the  $\text{H}_2\text{O}_2$  concentration was less than about 200 mM (Figure S4). The interaction between concentration of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  on TOC removal suggests that at low concentration of  $\text{H}_2\text{O}_2$ , the increase of  $\text{Fe}^{2+}$  concentration could not improve the TOC removal and the maximum TOC removal was obtained at  $\text{H}_2\text{O}_2$  concentration about 200 mM (Figure 3(a)).

For the UV-Cu-Fenton system, unlike the Fe-Fenton system, the interaction between UV irradiation and  $\text{H}_2\text{O}_2$  concentration or  $\text{Cu}^{2+}$  concentration is insignificant (Table S3 and Figure S5), implying a different mechanism for UV-Cu-Fenton reaction than UV-Fe-Fenton. Figure 3(b) shows that higher TOC removal was obtained at lower  $\text{Cu}^{2+}$  concentration and higher  $\text{H}_2\text{O}_2$  concentration at





**Figure 3** | (a) 3D response surface plot of TOC removal using UV Fe-Fenton and (b) 2D plot using UV Cu-Fenton as a function of  $\text{Fe}^{2+}$  or  $\text{Cu}^+$  and  $\text{H}_2\text{O}_2$  dosage (coded values as in Table S2, available online) at pH 3 and using 375 W of UV lamp.

constant UV irradiation intensity. Therefore, the optimized reaction parameters obtained from RSM are 176 mM  $\text{H}_2\text{O}_2$  and 9.6 mM  $\text{Fe}^{2+}$  using 500 W UV lamp for UV-Fe-Fenton process, and 276 mM  $\text{H}_2\text{O}_2$  and 2.95 mM  $\text{Cu}^{2+}$  using 480 W UV lamp for UV-Cu-Fenton process. The predicted TOC removal efficiency is 96% for both systems.

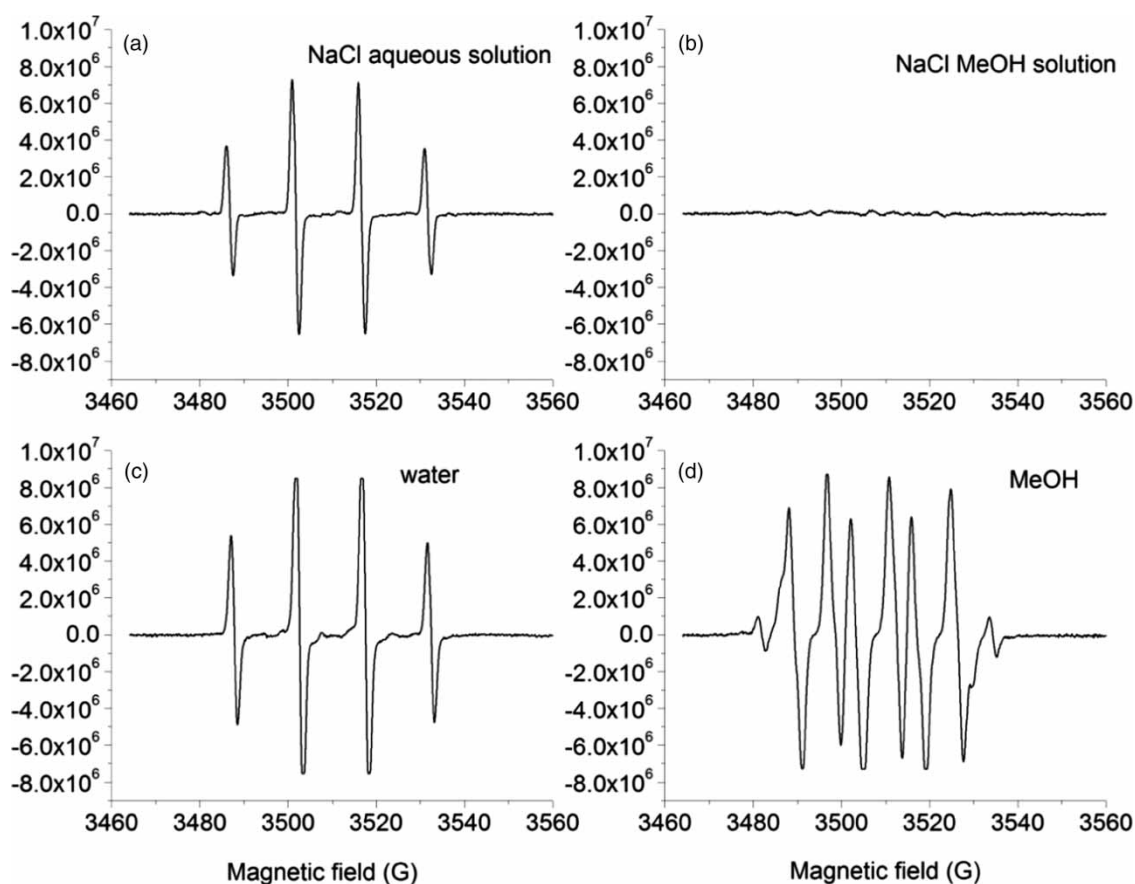
### Radicals identification and catalytic mechanism in UV-Fe/Cu-Fenton oxidation

ESR spectroscopy was used to clarify the  $\text{Cl}^-$  effect on the generation of radicals during the UV-Fenton reaction. As shown in Figure 4(a) and 4(c), DMPO-OH adduct was the only species observed for UV-Fe-Fenton system in aqueous solution with and without NaCl addition, the intensity of DMPO-OH was moderately inhibited by  $\text{Cl}^-$  ions (Moffett & Zika 1987; De Laat et al. 2004; Machulek et al. 2007). It should be noted that the  $\text{HO}_2\cdot/\text{O}_2\cdot^-$  may also contribute to the DMPO-OH adducts signal, since DMPO-OOH/ $\text{O}_2\cdot^-$  adducts readily decays into DMPO-OH in aqueous solution (Houriez et al. 2010). Accordingly, excess amount of methanol was used as the reaction matrix to examine the  $\text{HO}_2\cdot/\text{O}_2\cdot^-$ . As shown in Figure 4(d), DMPO-OOH or DMPO- $\text{O}_2\cdot^-$  adducts were detected, indicating the generation of  $\cdot\text{OOH}$  or  $\cdot\text{O}_2^-$  radicals (Bosnjakovic & Schlick 2006). When NaCl was added with methanol as solvent, almost no signal was detected at all (Figure 4(b)), revealing the inhibitive effect of NaCl on  $\text{HO}_2\cdot/\text{O}_2\cdot^-$  formation. Without NaCl, UV irradiation could promote the reduction of Fe(III)-aqua complexes as Equation (9) and generate superoxide radicals, however, in the presence of NaCl, the reduction of Fe(III)-Cl complexes occurred (Equation (11)). The calculation results in Table 1 show that  $\cdot\text{OH}$  radicals were dominant reactive oxygen species (ROS)

in the saline water. All these evidences suggested that the generation of  $\text{HO}_2\cdot/\text{O}_2\cdot^-$  from  $\text{Fe}^{3+}$  catalyzed  $\text{H}_2\text{O}_2$  decomposition was inhibited in hypersaline water, due to the complexation of  $\text{Cl}^-$  with  $\text{Fe}^{3+}$ , and thus the  $\cdot\text{OH}$  play a crucial role in organics oxidation.

Figure 5 shows the ESR spectra of DMPO-radical adducts formed in UV-Cu-Fenton system. DMPO-OH adducts were observed for Cu ions catalyzed  $\text{H}_2\text{O}_2$  decomposition in aqueous solution (Figure 5(a) and 5(c)), and the intensity of  $\cdot\text{OH}$  was greatly decreased and the signal shifted to lower magnetic field with addition of NaCl, indicating the suppression of  $\cdot\text{OH}$  generation besides scavenging of  $\cdot\text{OH}$  by  $\text{Cl}^-$  ions differently with UV-Fe-Fenton. The nine peaks in Figure 5(b) assigned to DMPO- $\text{O}_2\cdot^-$  (marked with \*) or DMPO- $\text{O}_2\text{H}$  adduct (marked with o) and other oxygen-centered radical adducts (marked with  $\Delta$ ), respectively (Kohno et al. 1994; Bosnjakovic & Schlick 2006). The dominant ROS are superoxide radicals in the presence of NaCl and methanol (Figure 5(b)). However, without NaCl, the multiple peaks in Figure 5(d) suggests a lower content of DMPO- $\text{O}_2\cdot^-$  or DMPO- $\text{O}_2\text{H}$  adducts (Table 1). The six peaks with hyperfine coupling constants  $a_N = 14$  G and  $a_H = 11$  G could be attributed to the DMPO- $\cdot\text{O}_2^-$  or DMPO- $\text{O}_2\text{H}$  adducts (marked with  $\clubsuit$  and  $\spadesuit$ ), the peaks marked with  $\blacklozenge$  and  $\square$  ( $a_N = 13.5$  G and  $a_H = 9$  G) were from DMPO- $\text{OCH}_3$  adduct, and the three peaks marked with  $\surd$  were from the degradation product of DMPO (Bosnjakovic & Schlick 2006). Therefore, it could be deduced that the  $\text{HO}_2\cdot/\text{O}_2\cdot^-$  are more important than  $\text{OH}\cdot$  in the UV-Cu-Fenton reaction, especially with the addition of NaCl, compared with the Fe-Fenton system.

Moreover, it was noted that the color of the reaction medium of UV-Cu-Fenton system changed from blue to yellow and finally returned to blue, indicating the disappearing



**Figure 4** | ESR spectra of DMPO-radical adducts of UV-Fe-Fenton reaction in (a) 20% w/v NaCl solution and (c) pure water, (b) 20% w/v NaCl solution in methanol matrix and (d) methanol without NaCl. Experiments in each graph were conducted under identical instrument parameters.  $[\text{Fe}^{2+}]_0 = 5 \text{ mmol/L}$ ,  $[\text{H}_2\text{O}_2]_0 = 0.1 \text{ mol/L}$ .

**Table 1** | Semi-quantitative analysis of the radicals generated using the highest ESR peak intensity

Peak intensity		$\cdot\text{OH}$ ( $\times 10^6$ )	$\text{O}_2\cdot$ ( $\times 10^6$ )	$\cdot\text{OH}/\text{O}_2\cdot$
UV-Fe-Fenton	without $\text{Cl}^-$	8.49	8.58	0.99
	with $\text{Cl}^-$	7.30	0.11	66
UV-Cu-Fenton	without $\text{Cl}^-$	0.76	0.40	1.9
	with $\text{Cl}^-$	0.22	0.45	0.49

of Cu-aqua complexes  $\text{Cu}(\text{H}_2\text{O})_4^{2+}$  and formation of CuOH or Cu-peroxide (Perez-Benito 2004; Lan et al. 2016). The formed Cu-peroxide intermediates could be decomposed to Cu(I) and  $\text{O}_2\cdot^-$  under UV irradiation (Lan et al. 2016). The formation of  $\text{Cu}^+$  was confirmed by XPS analysis of the Cu-sludge after reaction (Figure S6 in the Supplementary Material, available online).

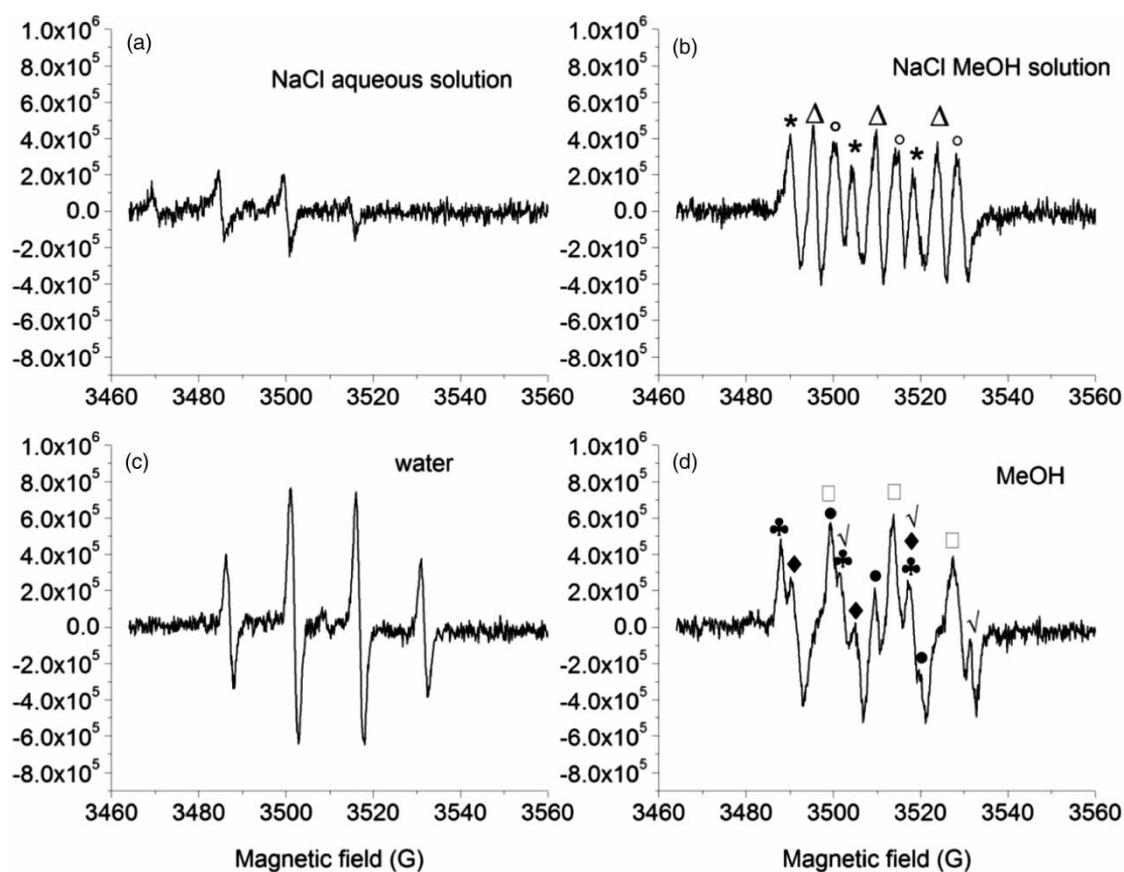
### Feasibility analysis of UV-Fe/Cu-Fenton reaction

The formation of iron (hydr)oxides precipitates on the UV lamp was a serious problem for UV assisted Fenton reaction,

by which the catalytic efficiency decreased after running several times. However, there was no scaling on UV lamp in UV-Cu-Fenton system, due to the formation of cupric salts other than hydroxides (Figure S7, available online). In addition, the formed iron (hydr)oxides precipitates cannot be reused easily and had to be treated as hazardous sludge. However, the cupric salt catalyst could be reused by precipitation, filtration and re-dissolution. Moreover, according to the optimization results from RSM, less amount of  $\text{Cu}^{2+}$  was need than  $\text{Fe}^{2+}$  to get adequate removal of TOC from the studied wastewater. Therefore, UV-Cu-Fenton is more promising for efficient mineralization of hypersaline wastewater from epoxy resin production.

### CONCLUSION

Hypersaline wastewater with high concentration of organic contaminants is a challenge for effective treatment. The high salinity of wastewater significantly inhibited the oxidation



**Figure 5** | ESR spectra of DMPO-radical adducts of UV-Cu-Fenton reaction in (a) 20% w/v NaCl aqueous solution and (c) pure water, (b) 20% w/v NaCl in methanol matrix and (d) methanol without NaCl. Experiments in each graph were conducted under identical instrument parameters.  $[Cu^{2+}]_0 = 5 \text{ mmol/L}$ ,  $[H_2O_2]_0 = 0.1 \text{ mol/L}$ .

efficiency of the organic pollutants, and the high TOC restrains the reuse of inorganic salts. Therefore, enhanced mineralization of hypersaline wastewater should be considered in the advanced treatment to provide a possibility for salt resources recovery. The UV assisted  $Fe^{2+}$  catalyzed and  $Cu^{2+}$  catalyzed Fenton oxidation of hypersaline wastewater both are efficient for TOC removal of hypersaline resin processing wastewater. Continuous dosing of Fenton's reagent and pH maintenance at 3 is beneficial for the  $Fe^{2+}$  catalyzed Fenton oxidation. With the use of RSM, the operation parameters were optimized as 176 mM  $H_2O_2$  and 9.6 mM  $Fe^{2+}$  using 500 W UV lamp for UV-Fe-Fenton process, and 276 mM  $H_2O_2$  and 2.95 mM  $Cu^{2+}$  using 480 W UV lamp for UV-Cu-Fenton process. The predicted TOC removal efficiency could reach 96% for both systems. However, the catalytic mechanisms involving radicals were different for UV-Fe-Fenton and Cu-Fenton reaction. Hydroxyl radical was dominant oxidant in UV- $Fe^{2+}$ -Fenton process, while  $HO_2\cdot/O_2\cdot^-$  played a more important role in the UV-Cu-Fenton system. Moreover, no scaling or

sludge problem makes UV-Cu-Fenton a promising alternative method for efficient mineralization of hypersaline industrial wastewater.

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