Studies on the reaction mechanism of Cu/SiC catalytic oxidation for degradation of methyl orange in presence of microwave

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ABSTRACT

The removal of methyl orange (MO) in a copper-loaded silicon carbide (Cu/SiC) system under microwave (MW) irradiation was studied. Cu/SiC was synthesized by employing an impregnation method and the effects of parameters such as reaction time, catalyst dosage, hydrogen peroxide (H_2O_2) dosage, microwave power and pH on the rate of degradation of MO were also studied. The obtained results showed that almost complete degradation was obtained in the presence of Cu/SiC catalyst within 8 min of irradiation when 100 mL of MO solution (20 mg/L), 3 ml/L of H_2O_2, 2 g/L of catalyst dose, 600 W of MW power, and pH 7 were applied. The Cu-bearing catalyst with H_2O_2 formed a Fenton-like system and the rate of generation of hydroxyl radicals (·OH) was also accelerated by subjecting to MW. From the kinetic analysis, it is revealed that the degradation of MO using the MW-Cu/SiC-H_2O_2 system follows the pseudo-first-order.

Key words | catalytic oxidation, Cu/SiC, methyl orange, microwave

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INTRODUCTION

Dyes from textile or dyestuff industries are becoming a serious environmental problem due to their inherent characteristics such as toxicity, high chemical oxygen demand and being refractory to biological degradation (Chen *et al.* 2013). Among various dyes, methyl orange (MO) is difficult to degrade and is often utilized as a model dye contaminant. Several techniques such as biodegradation, membrane method, adsorption, and photocatalytic oxidation have been applied for the degradation of the organic component from dyes (Xiao *et al.* 2009; Wang *et al.* 2009; Zhai *et al.* 2018). By contrast, the above-mentioned traditional methods also have inherent drawbacks. First, the pollutants are just transformed from one form into another instead of being completely changed into harmless compounds. Second, for the treatment of wastewater the biological methods may take a longer time with low efficiency. Besides, harsh reaction conditions of photocatalytic oxidation lead to high economic cost and limited industrial applications, and some of them cause secondary pollutants (Yin *et al.* 2016).

Fenton oxidation is an advanced oxidation technology decomposing hydrogen peroxide (H_2O_2) into hydroxyl radicals (·OH) in the presence of Fe^{2+} catalyst. Hydroxyl radicals (·OH) have the ability to break down large molecules of organic matter without any selectivity, which are then gradually degraded to small molecules and even can be mineralized to water and carbon dioxide. However, the degradation effects of the Fenton reaction on the pollutants can be significantly affected by the pH of the wastewater. According to previous studies, the optimal range of pH is not related to the types of pollutants to be treated, but is mainly restricted by the Fenton reagent itself. In the traditional Fenton system, the optimal pH is around 3, but the actual wastewater is not generally in that acidic pH, which requires adjustment of the pH of the wastewater either by adding acid or alkali. The cost of wastewater treatment is then significantly increased, which in turn limits the practical application of Fenton technology (Shi *et al.* 2014). Therefore, polyvalent metals such as cobalt, manganese, cerium and copper are also used as Fenton-like catalysts for the activation of H_2O_2 (Ma *et al.* 2015; Zhang *et al.* 2016; Gan *et al.* 2017; Zhao *et al.* 2017). Copper ions can be used as an intermediate

metal ion in the Fenton system to induce the decomposition of hydrogen peroxide to produce large amounts of hydroxyl radicals. But it is to be noted that under near-neutral pH, Cu is not as easy to hydrolyze and precipitate as ferrous ions. Therefore, if the ferric ions are replaced by copper ions as the catalyst in a Fenton system, the range of application of pH can be significantly expanded (Pham *et al.* 2013; Chen *et al.* 2017). In the wastewater treatment processes to reduce the secondary pollution, copper ions could be fixed in a carrier to catalyze the decomposition of hydrogen peroxide to generate ·OH. Hence, under mild conditions, the application of this technique can not only keep the traditional advantages of broad applicability and strong oxidizing ability of Fenton's treatment of wastewater but can also broaden the application areas of Fenton technique. Besides, the application of a carrier assists in recycling the catalyst and reduces the economic costs.

Fenton-like systems can also be combined with other processes such as electrochemistry, ultrasound, microwave (MW) and ultraviolet to accelerate the conversion and circulation of ions further. MW-induced oxidation is a new technology developed in recent years, which can oxidize or deoxidize organic pollutants at room temperature and ambient pressure (Remya & Lin 2011; Pan *et al.* 2018). Due to the unique properties of MW, it can selectively heat the donor material, where the heating starts from inside the material, so that heating can be started and stopped instantly compared to the conventional heating methods. On the other hand, MW radiation can cause the vibration of molecules, which helps to reduce the activation energy by reducing the size (Haque 1999). However, as indicated earlier, the application of MW radiation does not directly cause the degradation of organic pollutants, as its energy (0.98 J/mol at 2.450 GHz) is far below the energy of common chemical bonds present in the organic molecules (hundreds of kJ/mol) (Hu & Cheng 2014). Therefore, the combination of MW with adsorbent, catalyst and oxidant improves the treatment efficiency of various pollutants. CuO/AC catalyst was obtained from impregnation, which used active carbon (AC) as the support, and ·OH were generated during microwave catalytic oxidation degradation (MCOD) of crystal violet in the wastewater (Yin *et al.* 2016). The removal of arsenic (As) in an iron-loaded silicon carbide (Fe/SiC) under MW irradiation has been studied (Pan *et al.* 2018). Chen *et al.* (2016) applied MW-induced carbon nanotubes (MW/CNTs) in the treatment of organic pollutants, such as sodium dodecyl benzene sulfonate (SDBS), methyl parathion (MP),

methylene blue (MB), and bisphenol A (BPA) in aqueous solution. The degradation of 2-nitrophenol (2-NP) was studied using a heterogeneous system of MW-CuO/Al-H_2O_2 (Atta *et al.* 2012). In most cases, it has been noted that the application of MW for the removal of pollutants can reduce the reaction time without causing any secondary pollution (Lv *et al.* 2009). As for the choice of carrier, AC is an ideal choice because of its good adsorption property. The carrier used with MW should consider not only its adsorption performance, but also its good microwave absorption performance. Silicon carbide (SiC) is a type of non-oxide ceramic material with excellent properties, such as high hardness, heat resistance and corrosion resistance, as well as excellent thermal conductivity and good MW absorption performance. It is also an ideal carrier material, but only a few studies have been reported.

In this context, a Cu/SiC catalytic oxidative system for the degradation of MO under MW was established. The effects of catalyst dosage, MW power, H_2O_2 dosage and pH on the rate of degradation of MO were investigated along with the reusability of the catalyst as well as the mechanism of catalytic oxidation. Overall, this study provides the necessity for further optimization of the reaction conditions of catalytic oxidation and degradation of organic compounds in wastewater treatment.

MATERIALS AND METHODS

The experimental device and materials

The experimental device used was a microwave reactor which was refitted through a household microwave oven, where the power of the MW reactor can be continuously adjusted. The experiments were carried out in a 250 ml conical flask, which was placed in the microwave device having connected with a condensing reflux tube. The microwave power was controlled through setting the interface of the MW reactor. The schematic diagram of the experimental device is shown in Figure 1.

Cu $(NO_3)_2 \cdot 3H_2O$ was obtained from Tianjin Tianli Chemical Reagent Co., Ltd and powdered SiC (98% purity) with a diameter of 40 μm was purchased from China Building Materials Academy. MO was purchased from Sinopharm Chemical Reagent Co., Ltd. Hydrogen peroxide (30% w/w) and all other chemicals used were of analytical grade unless otherwise indicated. All the solutions were prepared using double distilled water.
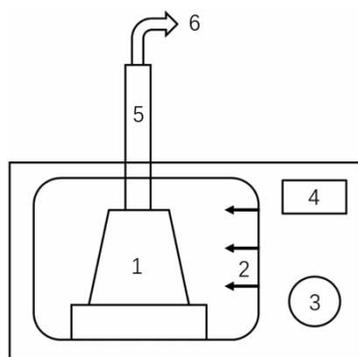
Figure 1 │ Schematic diagram of the MW-Cu/SiC-H$_2$O$_2$ system. (1) reaction vessel; (2) microwave generator; (3) power regulator; (4) display screen; (5) condenser pipe; (6) sample collector.

Preparation and characterization of Cu/SiC

The Cu/SiC catalysts were prepared through the impregnation method. First, a certain amount of SiC powder was weighed, added into distilled water and washed several times. Following this, 1% nitric acid solution was added and subjected to ultrasound for 30 min. Second, the obtained SiC powder was rinsed with distilled water until neutral and dried at 105 °C for 8 h. The pretreated SiC powder was then stored in a desiccator for further use. In the process of impregnation, 10 g of SiC powder was immersed in 100 ml (0.6 mol/L) copper nitrate solution for 24 h, and then dried at 80 °C for 8 h. It was then sintered at 300 °C for 3 h in a muffle furnace. After cooling, copper silicon carbide catalyst was obtained.

The surface morphology and elemental composition of SiC and Cu/SiC were observed and detected using a scanning electron microscope (SEM-EDS). The contents of Cu were detected by inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin Elmer 8300, PerkinElmer Corporation). Powder X-ray diffraction (XRD, RINT 2500, XRD-Rigaku Corporation, Japan) was used to analyze the crystalline phases of Cu/SiC. Thermo Scientific ESCALAB 250XI X-ray photoelectron spectrometer (XPS, Thermo Fisher Technology Co., Ltd) was used for analyzing the valence states of the elements present in the catalyst.

Experimental setup and procedure

The whole experiment was carried out in three stages. First, the combination of microwave, catalyst and oxidant in the MW-Cu/SiC-H$_2$O$_2$ system was applied to demonstrate the superiority of the overall process, along with carrying out the above elements individually as well as in the combination of two processes to treat the target pollutants. The specific processes followed are described as follows:

(1) Adsorption of Cu/SiC catalyst: the MW reaction was carried out for only 8 min, and within this time there was almost no change in the adsorption. Therefore, in the case of experiments in the absence of MW, a reaction time of 24 h was followed. 100 mL MO solution (20 mg/L) at pH 7.0 was mixed with 0.2 g Cu/SiC powder and placed for 24 h.

(2) Individual oxidation with H$_2$O$_2$ was carried out to check whether the organic pollutants can be oxidized to induce their degradation. The above solution at pH 7.0 was mixed with 0.3 mL H$_2$O$_2$ and placed for 24 h.

(3) Fenton-like reaction: the catalyst and oxidant reacted directly at standard temperature and atmospheric pressure, where copper ions react with hydrogen peroxide as a Fenton-like reaction. MO solution at pH 7.0 was mixed with 0.2 g Cu/SiC powder and 0.3 mL H$_2$O$_2$, which were then placed for 24 h.

(4) Microwave irradiation: 100 mL MO solution (20 mg/L) was irradiated only by MW (600 W) for 8 min.

(5) MW-Cu/SiC: in the absence of oxidants, the role of the MW to directly induce the catalysts in order to degrade the pollutants was investigated. An MO solution at pH 7.0 was mixed with 0.2 g Cu/SiC powder and irradiated for 8 min with 600 W of microwave power.

(6) MW-H$_2$O$_2$ treatment: in the absence of a catalyst, whether MW could directly stimulate the decomposition of oxidant in order to degrade the pollutants was investigated. An MO solution at pH 7.0 was mixed with 0.3 mL H$_2$O$_2$ and was irradiated for 8 min with 600 W of MW power.

(7) MW-Cu/SiC-H$_2$O$_2$ system: an MO solution at pH 7.0 was mixed with 0.2 g Cu/SiC powder and 0.3 mL H$_2$O$_2$, and the solution was irradiated for 8 min with 600 W of MW power.

(8) WB (water bath heating)-Cu/SiC-H$_2$O$_2$ system: the temperature of the solution increased during microwave irradiation, and the increased temperature is likely to improve the degradation rate. To separate the contributions of microwave irradiation and increased temperature to the enhanced rate, water bath heating was used instead of the MW. The MO solution at pH 7.0 was mixed with 0.2 g Cu/SiC powder and 0.3 mL H$_2$O$_2$, and the solution was heated in a water bath for 8 min.

Second, the degradation of methyl orange was affected by a variety of factors, including the amount of catalyst,

the amount of oxidant and the power of the MW. The effects of MW irradiation time (2, 4, 6, 8 min), H_2O_2 dose (1, 2, 3, 4 mL/L), Cu/SiC dose (1, 2, 3, 4 g/L), MW power (200, 400, 600, 800 W), pH (3, 5, 7, 9) on the degradation of MO were examined.

Finally, the reusability of catalysts was checked. In a typical experiment, 100 mL MO solution (20 mg/L) at pH 7.0 was mixed with 0.2 g Cu/SiC powder (2 g/L) and 0.3 mL H_2O_2 (3 mL/L), and the solution was irradiated by MW (600 W). The used Cu/SiC powder was separated from the treated solutions and dried at 45 °C in an oven after washing with distilled water. The dried Cu/SiC powder was used again to react under the same experimental conditions by following the same procedure, which was repeated five times.

Methods

(1) Calculation on the degradation rates of MO

The UV–Vis spectra of MO solutions were measured using a UV–Vis spectrophotometer (UV1780, SHIMADZU, Japan). In addition to the amount of catalyst and oxidant, MW power was also a key factor affecting the degradation of the MO solution. Based on the maximum absorbance at 465 nm for MO solutions of 0–20 mg/L, the percentage degradation was obtained as follows: % *degradation* $= [(C_0 - C_t)/C_0] \times 100\%$. Where, C_0 and C_t are the initial concentration and the concentration after a treatment time 't' of MO solution.

(2) The first order kinetic equation for degradation

$$Ln(C/C_0) = -kt \tag{1}$$

where, C_0 is the initial concentration of MO (mg/L); C is the concentration of MO after each reaction time (mg/L) and k is the rate constant.

RESULTS AND DISCUSSION

Characterization of catalysts

SEM shows the even distribution of cupreous species on the surface of supports. As can be clearly seen from SEM images, Cu particles are irregularly coated on the surface of Cu/SiC (Figure 2). The elemental analysis from EDS confirmed that SiC was relatively pure before loading, whereas the oxygen and copper contents increased after loading,

indicating that copper was loaded onto the surface of SiC in the form of oxide. The relative loading of copper was 2.43% as determined from ICP-OES.

There is no notable change in the number of diffraction peaks of Cu/SiC with respect to SiC (Figure 3). On one hand, it indicates that the loaded Cu species might be as non-crystalline phase. On the other hand, no crystalline peaks of Cu were observed in Cu/SiC which may be probably due to its good dispersion on the surface of SiC. The XRD patterns of Cu modified SiC agree well with that of the parent SiC.

As shown in Figure 4(a), the strength of the SiC peak increased after Cu loading, and the characteristic peak of $Cu2p_{3/2}$ appeared, showing that copper ions were loaded on the surface of SiC. The characteristic CuO peaks in the Cu/SiC were observed at 934.7 eV, which is close to the previously reported value for CuO (Chen *et al.* 2017). The other two peaks at 941.3 and 943.9 eV were the characteristic shake-up satellites that accompany the main Cu $2p_{3/2}$ line of CuO (Figure 2(b)). These observations prove that Cu has been successfully loaded onto the surface of SiC in the form of Cu^{2+}.

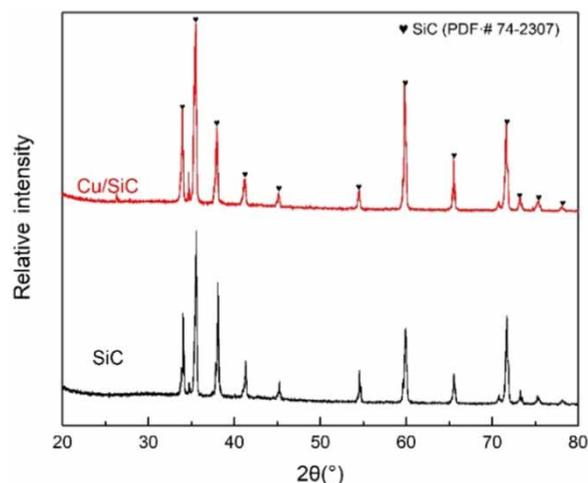## The removal behavior of MO in different systems

The adsorption experiments were conducted at room temperature and it can be seen from Table 1 that with the addition of Cu/SiC the removal rate through adsorption was only 1% after 24 h, indicating that the main route on the removal rate of MO was not adsorption in different systems. The addition of H_2O_2 alone also showed no degradation of MO indicating that H_2O_2 could not oxidize organics without any catalyst. Thus, with the addition of catalyst, the degradation was significantly improved. Since a Fenton-like reaction was developed between copper and H_2O_2 in which ·OH were generated that could degrade various organic pollutants. After the introduction of MW irradiation, the time for all the reactions was reduced to 8 min and the effect of removal rate of MO in different reaction systems is shown in Figure 5. In the presence of MW alone, the removal rate of MO was about 3.5%, indicating that MW irradiation alone could not destroy the organic components of wastewater and has only a slight degradation effect on MO. When MW was introduced along with the catalyst but without the addition of oxidant, no change in the degradation effect was observed. It shows that the MW was not able to stimulate the catalyst to generate free radicals to decompose MO In MW-H_2O_2 system, the degradation effect was significantly increased after H_2O_2
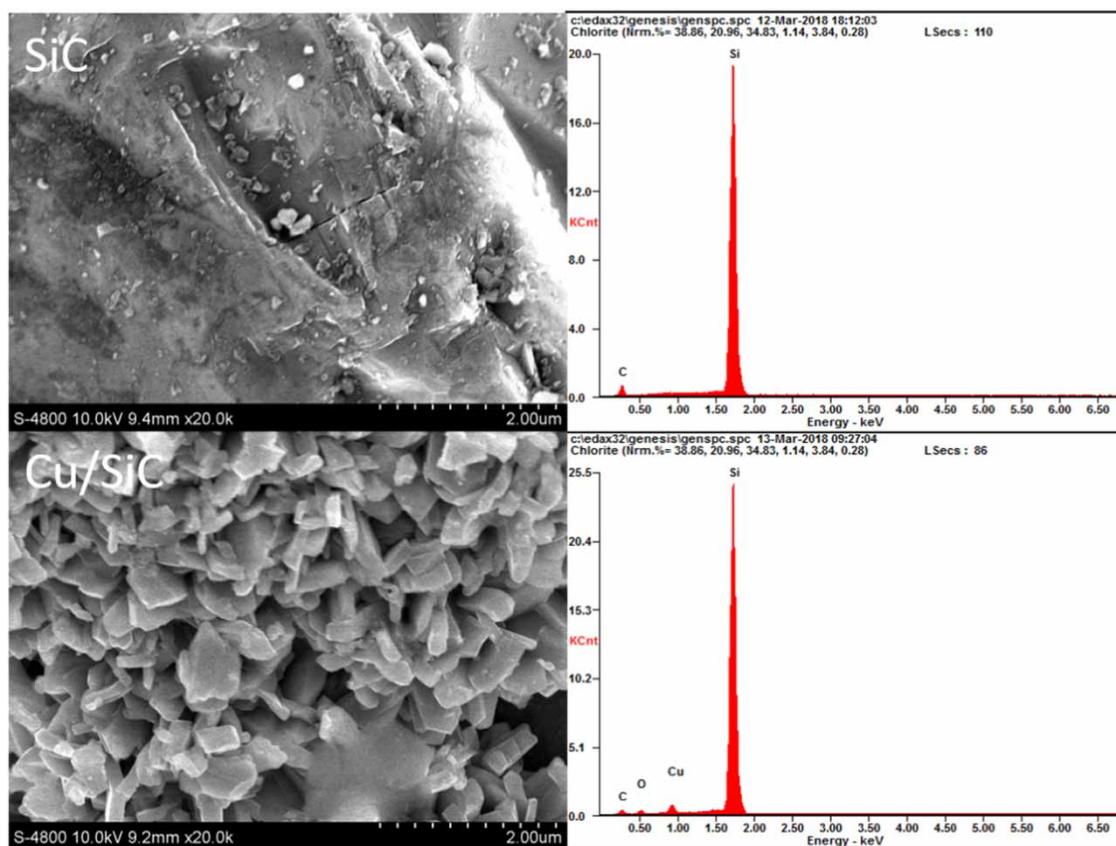
Figure 2 │ SEM images of the Cu/SiC sample and matching EDS data for the analysis of element content.

was added, where the degradation rate reached over 40% after 8 min. It could be probably that microwave induces the decomposition of H_2O_2 directly and ·OH were then generated (Ravera *et al.* 2009; Hong *et al.* 2012). The removal

Figure 3 │ XRD patterns of SiC and Cu/SiC.

rate of methyl orange was greatly increased to reach 97.5% in the MW-Cu/SiC-H_2O_2 system, which could be due to the addition of the Cu-bearing catalyst to form a Fenton-like system with H_2O_2, and the generation rate of ·OH was also increased by MW (Wang & Wang 2016). In order to separate the contributions of MW irradiation and increased temperature to the enhanced rate, water bath heating was used instead of MW and the degradation rate reached over 28.9%. The above shows that the role of the MW is not only heating, but there is a synergistic effect between MW, catalyst and oxidant.
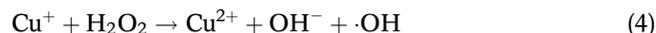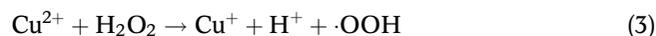
The system consisted of MW, catalyst and oxidant in MW-Cu/SiC-H_2O_2. H_2O_2 and Cu-loaded catalysts under normal temperature and pressure formed Fenton-like reactions that generated free radicals to degrade the target pollutants. Both the monovalent (Cu^+) and divalent (Cu^{2+}) reacted easily with H_2O_2 (Equations (3) and (4)), which is analogous to Fe^{2+}/H_2O_2 and Fe^{3+}/H_2O_2 reaction systems respectively (Bokare & Chio 2014). H_2O_2 does not break down directly to produce free radicals, where MW could directly induce the decomposition of H_2O_2 to generate
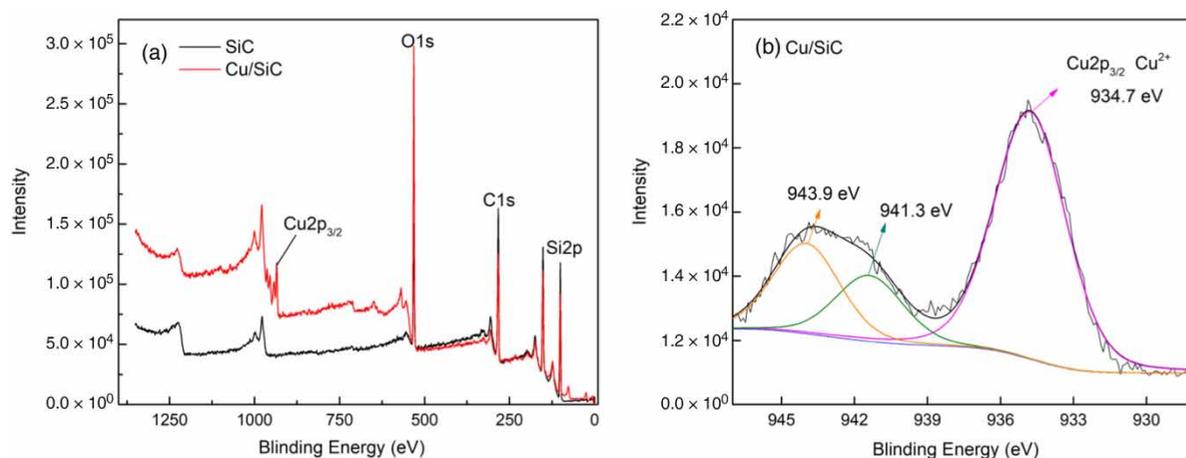
Figure 4 │ (a) XPS of SiC and Cu/SiC and (b) Cu2p spectra XPS of Cu/SiC.

·OH (Equation (2)). The partial removal of MO in the MW H_2O_2 system could also be observed (Ravera et al. 2009; Hong et al. 2012). Studies have shown that under MW irradiation, the effect of "hot spots" generated by the support material may be able to promote the capability of the catalyst via high temperature and the degradation of organic pollutants could take place easily due to the strong absorption capacity of the MW-absorbent (Remya & Lin 2011). However, in this study, no supporting results to prove the existence of the effect of 'hot-spot' could be noted. Apparently, no significant degradation of MO was found out in the MW-Cu/SiC system. This further illustrates that in this experimental system oxidants are necessary. However, the electron movement of Cu/SiC could be accelerated by MW radiation and the high temperature on the surface of the MW absorbent can also promote the catalysis capacity of a catalyst which is loaded on the surface of an MW absorbent (Remya & Lin 2011). MW catalytic reactions to generate ·OH followed by

the oxidative degradation of MO over ·OH are shown in the following reactions:

$$H_2O_2 \rightarrow 2 \cdot OH \tag{2}$$

$$Cu^{2+} + H_2O_2 \rightarrow Cu^+ + H^+ + \cdot OOH \tag{3}$$

$$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + OH^- + \cdot OH \tag{4}$$

Effect of parameters on the degradation in MW-Cu/SiC-H_2O_2 system

The amount of oxidant and catalyst were the key factors in the microwave catalytic oxidation process. It is significant to minimize the dosage in order to reduce the economic costs. The rate of degradation of MO was investigated, varying the amount of catalyst from 0.1 to 0.4 g. The obtained results reflected that the rate of degradation of MO in wastewater increased slowly with an increase in

Table 1 │ Conditions and the effect of different treatment processes on the degradation of MO

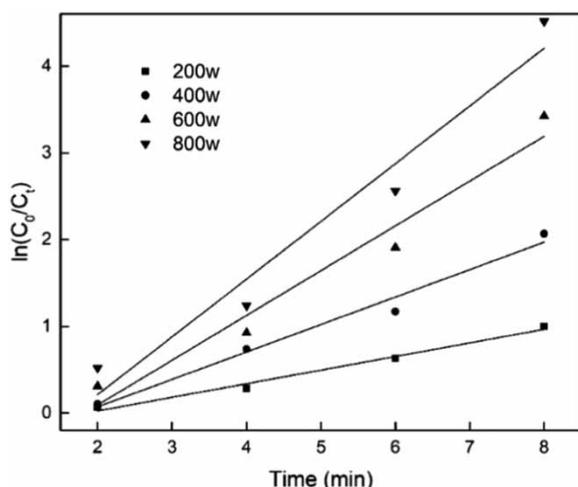| Number	System	WB (°C)	MW (W)	Catalyst (g)	Amount of oxidant (ml)	Time	Degradation (%)
1	Cu/SiC	–	–	0.2		24 h	1.0
2	H_2O_2	–	–	–	0.3	24 h	1.7
3	Cu/SiC-H_2O_2	–	–	0.2	0.3	24 h	26.5
4	MW	–	600	–	–	8 min	3.5
5	MW-Cu/SiC	–	600	0.2	–	8 min	3.6
6	MW-H_2O_2	–	600	–	0.3	8 min	46.9
7	MW-Cu/SiC-H_2O_2	–	600	0.2	0.3	8 min	97.5
8	MB- Cu/SiC-H_2O_2	100	–	0.2	0.3	8 min	28.9
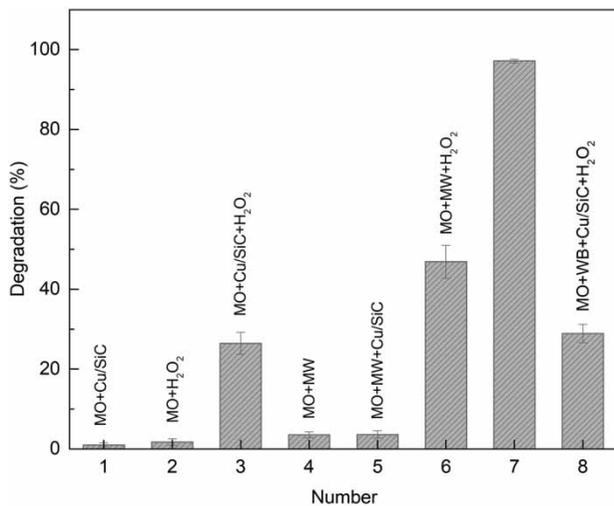
Figure 5 | Effect of different treatment processes on the degradation of MO: (1) adsorption of Cu/SiC catalyst; (2) H_2O_2 oxidation; (3) Fenton-like reaction; (4) MW irradiation; (5) MW-Cu/SiC treatment; (6) MW-H_2O_2 treatment; (7) MW-Cu/SiC-H_2O_2 system; (8) WB- Cu/SiC-H_2O_2 system.

the dosage of Cu/SiC. The rate of degradation reached 82.46% after 8 min with 0.1 g Cu/SiC. With an increase in the dosage of catalyst, the reaction time will be significantly shortened to achieve the same removal rate, as with an increase in the dosage of the catalyst, the contact area of the catalyst, oxidant and reaction solution is increased, and the reaction rate is increased.

The effect of dosages of oxidant (1–4 ml/L) with a MW power of 600 W, on the degradation of MO in MW-Cu/SiC-H_2O_2 system has been presented in Figure 6(b). The rate of removal of methyl orange increased with an increase in the amount of H_2O_2, where the rate of degradation of MO increased from 78.6 to 98.5%, with the dosage of H_2O_2 increasing from 0.1 to 0.3 mL. This could be due to the fact that H_2O_2 is rapidly decomposed by the Cu/SiC catalyst under MW radiation and at the same time large amounts of ·OH, with strong oxidation ability, develops. With an increase in H_2O_2 dosage, the removal
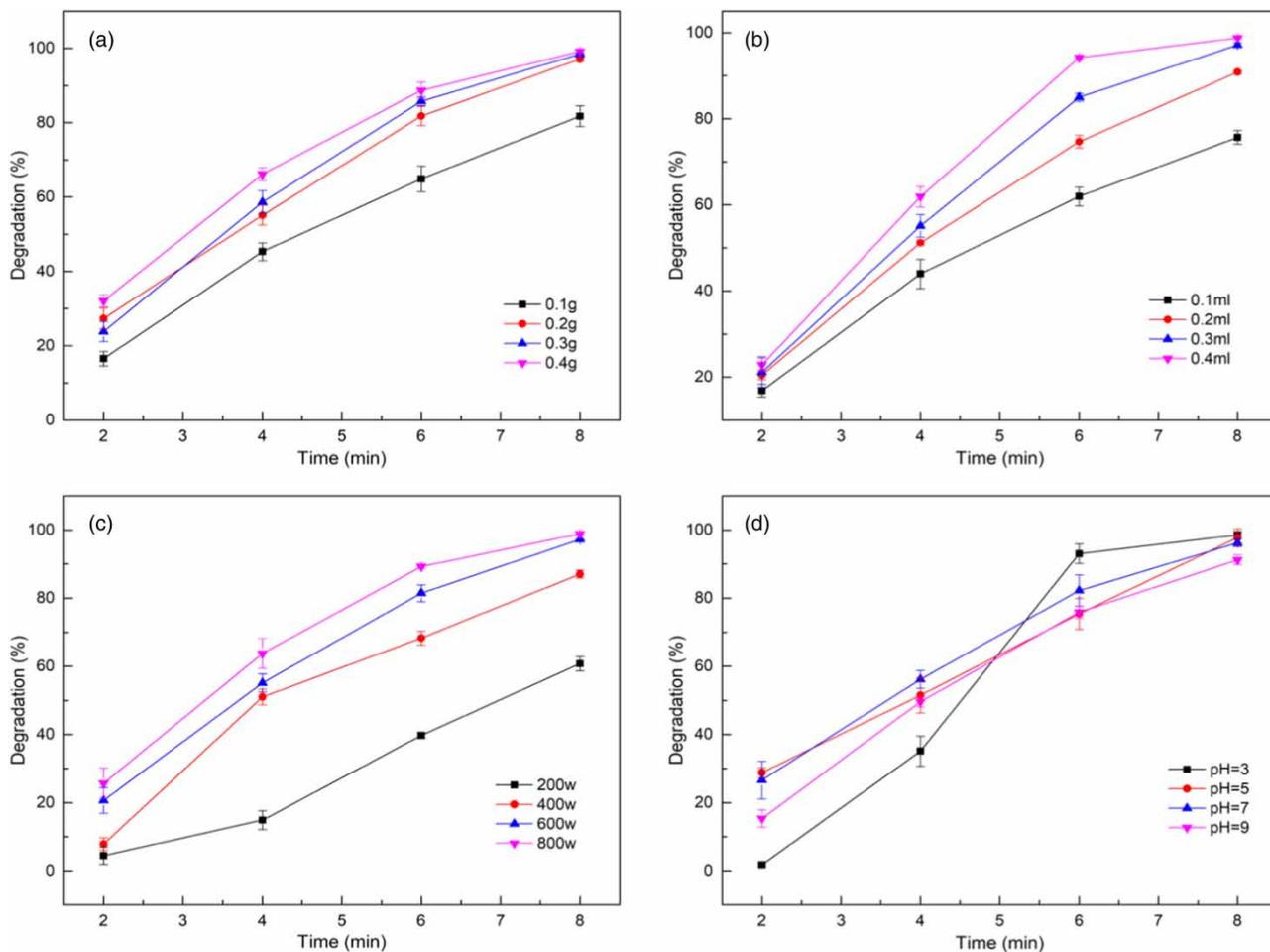
Figure 6 | Effects of different parameters on the degradation of MO using MW-Cu/SiC-H_2O: (a) effect of dosage of catalyst on the degradation; (b) effect of dosage of oxidant on the degradation; (c) effect of microwave power on the degradation; (d) effect of pH on the degradation.

Figure 7 │ The relationship between C/C_0 of MO and reaction time.

Table 2 │ Kinetic parameters of MO degradation at various MW powers

MW power (W)	Kinetic parameter	R^2	$k \times 10^{-2}$ (min^{-1})
200	y = 0.15672x-0.28861	0.98057	15.672
400	y = 0.3162x-0.56037	0.97106	31.62
600	y = 0.51611x-0.93954	0.94462	51.611
800	y = 0.66517x-1.11733	0.93805	66.517

rate of MO became higher, owing to the increased amount of ·OH in the oxidative degradation of MO. Therefore, in view of the degradation effect of MO and the cost of hydrogen peroxide, 0.3 mL was selected as the optimal dosage of H_2O_2.

In order to evaluate the influence of microwave power on the degradation of MO, microwave powers of 200, 400, 600 and 800 W were selected with the catalyst dosage of 0.2 g and the obtained results are shown in Figure 6(c), where an increase in the degradation rate with an increase in MW power can be noted. Obviously, in the whole process, MW power is a unique energy source and the rate of degradation of MO in the wastewater increased as the power also increased. With higher MW power, more molecules can absorb the MW energy. Polar molecules make the temperature of the system increase rapidly throughout the whole system, and under the action of MW energy, the higher the temperature, the higher the activity of hydroxyl radicals, and the greater the oxidation.

During the reaction, the degradation was greatly affected by the solution pH. The results after 8 min showed that the degradation rate of MO reached the highest point, 98.5%, at pH 3. Although the optimal pH in the MW-Fenton process is still about 3, which is similar to the Fenton reaction, the acceptable pH has been extended to include the intermediate alkaline conditions. Under pH 9, the degradation rate can still reach 91.2%, thus completely proving that this process can be directly used to treat wastewater without adjusting the pH of wastewater containing organic components. The stimulation of hydrogen peroxide by MW irradiation may account for a wide range of suitable pH values (Mauro *et al.* 2009).

Radical scavenging tests under the same conditions as that of MW catalytic oxidation systems for identifying the effect of radicals on the degradation of MO were performed. In the experiments on MW catalytic oxidation, an excessive amount of t-butanol (20 mL) was added and the concentrations of MO in the solution were monitored. Radical scavenging tests showed that in the MW-Cu/SiC-H_2O_2 system with the addition of t-butanol, the degradation efficiencies of MO decreased by 81% (data not shown). This also indirectly proved that the MW catalytic oxidation generated ·OH, which is responsible for the direct oxidation and degradation of MO.

The kinetic equation of microwave catalytic degradation

Under the following conditions of MO concentration of 20 mg/L, catalyst dosage of 0.2 g, hydrogen peroxide dosage of 0.3 mL, the relationship between the concentration and time at different microwave powers are shown in Figure 7. The activity of Cu/SiC in the MW-Cu/SiC-H_2O_2 process was studied. According to Equation (1), the rate constant k could be calculated from the slope and the
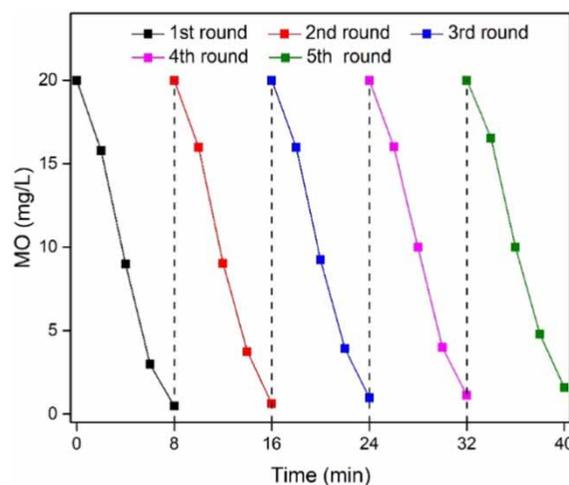
Figure 8 │ Removal of MO in different batches during MW catalytic oxidation process.

larger the value of the rate constant, the faster the reaction. As can be seen from Table 2, the rate constant increases with an increase in microwave power and when the power was 800 W, the rate constant reached up to $66.517 \times 10^{-2} \, min^{-1}$. From the kinetic analysis, it could be noted that the degradation of MO in an MW-Cu/SiC-H_2O_2 system agrees with the pseudo-first-order kinetics.

The reusability and utilization of the Cu/SiC

The reusability of Cu/SiC played a significant role for the practical application of MW catalytic oxidation technology. The reusability of Cu/SiC indicates that the catalyst in a batch can be used over several cycles for MW catalytic oxidation. For this, the used Cu/SiC was dried at 45 °C in an oven after washing with distilled water. A degradation efficiency of 92% was obtained for MO after five cycles of degradation, demonstrating that the catalyst retained similar degradation efficiency as that of the fresh catalyst (Figure 8). These results clearly proved that Cu/SiC has excellent recycling capability and broader application prospects to further exploit in various degradation reactions.

CONCLUSIONS

In this study, a new strategy of Cu/SiC catalytic oxidation degradation under MW condition was established for the effective degradation of MO. Some important conclusions achieved from the present work are as follows:

(1) A degradation rate of up to 97.5% within 8 min was observed using 0.2 g of catalyst, 0.3 ml of oxidant and 600 W of microwave power, to degrade 20 mg/L of MO in the wastewater.

(2) From these experiments, the degradation process could be divided into two steps: MW catalytic reaction to generate ·OH followed by the oxidative degradation of MO over ·OH; the addition of Cu-bearing catalyst formed a Fenton-like system with H_2O_2 and the rate of generation of ·OH was accelerated by MW.

(3) From the kinetic analysis, it was revealed that the degradation of MO in an MW-Cu/SiC-H_2O_2 system agrees with pseudo-first-order kinetics and the reaction rate constant increased with an increase in the microwave power.

(4) The proposed MW catalytic oxidation has significant advantages in the wastewater treatment and whether MW has any non-thermal effect in the process of decomposition deserves further research in the future.

(5) Recovering heat from treated wastewater using heat exchangers is recommended because this can save economic cost and avoid heat pollution of the environment.

ACKNOWLEDGEMENTS

REFERENCES

Atta, A. Y., Jibril, B. Y., Al-Waheibi, T. K. & Al-Waheibi, Y. M. 2012 Microwave-enhanced catalytic degradation of 2-nitrophenol on alumina-supported copper oxides. *Catalysis Communications* **26** (35), 112–116.

Bokare, A. D. & Choi, W. 2014 Review of iron-free Fenton-like systems for activating H_2O_2 in advanced oxidation processes. *Journal of Hazardous Materials* **275** (2), 121–135.

Chen, Z., Wang, T., Jin, X., Chen, Z., Megharaj, M. & Naidu, R. 2013 Multifunctional kaolinite-supported nanoscale zero-valent iron used for the adsorption and degradation of crystal violet in aqueous solution. *Journal of Colloid & Interface Science* **398** (19), 59–66.

Chen, J., Pan, H., Hou, H., Li, H., Yang, J. & Wang, L. 2017 High efficient catalytic degradation of PNP over Cu-bearing catalysts with microwave irradiation. *Chemical Engineering Journal* **323**, 444–454.

Chen, J., Xue, S., Song, Y., Shen, M., Zhang, Z. & Yuan, T. 2016 Microwave-induced carbon nanotubes catalytic degradation of organic pollutants in aqueous solution. *Journal of Hazardous Materials* **310**, 226–234.

Gan, G., Liu, J., Zhu, Z., Yang, Z., Zhang, C. & Hou, X. 2017 A novel magnetic Fe_3O_4/CeO_2 composite prepared by oxidation-precipitation process and its application for degradation of orange G in aqueous solution as Fenton-like heterogeneous catalyst. *Chemosphere* **168**, 254–263.

Haque, K. E. 1999 Microwave energy for mineral treatment processes-a brief review. *International Journal of Mineral Processing* **57** (1), 1–24.

Hong, J., Yuan, N., Wang, Y. & Qi, S. 2012 Efficient degradation of Rhodamine B in microwave-H_2O_2 system at alkaline pH. *Chemical Engineering Journal* **191** (19), 364–368.

Hu, E. & Cheng, H. 2014 Catalytic effect of transition metals on microwave-induced degradation of atrazine in mineral micropores. *Water Research* **57** (12), 8–19.

Lv, S., Chen, X., Ye, Y., Yin, S., Cheng, J. & Xia, M. 2009 Rice hull/$MnFe_2O_4$ composite: preparation, characterization and its rapid microwave-assisted COD removal for organic wastewater. *Journal of Hazardous Materials* **171** (1), 634–639.

Ma, Z., Ren, L., Xing, S., Wu, Y. & Gao, Y. 2015 Sodium dodecyl sulfate modified $FeCo_2O_4$ with enhanced Fenton-like activity at neutral pH. *Journal of Physical Chemistry C* **119** (40), 23068–23074.

Mauro, R., Alessandra, B., Fabio, G., Claudio, C., Davide, M. & Domenico, O. 2009 Oxidative degradation of 1,5-naphthalenedisulfonic acid in aqueous solutions by microwave irradiation in the presence of H_2O_2. *Chemosphere* **74**, 1309–1314.

Pan, H., Hou, H., Shi, Y., Li, H., Chen, J., Wang, L. & Crittenden, J. C. 2018 High catalytic oxidation of As(III) by molecular oxygen over Fe-loaded silicon carbide with MW activation. *Chemosphere* **198**, 537–545.

Pham, A. N., Xing, G., Miller, C. J. & Waite, T. D. 2013 Fenton-like copper redox chemistry revisited: hydrogen peroxide and superoxide mediation of copper-catalyzed oxidant production. *Journal of Catalysis* **301** (5), 54–64.

Ravera, M., Buico, A., Gosetti, F., Cassino, C., Musso, D. & Osella, D. 2009 Oxidative degradation of 1,5-naphthalenedisulfonic acid in aqueous solutions by microwave irradiation in the presence of H_2O_2. *Chemosphere* **74** (10), 1309–1314.

Remya, N. & Lin, J. G. 2011 Current status of microwave application in wastewater treatment-a review. *Chemical Engineering Journal* **166** (3), 797–813.

Shi, J., Ai, Z. & Zhang, L. 2014 $Fe@Fe_2O_3$ core-shell nanowires enhanced Fenton oxidation by accelerating the Fe(III)/Fe(II) cycles. *Water Research* **59** (4), 145–153.

Wang, N. & Wang, P. 2016 Study and application status of microwave in organic wastewater treatment-a review. *Chemical Engineering Journal* **283**, 193–214.

Wang, S., Gong, Q. & Liang, J. 2009 Sonophotocatalytic degradation of methyl orange by carbon nanotube/TiO_2 in aqueous solutions. *Ultrasonics Sonochemistry* **16** (2), 205–208.

Xiao, M., Li, L., Zhong, L., Chen, G., Hang, Z. & Su, X. 2009 Study on treatment of printing and dyeing wastewater by activated carbon adsorption. *Liaoning Chemical Industry* **38** (8), 537–539.

Yin, J., Cai, J., Yin, C., Gao, L. & Zhou, J. 2016 Degradation performance of crystal violet over CuO@AC and CeO_2-CuO@AC catalysts using microwave catalytic oxidation degradation method. *Journal of Environmental Chemical Engineering* **4** (1), 958–964.

Zhai, L., Bai, Z., Zhu, Y., Wang, B. & Luo, W. 2018 Fabrication of chitosan microspheres for efficient adsorption of methyl orange. *Chinese Journal of Chemical Engineering* **26**, 657–666.

Zhang, Y., Liu, C., Xu, B., Qi, F. & Chu, W. 2016 Degradation of benzotriazole by a novel Fenton-like reaction with mesoporous Cu/MnO_2: combination of adsorption and catalysis oxidation. *Applied Catalysis B Environmental* **199**, 447–457.

Zhao, W., Liang, C., Wang, B. & Xing, S. 2017 Enhanced photocatalytic and Fenton-like performance of CuO_x decorated $ZnFe_2O_4$. *ACS Applied Materials & Interfaces* **9** (48), 41927–41936.