Microwave-assisted method to degrade phenol using persulfate or hydrogen peroxide catalyzed by Cu-bearing silicon carbide

Jie Sun, Guotong Xia, Wenjin Yang, Yue Hu and Weibo Shen

ABSTRACT

The radical generation properties of hydrogen peroxide and persulfate for phenol degradation were investigated under microwave irradiation using copper-doped silicon carbide (Cu/SiC) composites as catalyst. The results showed that 90% and 70% of phenol and total organic carbon (TOC), respectively, were removed within 7 min. Microwave activation of hydrogen peroxide and sodium persulfate in terms of thermal effects and accelerated electron transfer was analyzed by degradation kinetics and X-ray photoelectron spectroscopy (XPS). The microwave activation of $Na_2S_2O_8$ demonstrated that the hot spots promote decomposition of persulfate more rapidly and the rate of persulfate decomposition was more than three times the activation rate of a normal heating method. There is a synergistic effect between Cu and microwave radiation, which is highlighted by the H_2O_2 activation; ·OH was generated due to the redox cycle between Cu(I)/Cu(II) and was responsible for phenol degradation using H_2O_2. High performance liquid chromatography (HPLC) analysis indicated that hydroxylation and sulfate radicals addition of phenol were the initial oxidation reaction steps of hydrogen peroxide and persulfate, respectively, followed by further oxidation to form short-chain carboxylic acids.

Key words | catalytic mechanism, catalytic wet peroxide oxidation, copper, microwave activation, persulfate

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HIGHLIGHTS

- The kinetic advantages of microwave-assisted reactions.
- The activation of persulfate involved thermal gradients and redox reaction simultaneously.
- The reaction mechanism in $Na_2S_2O_8$-Cu/SiC system was examined.

INTRODUCTION

Phenols are important chemical and pharmaceutical raw materials and function as intermediates in the synthesis of many high molecular weight aromatic hydrocarbons (Santos *et al.* 2002). Phenol is a major environmental pollutant, and its high biotoxicity makes it impossible for the biochemical methods to completely mineralize it. Advanced oxidation technologies for water treatment using sulfate and hydroxyl radicals have been developed for the remediation of contaminated groundwater and the degradation of wastewater containing dyes, chlorophenol, and phenol. Liou and Chen mineralized phenol in wastewater using a copper/activated carbon (Cu/AC) composite catalyst in the presence of H_2O_2; experiments have shown that the Cu/AC has a higher utilization rate of hydroxyl radicals than ordinary iron oxides and can degrade pollutants faster, like complete degradation of phenol within 30 min. Additionally, more than 90% of the chemical oxygen demand (COD) from the intermediate compounds was also reduced (Liou & Chen 2009).

Microwave (MW) radiation catalysis is a technology for the degradation of organic pollutants where traditional advanced oxidation technologies are combined with the

microwave irradiation that converts microwave electromagnetic energy into heat. It has high selectivity between the heated materials due to the differences in dielectric loss (such as water and SiC). Chen *et al.* reported that the microwave heating leads to the formation of 'hot spots', locations where non-uniform heating occurs with the formation of high temperature regions that provide active sites for the reactions and more effective chemical reactions (Chen *et al.* 2017). In the catalytic processes, microwave radiation also has non-heating effects. For instance, Qiu *et al.* reported that the microwave radiation induced the formation of electron–hole pairs in the semiconductor catalysts and dramatically enhanced the catalytic capacity (Qiu *et al.* 2016).

Previous studies have shown that the catalysts combined with other reagents can greatly improve the removal efficiency of contaminants under microwave irradiation (Xia *et al.* 2019), and the descriptions of the mechanisms involved are mostly discussed at a certain point but not summarized. Herein, copper-based silicon carbide (Cu/SiC) catalysts were prepared by an impregnation method. Catalytic performance and repeatability of the as prepared catalyst was studied using phenol was as a model pollutant under microwave irradiation. Instrumental techniques like scanning electron microscopy (SEM), energy dispersive spectrometer (EDS), and X-ray photoelectron spectroscopy (XPS) were used to characterize the structure and components of the catalyst along with the valence state analysis to study the formation of radicals. The intermediates corresponding to the phenol degradation were determined, and the formation and mineralization mechanisms of the different intermediates were proposed. By comparing the results, the activation modes of different oxidants under the same catalytic environment were discussed to determine the favorable catalytic conditions for the efficient degradation of pollutants.

METHODS

Materials

Phenol, quinone, catechol and hydroquinone were purchased from Aladdin. H_2O_2 and $Na_2S_2O_8$ were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Methanol was purchased from TEDIA. *Tert*-butyl alcohol and ethanol were procured from Chengdu Kelong Chemical Reagent Factory. Cupric nitrate and nitric acid were purchased from Kemiou Chemical Reagent Co., Ltd (Tianjin, China) and were used for the catalyst synthesis. β-SiC was obtained from the Institute of China Building

Materials Academy. All other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All the chemicals were of analytical grade and used without further purification. All the solutions were prepared with ultrapure water.

Catalyst preparation

The Cu/SiC composites were prepared by an impregnation method using SiC as the catalyst support. Copper was loaded using an impregnation method. First, SiC was ultrasonically washed in 1% HNO_3 for 30 min, followed by washing with deionized water for five times and then dried at 105 °C for 8 h. Then, the obtained Cu/SiC was blended with 100 mL of 0.7 mol L^{-1} or 1.5 mol L^{-1} $Cu(NO_3)_2$ solution and then stirred for 2 h. Finally, the slurry was dried at 105 °C for 8 h and then the mixture was calcined at 300 °C in air for 4 h. The prepared materials Cu/SiC 2 and Cu/SiC 4 with respective copper mass fractions of 2.43% and 4.14% were used as catalysts.

Experimental procedures

To evaluate the effect of catalyst adsorption on the degradation process, Cu/SiC (1 g) was mixed with phenol-containing solution (200 mg L^{-1}, 100 mL) using a shaking-table for desired time interval. Microwave catalytic experiments were conducted in aqueous solution using a modified domestic microwave (microwave power: 0–900 W) (Chen *et al.* 2017). The catalytic performance of Cu/SiC in the oxidation of phenol by H_2O_2 or $Na_2S_2O_8$ was evaluated in a 100 mL batch reactor system. The optimum quantity of H_2O_2 or $Na_2S_2O_8$ was determined under the same conditions at 98 °C, and the temperature of the solution and catalyst during the catalytic process was recorded with a K-type thermocouple probe. After mixing phenol and the catalyst, volatile organic compounds were formed as a result of phenol decomposition which was refluxed into a quartz reactor through a condensing unit, under microwave irradiation (600 W). Samples (1 mL) were withdrawn from the reactor at set intervals and immediately filtered through a 0.22 μm filter. Reusability of the catalyst was verified by using the catalyst in successive catalytic experiments under the same optimized conditions. After each cycle, the catalysts were collected and rinsed three times with deionized water, dried, and then were subjected to another catalytic cycle. After each catalytic cycle, XPS was used to characterize the chemical composition and valence states of the elements on the catalyst surfaces. The copper content in

the recovered catalysts was determined to estimate the stability of the catalysts.

The active species present in the peroxide catalytic system were also studied. Ethanol, *tert*-butanol (·OH and ·SO_4^- scavenger), and *p*-benzoquinone (·O_2^- scavenger) were added to the catalytic systems, and then the phenol concentrations in the solution were measured (Wang *et al.* 2018).

Analytical methods

After microwave treatment, the phenol and degradation products were analyzed using reverse-phase high performance liquid chromatography (HPLC, Agilent 1200) equipped with an Agilent 5 TC-C18 column (5 μm, 250 × 4.6 mm) at a wavelength of 254 nm. Methanol and pure water in a ratio of 40:60 were used as the mobile phase. The standard solutions of phenol, catechol, hydroquinone, resorcinol and benzoquinone were prepared to obtain the standard curves and the retention time for individual component was 8.869 min, 4.254 min, 3.181 min, 3.562 min, and 3.962 min, respectively. The solution pH was measured by a pH meter (Mettler Toledo, FE28), the TOC was measured using a Multi TOC Analyzer (2100, Analytik Jena, Germany).

The surface morphology, size distribution of the prepared and reacted copper oxides and the elemental composition of the catalysts were followed by a scanning electron microscope (SEM, S-4800, Hitachi Corporation) equipped with an EDS. The Cu contents were detected by an inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin Elmer 8300, PerkinElmer Corporation). The surface chemical composition was further analyzed by X-ray photoelectron spectroscopy (XPS, AXIS Supra, Kratos Corporation).

RESULTS AND DISCUSSION

Catalyst characterization

The distribution of copper oxides and copper on the surface of the prepared and reacted Cu/SiC were investigated by SEM-EDS. The SEM images in Figure 1 indicate that the calcination process did not destroy the honeycomb structure of the SiC. The highly-dispersed Cu species increased the number of exposed active sites which improved the catalytic performance. The XPS spectra of the catalyst surface in Figure S1 (Supplementary Information) shows that the oxygen was contributed mainly by two species: hydroxyls/

carbonates (532 eV) and a mixture of copper oxides (529.9 eV) (Sutthiumporn & Kawi 2011; Rat'ko *et al.* 2012). The XPS spectrum in Figure 2 shows the chemical states of the metal oxides in the prepared catalyst samples. The Cu $2p_{3/2}$ characteristic peak at 934.5 eV along with the presence of the characteristic shake-up satellite peaks at 941.8 eV and 944.1 eV demonstrated the existence of Cu(II) (Velu *et al.* 2005; Wadekar *et al.* 2005; Wang *et al.* 2018). The presence of a peak at 933.3 eV in the H_2O_2 reaction system after five consecutive catalytic experiments indicates the appearance of Cu(I) (Figure 2(b)), but presence of Cu(I) was not detected on the catalyst surface for the $S_2O_8^{2-}$ system (Figure 2(c)).

The surface area of the catalyst was determined to be 230 $m^2 g^{-1}$. The ICP-OES analysis showed that the amount of copper increased with increasing copper nitrate concentration. After five successive catalytic cycles in the presence of H_2O, the weight ratio of copper in the reacted catalyst was nearly the same as to that of the fresh catalyst (2.4 – 2.43 wt%). However, in the $Na_2S_2O_8$ system, the weight ratio of copper was reduced to 1.8 wt%.

Catalytic mechanism of Cu/SiC

Figure 3 shows the effect of the initial oxidant concentration on phenol degradation in presence of Cu/SiC catalyst under microwave irradiation. As can be seen from Figure 3(b), the degradation of phenol increased from 30% to 90% with increasing $Na_2S_2O_8$ dose from 1 mmol L^{-1} to 6 mmol L^{-1}, and to obtain the same removal efficiency in the presence of H_2O_2, 20 mmol L^{-1} of H_2O_2 was required (Figure 3(a)). In a control experiment without microwave radiation for Cu/SiC 2 reaction system, the phenol conversion after 6 h was around 90% (6 mmol L^{-1} $Na_2S_2O_8$ or 30 mmol L^{-1} H_2O_2). Therefore, the binding of H_2O_2 to copper ions significantly enhanced the degradation of phenol under microwave irradiation, with $Na_2S_2O_8$ having higher degradation efficiency. The superior performance of $Na_2S_2O_8$ can be attributed to its better thermal activation properties compared to H_2O_2 under microwave irradiation (Equation (1)). The microwave heating of $Na_2S_2O_8$ in the presence of SiC resulted in the degradation rate of about 60% for phenol (6 mmol L^{-1} $Na_2S_2O_8$), which was higher than the degradation rate in the presence of H_2O_2 (16%, 30 mmol L^{-1} H_2O_2). In a recent report, Wang *et al.* suggested that Mn_3O_4 showed higher degradation rate of phenol, with 20 ppm phenol being removed within 60 min in the presence of 6.5 mM persulfate (Wang *et al.* 2019). In comparison, microwave irradiation assisted activation of persulfate by CuO has more advantages in the treatment
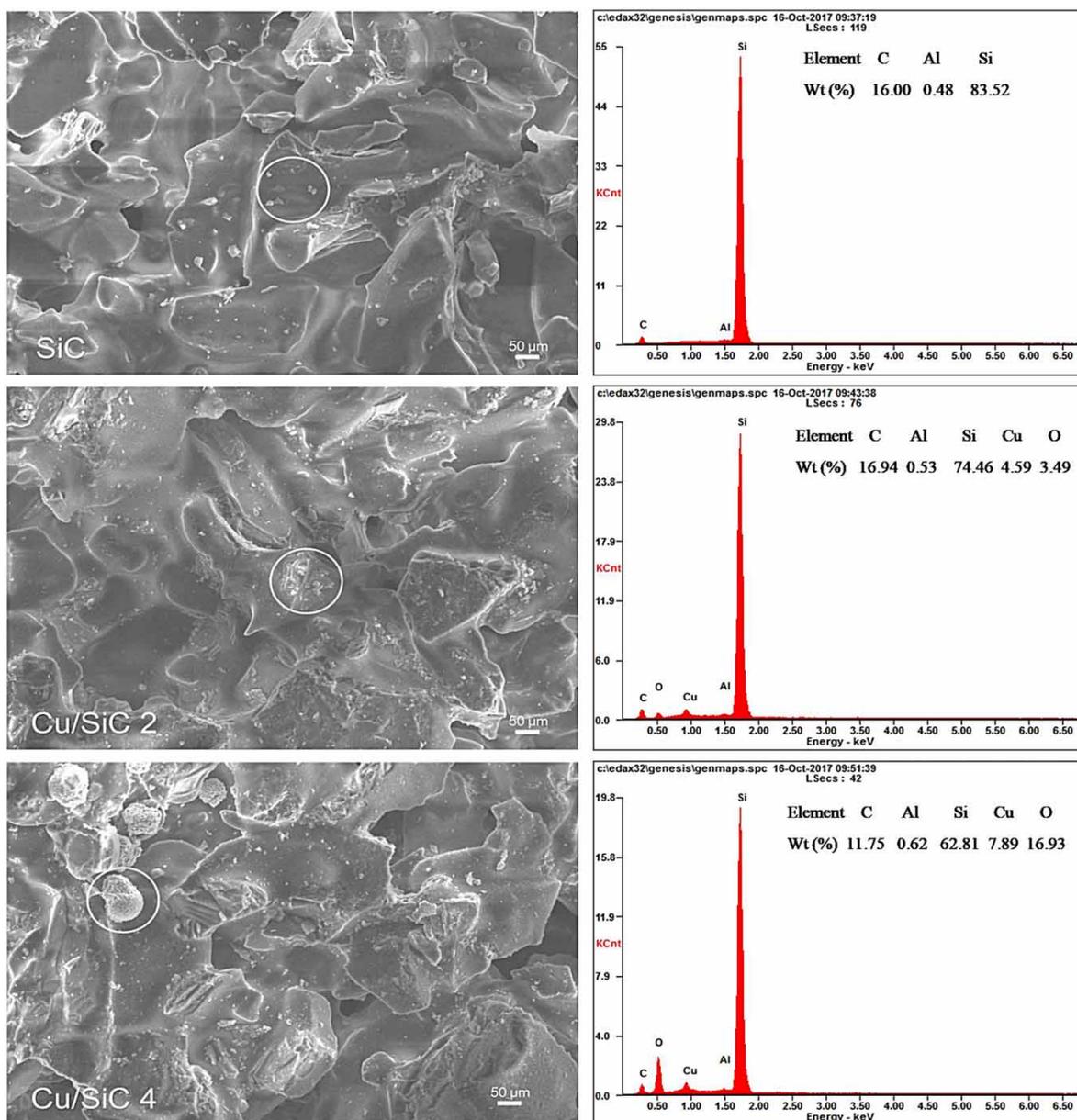
Figure 1 │ SEM images of the Cu/SiC sample and corresponding EDS data (SiC: silicon carbide unloaded copper; Cu/SiC 2: Cu mass fraction was 2.43%; Cu/SiC 4: Cu mass fraction was 4.14%).

of high-concentration wastewater.

$$S_2O_8^{2-} \xrightarrow{\text{Heat}} 2 \cdot SO_4^{-} \qquad (1)$$
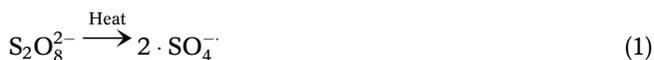
With respect to the mechanistic aspect of phenol degradation, it can be divided into two steps; the generation of radicals and the oxidation of phenol by the generated radicals. The reaction rates of $\cdot SO_4^-$ and $\cdot OH$ with phenol were reported to be $8.8 \times 10^9 \, M \cdot s^{-1}$ and $6.6 \times 10^9 \, M \cdot s^{-1}$,

respectively (Du *et al.* 2017), so the rate determination step for the degradation of phenol was the production of radicals, and the action of microwaves was considered to enhance the rate of radical production. To verify the effect of microwaves on the catalytic activity in this experiment, kinetics of degradation was studied. Figure 4 shows the phenol removal rate with time along with the fitting of kinetic model from the experiments carried out in a water bath containing aqueous solution (SiC, 98 °C) and in presence of MW (SiC or Cu/SiC 2); Table 1 presents a comparison of the kinetic
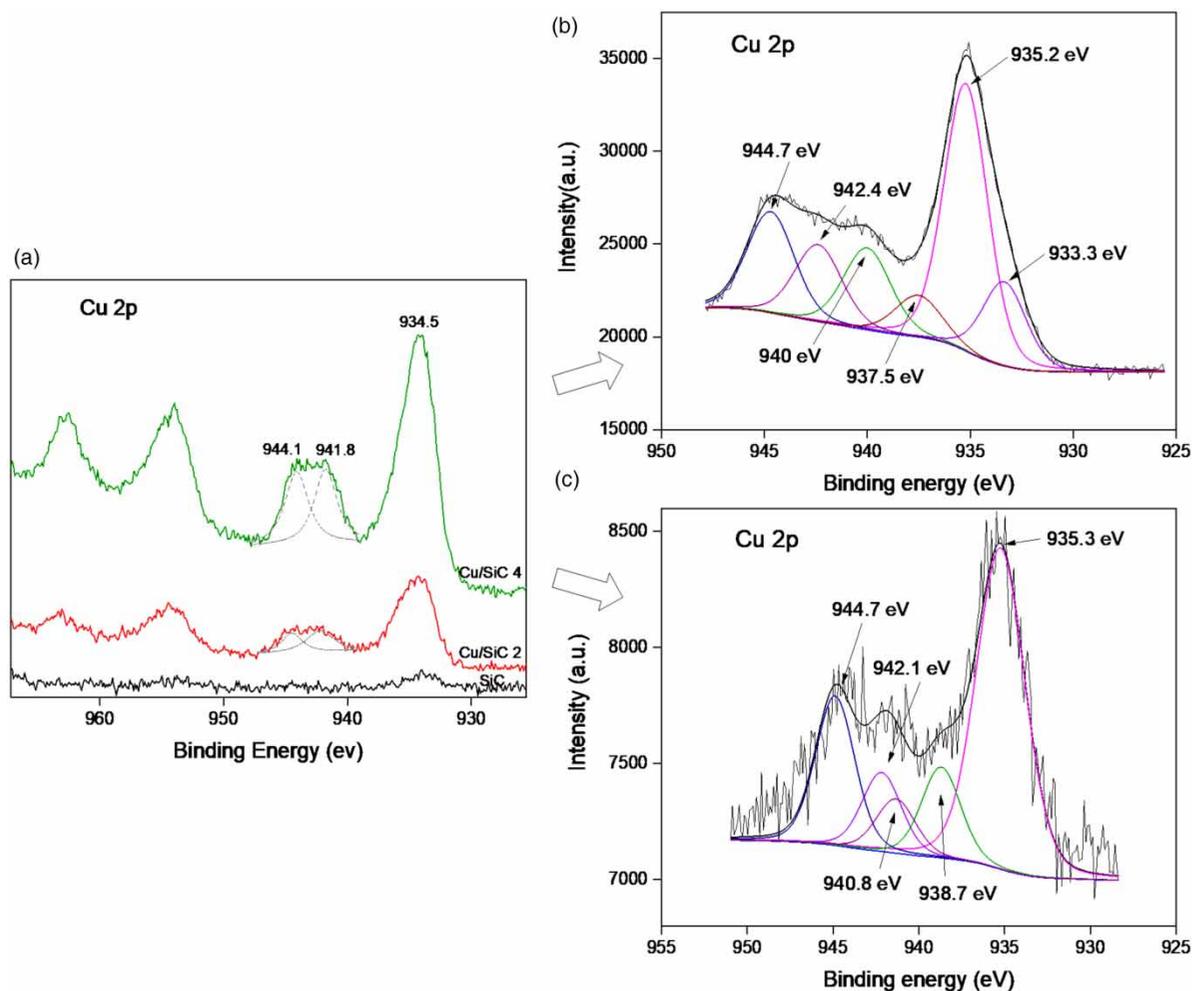
Figure 2 │ Cu2p XPS spectra of fresh Cu/SiC (a), Cu/SiC 2 after five catalytic reactions using H_2O_2 (b) or $S_2O_8^{2-}$ (c).
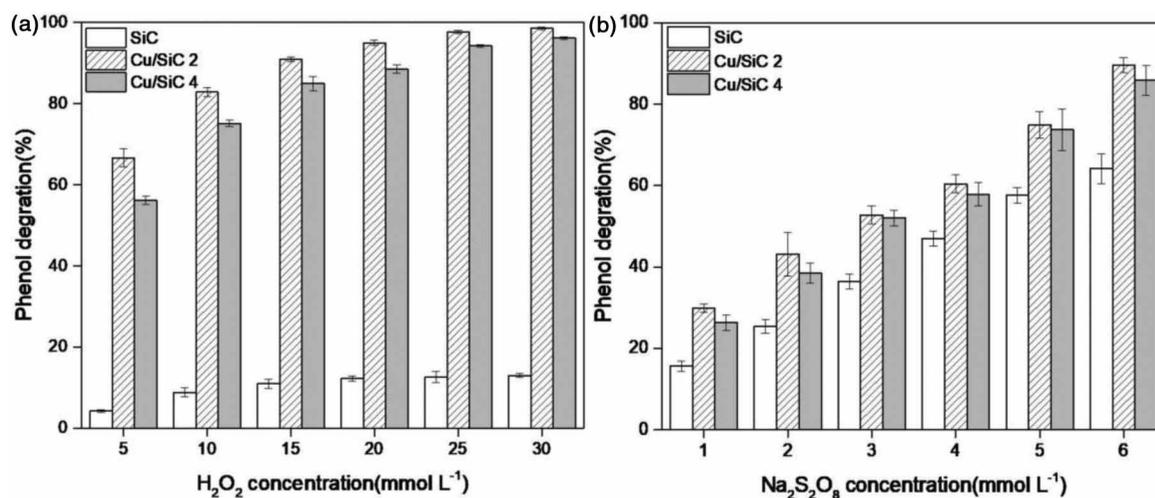
Figure 3 │ (a) Phenol degradation efficiencies in H_2O_2 catalytic systems (5–30 mmol L^{-1}); (b) Phenol degradation efficiencies in $Na_2S_2O_8$ catalytic systems (1–6 mmol L^{-1}, 200 mg L^{-1} phenol, catalyst dosage = 1 g, MW power = 600 W, time = 7 min).
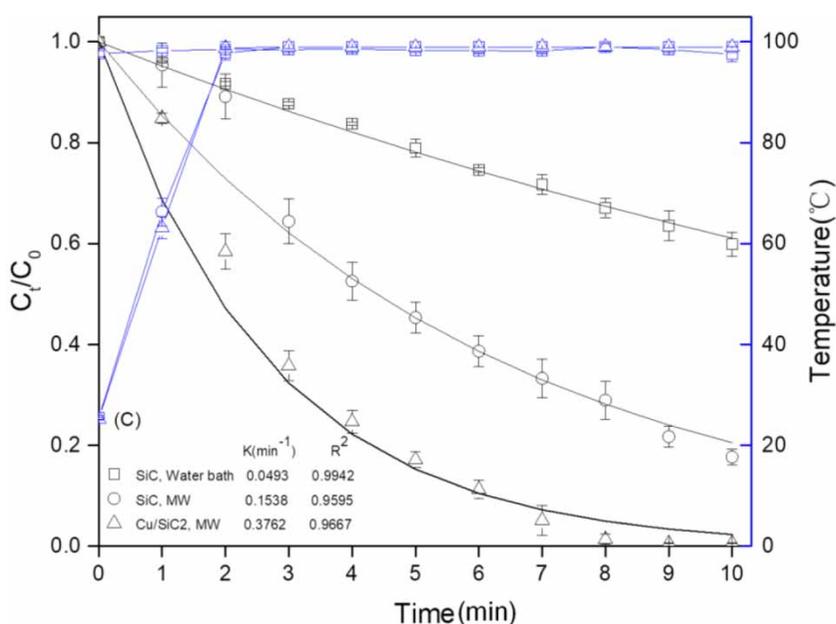
Figure 4 | Phenol conversion over time at different reaction conditions, the black lines represent kinetic model fitting (200 mg L^{-1} phenol, Na$_2$S$_2$O$_8$ = 6 mmol L^{-1}, catalyst dosage = 1 g, MW power = 750 W).

curves and rate constants for the phenol removal under three different conditions studied. The phenol degradation in this study followed a pseudo-first-order kinetics model, and the kinetic coefficients of phenol degradation for SiC in water bath, SiC in MW and Cu/SiC in MW were 0.0493 min^{-1}, 0.1538 min^{-1}, and 0.3762 min^{-1}, respectively. Among them lower $R^2 \geq 0.9595$ under microwave radiation was due to the influence of temperature during the initial duration of 2 min and as the temperature in the solution reaches 98 °C, phenol achieves a steady increase in mineralization efficiency; the rate of reaction catalyzed by SiC in the presence of microwave was about 3.12 times higher than that of the water bath heating (Table 1). There are some plausible mechanisms for this enhancement under microwave irradiation. First, the rate of temperature rise under microwave irradiation varies in different media, and the heterogeneous reaction system presents a thermodynamic non-equilibrium state. In particular, the surface micro-regions of the solid-phase catalysts had a steep thermal gradient (hot spots) due to the interface polarization.

The molecules were activated easily in the high-temperature micro-regions. Secondly, it has been reported that the microwave could reduce or increase the activation energy (Costa *et al.* 2009), which could be explained based on the temperature gradient. Based on the Arrhenius reaction rate equation, the activation energy is related to the localized microscopic high temperatures, rather than the overall temperature. In fact, only the bulk temperature was measured and the microscopic temperature could not be assessed and if the temperature range was large, an error will occur in the calculation of the activation energy.

The presence of Cu(I) in the Cu/SiC samples recovered after five catalytic cycles was confirmed by XPS (Figure 2(b)), which showed that a copper-redox cycle occurred during the microwave assisted catalysis. Theoretically, microwave can speed up the separation of holes and electrons by SiC, and the transferred electron could induce the redox reaction of Cu(II) (Chen *et al.* 2017). Although Cu(I) was not detected in the persulfate system, the occurrence of electron transfer was not excluded due to its strong oxidation behavior. In addition, Cu/SiC 2 exhibited a higher catalytic activity towards phenol than Cu/SiC 4, indicating that the dispersion of active Cu species also significantly affected the catalytic activity. Hence, smaller quantity of Cu displayed superior catalytic effect. In contrast, aggregation of the active copper species occurring in the cavities of the carbon sphere, decreases the number of exposed active sites and thus reducing its utilization rate at higher quantity (Figure 1).

Table 1 | Degradation rate constant (K_n) of phenol obtained experimentally

|	Solution temperature (°C)	K_n (min^{-1})	$K_{(n+1)}/K_n$
1 Water bath + SiC	98 ± 2	0.0493	–
2 Microwave + SiC	98 ± 2	0.1538	3.12
3 Microwave + Cu/SiC 2	98 ± 2	0.3762	2.45

Phenol degradation pathway

The phenol degradation process with respect to time is shown in Figure 5. HPLC analysis indicated that the oxidation of phenol was 95% complete within 4 min and was converted to benzoquinone, hydroquinone, and catechol. These compounds were detected after 1 min of microwave irradiation and reached their maximum concentrations in solution after 3 min (Figure 5(a)). The oxidative degradation process of phenol is related to its molecular structure, the position of the hydroxyl group on the benzene ring. When the hydrogen atom on the benzene ring was replaced by a hydroxyl group, the electron cloud density became unevenly distributed. During the reactions with phenolic substances, hydroxyl radicals first attacked the ortho or para position due to a higher electron cloud density. During the degradation process, phenol is first oxidized to hydroquinone or catechol, and then the generated aromatic intermediates were transformed into organic acids via ring-opening reactions (such as maleic acid, oxalic acid, etc.). The above process agrees with the general phenol degradation mechanism (Wang *et al.* 2011; Singh *et al.* 2016).

$$C_6H_5OH + \cdot SO_4^- \rightarrow C_6H_5O \cdot + HSO_4^- \tag{2}$$

$$\begin{aligned} C_6H_5OH + \cdot SO_4^- &\rightarrow C_6H_5OH \cdot + SO_4^{2-} \\ &\rightarrow C_6H_5O \cdot + H^+ + SO_4^{2-} \end{aligned} \tag{3}$$

$$\begin{aligned} C_6H_5OH + \cdot SO_4^- &\rightarrow C_6H_5OHSO_4^- - adduct \\ &\rightarrow C_6H_6O_2 + SO_3^- \end{aligned} \tag{4}$$
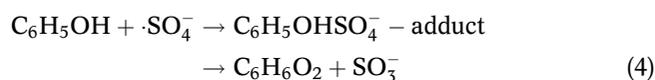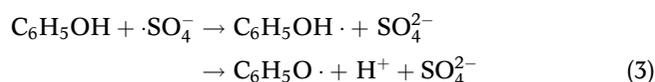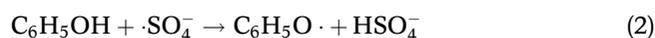
The reactions of sulfate radicals with organic matter mainly include hydrogen extraction (Equation (2)), electron mobility (Equation (3)), and addition mechanisms (Equation (4)). Catechol and benzoquinone were detected in the $Na_2S_2O_8$-Cu/SiC 2 reaction system within 3 and 4 min, respectively (Figure 5(b)), and the addition mechanism was verified by the determination of the product catechol. First, $\cdot O\text{-}SO_3^-$ was generated at the beginning due to the interactions between $\cdot SO_4^-$ and organic matter. Then the O side (containing a single electron) was added to the benzene ring and separated a H. Then one O-S bond was broken and the formed -O· combined with the H atom to form a new hydroxyl group (-OH), resulting in the formation of catechol. The subsequent degradation was similar to the degradation of the organic compounds in presence of the hydroxyl radicals. In order to comprehensively evaluate the degradation effect of phenol, TOC degradation experiment was carried out further (Figure S2, Supplementary Information). The remaining amount of TOC was maintained at 20–35%, phenol did not completely degrade into carbon dioxide and water, but instead generated corresponding organic acids. This result validates the viewpoint of M. Sillanpää *et al.* that the AOPs oxidize organic matter to low molecular weight organic matter in practical applications (Sillanpää *et al.* 2018).
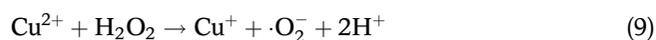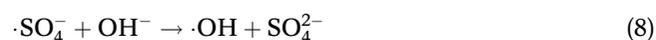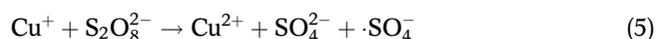
Identification of reactive species

The initial experimental results showed that the microwave irradiation during catalysis using $S_2O_8^{2-}$ involved thermal activation and copper ion addition. The XPS results revealed that the Cu/SiC catalysts contained Cu(II) oxides
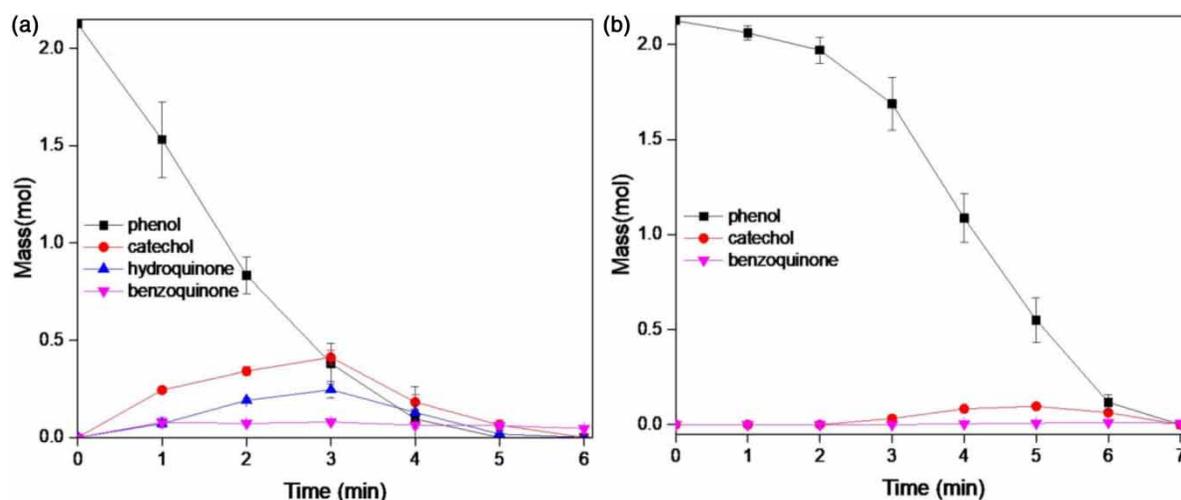

Figure 5 │ (a) Evolution of the major degradation intermediates of phenol in solutions in the H_2O_2-Cu/SiC 2 system; (b) the major degradation intermediates of phenol in the $Na_2S_2O_8$-Cu/SiC 2 system (200 mg L^{-1} phenol, catalyst dosage = 1 g, MW power = 600 W, H_2O_2 = 30 mmol L^{-1} or $Na_2S_2O_8$ = 6 mmol L^{-1}).

and there were many possibilities for a Cu(II)-catalyzed $S_2O_8^{2-}$ reaction, showing that the high phenol removal efficiency in the $Na_2S_2O_8$ system was likely due to $\cdot SO_4^-$, $\cdot O_2^-$, and $\cdot OH$ (Equations (5)–(9)) (Wang *et al.* 2018). The determination of the active species can clarify the reaction mechanism. According to the radical scavenging studies, three primary types of radicals were generated in the systems activated by $S_2O_8^{2-}$ and H_2O_2: $\cdot SO_4^-$, $\cdot OH$, and $\cdot O_2^-$ (Zhao *et al.* 2013).

$$Cu^+ + S_2O_8^{2-} \rightarrow Cu^{2+} + SO_4^{2-} + \cdot SO_4^- \qquad (5)$$

$$\cdot SO_4^- + H_2O \rightarrow HSO_4^- + \cdot OH \qquad (6)$$

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \qquad (7)$$

$$\cdot SO_4^- + OH^- \rightarrow \cdot OH + SO_4^{2-} \qquad (8)$$

$$Cu^{2+} + H_2O_2 \rightarrow Cu^+ + \cdot O_2^- + 2H^+ \qquad (9)$$

$$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + \cdot OH + OH^- \qquad (10)$$

$$Cu^{2+} + \cdot O_2^- \rightarrow Cu^+ + O_2 \qquad (11)$$

$$Cu^+ + \cdot O_2^- \rightarrow Cu^{2+} + H_2O_2 \qquad (12)$$

Ethanol (EtOH) and *tert*-butyl alcohol (TBA) were used as the scavengers and their rate constants are shown in Table S1 (Supplementary Information). Both the EtOH and TBA captured $\cdot OH$ and $\cdot SO_4^-$, while TBA scavenged $\cdot OH$ approximately 1000-times faster than that of $\cdot SO_4^-$. Thus, these compounds can be used to distinguish $\cdot SO_4^-$ from $\cdot OH$. According to the results, $\cdot OH$ and $\cdot SO_4^-$ were the dominant oxidizing species in the H_2O_2 and $Na_2S_2O_8$ systems, respectively (Figure 6). Meanwhile, *p*-benzoquinone (BQ), acted as an $\cdot O_2^-$ scavenger, and inhibited the degradation of phenol, suggesting that $\cdot O_2^-$ was present in both the reaction systems. Therefore, it was presumed that the generation of $\cdot O_2^-$ occurred due to the redox reaction of H_2O_2 and Cu(II), and the resulting Cu(I) reacted with the $S_2O_8^{2-}$ to produce $\cdot SO_4^-$ (Equations (5), (6), (7), (9)). Fig. S3 shows that in the presence of $S_2O_8^{2-}$, the pH was decreased to reach a minimum value of 2.0 after 8 min and then remained in a relative stable state until the end of the reaction, which was directly related to the formation of HSO_4^- (Equation (6)). Referring to previous reports, $\cdot SO_4^-$ was the predominant radical species at pH 5, while $\cdot SO_4^-$ and $\cdot OH$ were the radical species in the $S_2O_8^{2-}$ system at pH 9 (Li *et al.* 2018) and the conversion of $\cdot SO_4^-$ to $\cdot OH$ was lesser under acidic conditions (Equation (8)). The results suggest that Cu(II) and Cu(I) cycles were formed and $\cdot SO_4^-$ were continuously generated.
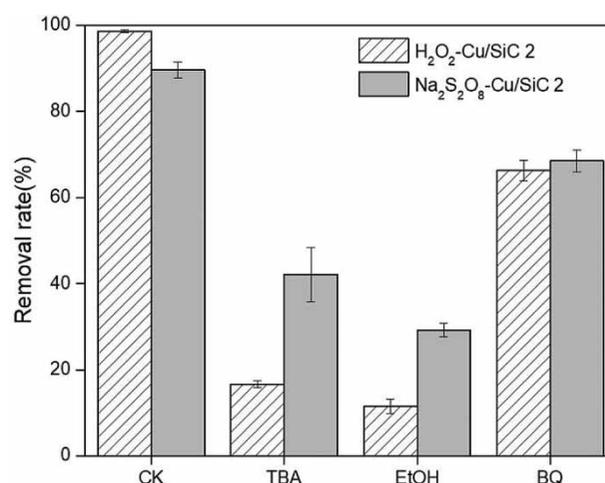
Figure 6 | Effect of scavengers on the catalytic degradation of phenol by Cu/SiC 2 (200 mg L^{-1} phenol, catalyst dosage = 1 g, MW power = 600 W, H_2O_2 = 30 mmol L^{-1} or $Na_2S_2O_8$ = 6 mmol L^{-1}, EtOH = 100 mmol L^{-1}, TBA = 100 mmol L^{-1}, BQ = 5 mmol L^{-1}).

In the H_2O_2 reaction, reduction of Cu(II) species was known to be the dominant process as per the XPS analysis and all the reactions involving $\cdot O_2^-$ and $\cdot OH$ occur (Equations (9)–(12)). But, at these high concentrations of H_2O_2, $\cdot O_2^-$ was insignificant oxidant of Cu(I) with H_2O_2-mediated oxidation-reduction being the dominant, particularly in the early stage of the reaction process. Cu(II) first react with hydrogen peroxide to produce Cu(I), reflecting the reducibility of hydrogen peroxide and then reacted with hydrogen peroxide to regenerate Cu(II) (Equations (9) and (10)). The radical generation and phenol degradation mechanisms are illustrated in Figure 7.

Catalyst reusability

As shown in Figure S4, the catalysts showed good reusability and stability over five successive experiments. The degradation efficiency of phenol in the H_2O_2-Cu/SiC 2 system was stable during each cycle, remaining almost as high as the fresh catalyst. The dephenolation efficiency of the $Na_2S_2O_8$ system in the fourth and fifth cycles decreased to 87% and 86%, respectively (Figure 8). Some studies have shown that the catalytic reaction rate increases with the increase of the mobility of metal ions (Ivanets *et al.* 2019), and the copper ion dissolved from the CuO under strongly acidic conditions (pH < 3.0) promotes the catalytic reaction in the persulfate system. However, with the increasing reaction time, there was gradual decrease in the release of Cu ions with the corresponding decrease in the degradation efficiency of phenol, which explains why the degradation rate
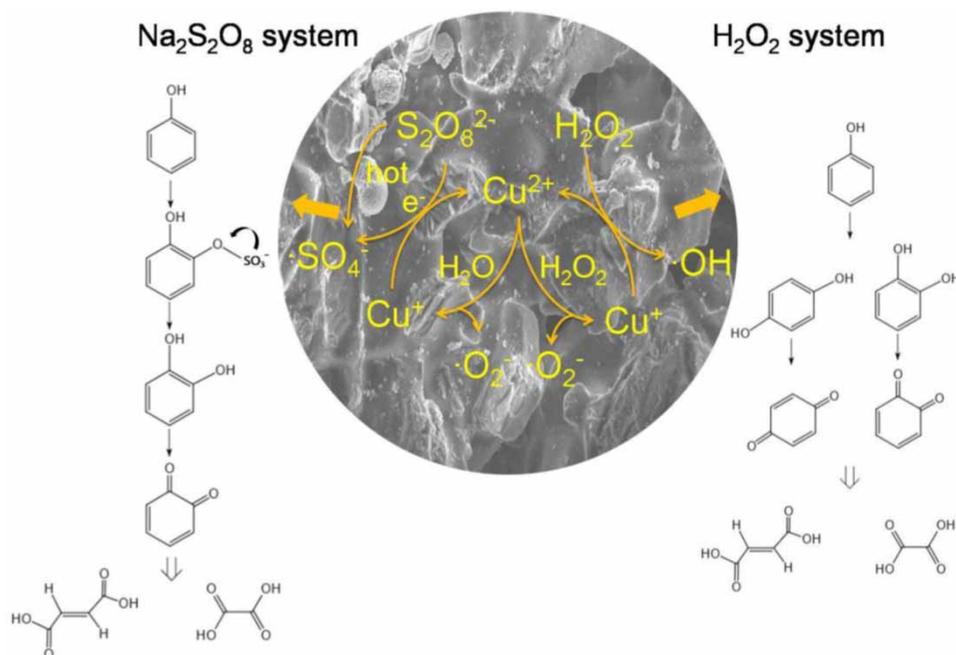
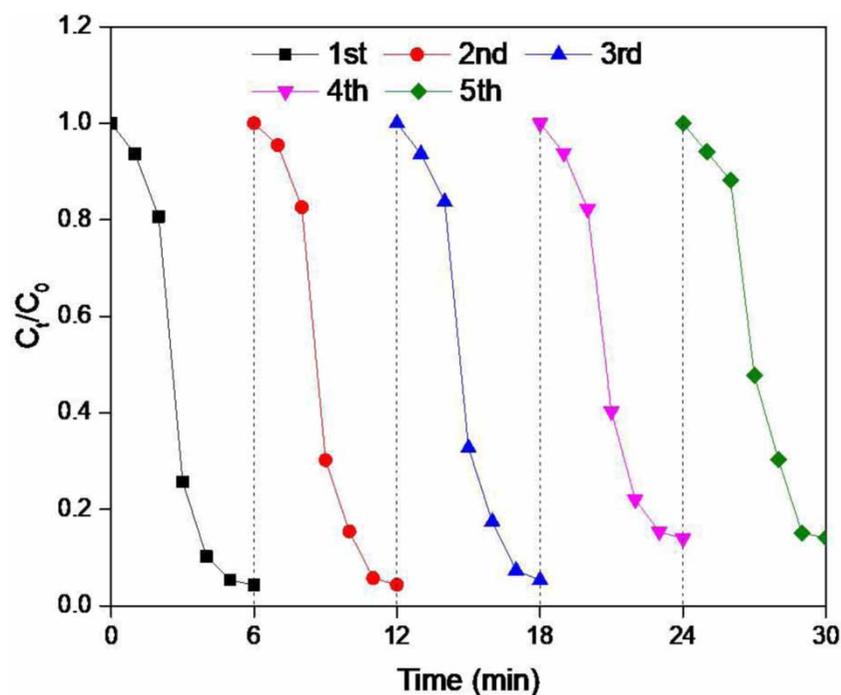**Figure 7** | Mechanism of radical generation and phenol degradation.

Figure 8 | Degradation of phenol for different cycles in the $Na_2S_2O_8$-Cu/SiC 2 system (200 mg L^{-1} phenol, catalyst dosage $=$ 1 g, MW power $=$ 600 W, $H_2O_2 =$ 30 mmol L^{-1} or $Na_2S_2O_8 =$ 6 mmol L^{-1}).

of phenol decreased in repeated degradation experiments (Figure 6). According to the ICP-OES analysis after five catalytic cycles, the mass loss of copper (0.6 wt%) was most likely responsible for the decreased catalytic activity. Previous experiments had demonstrated that the presence of copper ions enhanced the degradation rate of phenol by

persulfate (2.45 times, Table 1), but the results of XPS showed insignificant valence changes of Cu on the catalyst surface after five catalytic cycles (Figure 2(c)). The analysis concluded that a portion of copper ions diffused to the $Na_2S_2O_8$ solution and participated in the homogeneous reaction. In addition, the Cu(I) on the surface of the catalysts was oxidized by strong oxidizing agents and no valence changes compared with the reaction of copper ions and hydrogen peroxide. The release of copper ion leads to the acceleration of the reaction rate, but at the same time reduces the life of catalyst. It is worth noting that the process of reloading Cu ion on SiC is simple. In addition, how to improve the combination of Cu ion and SiC is an important direction to improve the economic benefits.

CONCLUSIONS

From the current research results, persulfate benefits from the high rate of free radical production, which shows higher degradation efficiency than hydrogen peroxide and has strong application potential. This work provided evidence that ·OH and $\cdot SO_4^-$ were the main active species during the degradation of phenol, which predominantly occurred at the ortho-position. The decomposition of persulfate depends on the reaction temperature, and the efficient degradation caused by the microwave irradiation was attributed to the hot spots caused by a local thermal imbalance. The valence analysis and kinetic experiments were conducted to demonstrate that the microwave radiation acts on the degradation process in two ways: electron transfer and thermal activation. In addition, due to the thermal effect of microwave, the process of temperature rise will inevitably bring great energy loss in this experimental process. It is a feasible way to increase the temperature of the wastewater containing phenol entering the reactor through the high temperature degradation wastewater heat exchange. From the perspective of the economic benefits of degradation, hydrogen peroxide has a low cost, does not introduce new sulfate ions and does not require subsequent treatment, so it is an environmentally friendly oxidant. However, its insensitivity to temperature makes it limited in microwave radiation. From the perspective of the degradation efficiency, persulfate was more suitable for the degradation of phenol under microwave environment. However, preliminary experiments showed that Cu/SiC was unstable in the presence of persulfates, suggesting a limitation in this regard. Nevertheless, this scheme may prove useful in applications where sulfates are highly used,

and further experiments are required to improve the binding of copper to improve the efficiency of continuous treatments. The stability and regeneration of the catalyst is also a major way to improve the economic efficiency.

DATA AVAILABILITY STATEMENT

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

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