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RESEARCH ARTICLE

Intensification of sonochemical degradation of methylene blue by adding carbon tetrachloride

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KEYWORDS

Methylene blue; Sonochemical degradation; Carbon tetrachloride; Intensification; Spectral shift Abstract With the emphasis of governments on environmental protection, the treatment of dye wastewater has received extensive attention. Methylene blue (MB) is a typical dye in industrial wastewater. Sonochemical degradation of methylene blue (MB) was investigated by the addition of CCl₄ in the present work. The effects of operation parameters were examined including the concentration of CCl₄, temperature, initial pH of the solution, and ultrasonic power on the degradation of MB. The concentration of CCl₄ and the initial pH of the solution exhibited a more significant effect on MB degradation than the effect on that exhibited by ultrasonic power and temperature. Under the optimum experimental conditions, MB was degraded completely after 30 min of ultrasound irradiation. Considering the costs in practical applications, the ultrasonic power intensity and CCl₄ concentration can be further optimized to 60 W/L and 0.05% (35 min degrade 98.6%), respectively. The total organic carbon (TOC) and Cl⁻ concentrations from CCl₄ in the degraded solution were 0.23 and 0.13 mmol/L respectively. The red-shift of MB absorption peak (from 665 to 679 nm) was observed during the process of degradation. The identification of the intermediates and degradation pathways by liquid chromatography coupled with mass spectrometry (LC-MS) shows that the n-electron-containing group -Cl is connected with the chromophore groups causing the absorption peak to shift towards the long-wave.

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1. Introduction

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Dyes are usually served as colorants in various industries related to daily life, such as food, printing, cosmetics, and textiles (Ghodbane and Hamdaoui, 2009). The utilization rate of dyes is low in the dyeing process, and about 15% of the dyes are discharged into the environment without being used (Ma et al., 2009). Methylene blue (MB) is a typical synthetic dye, which may destroy the growth environment of aquatic animals and plants and cause series damage to human if intaking excessively (Khanday et al., 2016a; Vadivelan and Kumar, 2005). However, traditional wastewater treatment technologies, such

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as biological treatments, cannot effectively degrade MB (Byun and Kwak, 2005). More importantly, governments of countries have become more and more stringent in the control of wastewater discharge. Therefore, a simple and efficient method should be developed to convert hazardous dyes of wastewater into harmless products.

Recently, the research focus of dye removal is catalyst degradation (Fatimah et al., 2020; Mancuso et al., 2020) and adsorption (Khanday et al., 2016b; Marrakchi et al., 2017; Marrakchi et al., 2016). However, the process of synthesizing catalyst and adsorbent is complicated. Over the past few decades, the advanced oxidation process (AOPs) has progressively been applied to wastewater treatment and has attained remarkable developments (Sani et al., 2020; Wang and Xu, 2012; Wang et al., 2020). Many methods used alone or combined with other technologies, such as electrochemical oxidation, photocatalytic oxidation, and ultrasonic oxidation, have been applied to degrade MB (Ahmad et al., 2020; Botsa et al., 2020; Ma et al., 2009; Samarghandi et al., 2020; Shimizu et al., 2007; Xiong et al., 2012). Ultrasound AOP has a wide adaptability to degrade various organic pollutants. especially for the advanced treatment of high concentrations of refractory organic pollutants. Sonochemical technique can accelerate the rate of chemical reactions and initiate new reaction pathways. Acoustic cavitation, is the basis of sonochemistry characterized by the formation, growth, and collapse of cavitation bubbles. The collapse of cavitation bubbles will induce extremely high temperature and pressure (up to 5000 K and 1000 atm), and an extremely strong microjet. The main reactions during the collapse of cavitation bubbles are shown below (reactions (1)-(4)) (Makino et al., 1983; Suslick, 1990; Thompson and Doraiswamy, 1999). Oxidizing substances that may react with MB molecules such as 'OH and H₂O₂ are formed during acoustic cavitation.

$$H_2 O \xrightarrow{)))} H \cdot + \cdot O H \tag{1}$$

$$H \cdot + O_2 \to \cdot OOH \tag{2}$$

$$2 \cdot OH \to H_2 O_2 \tag{3}$$

$$2 \cdot OOH \to H_2 O_2 + O_2 \tag{4}$$

Although sonochemical degradation of MB is effective, the degradation rate is unsatisfactory. Hence, some measures should be taken to strengthen the ultrasonic AOP. As an important organic compound, CCl₄ is extensively applied in industry (Luo et al., 2007). CCl₄ sonolysis products with strong oxidizing can strengthen the sonochemical reaction in the solution and promote the generation of OH (Chakinala et al., 2008; Wang et al., 2007). Many researchers have demonstrated that CCl₄ is beneficial to enhance the efficiency of the sonochemical degradation of dyes (Bejarano-Pérez and Suárez-Herrera, 2008; Ghodbane and Hamdaoui, 2009; Mishra and Gogate, 2011; Wang et al., 2007). Uddin and Okitsu (Uddin and Okitsu, 2016) illustrated that the addition of CCl₄ can promote the sonochemical degradation of MB, whereas the degradation mechanism has not been demonstrated, the toxicity of the solution is unclear after degradation, and degradation intermediates have not been identified.

The main purpose of this study is to investigate the effect of adding CCl_4 on the sonochemical degradation of MB. For the

sake of optimizing the degradation process and clarifying the degradation mechanism, the parameters of temperature, initial pH, ultrasonic power, the concentration of CCl₄ and *tert*butanol on the degradation of MB were investigated. An unreported phenomenon of MB absorption peak shifting during degradation was observed, which help to determine MB concentration accurately and discuss the ultrasonic degradation mechanism. The approach of LC-MS was adopted to identify the intermediates of MB degradation and infer three possible degradation pathways. Considering the toxicity of the solution after degradation, the CCl₄ addition amount and operating conditions were optimized and the concentrations of Cl⁻ and TOC after degradation were analyzed.

2. Experimental

2.1. Reagents

The chemical reagents used for the experiment were purchased from Sinopharm Chemical Reagent Company, including methyl blue ($C_{16}H_{18}ClN_3S$), carbon tetrachloride, ethanol, silver nitrate, potassium chromate, sodium hydroxide, potassium iodide, sodium thiosulfate and hydrochloric acid. All chemicals were analytical grade and were used without pretreatment. Deionized water was used to prepare solutions.

2.2. Reactor

The experiment was carried out in a 250 mL three-port waterjacketed glass reactor (Fig. 1). Ultrasound (20 kHz) is emitted from the top of the reactor through a horn. The power of the ultrasonicator (JY98IIIDN, Shanghai Bingyue Electronic Instrument Co., Ltd., China) is adjustable from 12 to 1200 W.

2.3. Procedure

The initial pH of the solution was adjusted by HCl and NaOH. In the presence or absence of CCl₄, 200 mL MB solution was



Fig. 1 Schematic of the sonochemical reactor used for MB degradation.

used for degradation under isothermal conditions, and then samples were taken from the reactor and analyzed for concentration. An UV–Vis spectrophotometer (UV5, Mettler Toledo) was used to determine the MB concentration in the solution before and after sonochemical degradation.

The solution became turbid after ultrasonic irradiation of deionized water containing CCl_4 (UI solution). In addition, when ethanol was added, the irradiated solution became clear. The MB calibration curve with the maximum wavelength at 679 nm was plotted by mixing UI solution and ethanol as a solvent. In the solution, ethanol and UI solution accounted for 33% and 30%, respectively. Since UI solution was oxidized, measurements should be taken immediately after the preparation of the standard solution.

The intermediates of MB degradation were analyzed by a reversed phase liquid chromatograph (UltiMate 3000 UHPLC system, Thermo Scientific, San Jose, CA, USA) and a linear ion trap-orbitrap high resolution mass spectrometer (LTQ Orbitrap Velos PRO, Thermo Fisher Scientific, San Jose, CA, USA) equipped with a heated electrospray ionization



Fig. 2 Spectra of MB solutions (a) in the absence, (b) presence of CCl_4 during degradation, (c) at 665 nm, and (d) at 679 nm.

source. The mobile phase consists of 0.1% formic acid solution and acetonitrile solution.

Cl⁻ and ClO⁻ in the solution after degradation were determined by titration. The TOC in the solution after degradation was measured by a total organic carbon analyzer (Elementar vario Toc, Germany). Oxidative reductive potential (ORP vs. Ag/AgCl) of the solution was measured by a potentiometer (PHS-3E, INESA).

3. Results and discussion

3.1. Preliminary degradation test

A preliminary degradation test was conducted to verify the feasibility of CCl_4 intensifying degradation. As shown in Fig. 2a and b, the absorbance of the MB solution drops rapidly due to the existence of CCl_4 . It is worth noting that the absorption peak shifts from 665 to 679 nm when CCl_4 is present. And the absorbance of same solution between the 665 and 679 nm has an obvious disparity. But when CCl_4 is absent, the absorption peak of the MB solution before and



Fig. 2 (continued)

after ultrasonic irradiation is 665 nm. Accordingly, calibration curves of MB at 665 and 679 nm should be plotted to analyze the concentration of MB accurately. The calibration curves with absorption peak at 665 and 679 nm, and spectra are shown in Fig. 2c and d.

3.2. Mechanism of red-shift

The influence of oxidizing substances on MB spectrum was examined to illustrate the reason of red-shift. As shown in Fig. 3a-c, after mixing with deionized water, both the absorbance and absorption peak of solution are essentially unchanged. But after mixing with UI solution, the absorbance of the solution decreases, and the absorption peak shifts from 665 to 679 nm. Additionally, after 40 min of mixing, the color of the mixed solution becomes obviously lighter, which indicates that UI solution has strong oxidizing properties due to the sonolysis decomposition of CCl_4 . Let stand for 15 days,



Fig. 3 Spectra of the solution after mixing MB with (a) deionized water, and (b) UI solution; (c) color comparison of MB solution after mixing for 40 min; (d) spectra of the solution after mixing the non-oxidizing UI solution with the MB solution.





the ORP value of UI solution drops from 1061 to 395 mV. And I_2 is not generated after mixing the UI solution with KI solution, which proves that UI solution lost its oxidizing properties. The absorption peak of MB solution mixed with nonoxidizing UI solution still is 665 nm (Fig. 3d). This indicates that when CCl₄ is added to sonochemically degrade MB, the oxidizing substances produced by sonolysis of CCl₄ are the fundamental cause of the red-shift of the absorption peak.

The oxidizability of the UI solution may be caused by the sonolysis product HClO of CCl₄ or residual H_2O_2 produced by the cavitation. By using NaClO or H_2O_2 to oxidize MB solution, the mechanism of red-shift was further investigated. As shown in Fig. 4, oxidized by NaClO and H_2O_2 for 720 min, the absorbance only decreased by 51.7% and 5.3%, respectively. Then adjusting the pH of containing NaClO solution from 10.88 to 2.53 by HCl, the concentration of HClO in the solution enormously increases. Accordingly, the absorbance drops sharply and the absorption peak shifts from 665



Fig. 4 Spectra of MB solution oxidized by (a) NaClO or (b) H_2O_2 .

to 679 nm instantly in the solution with NaClO. In the solution of H_2O_2 , HCl was added to adjust the pH from 5.15 to 2.33. But after 5040 min, the absorption peak of the solution is still at 665 nm and the absorbance only drops by 28.4%. These results indicate that the existence of chlorine substances (e.g. HClO, Cl₂, HCl) intensifies the oxidation capacity, causes the red-shift of the absorption peak during sonochemical degradation and enhances degradation process.

3.3. Effect of CCl₄

The effect of CCl₄ concentration on MB degradation was examined in the range of 0–1.0%. As shown in Fig. 5a, the MB degradation rate increases obviously when the concentration of CCl₄ increases from 0 to 0.1%, then it is nearly constant when the concentration further increases from 0.1 to 1.0%. The results demonstrate that the amount of CCl₄ required for the complete degradation of MB have a saturation value, which is similar to previous work (Ghodbane and



Fig. 5 (a) Effect of CCl₄ concentration on MB degradation and (b) the pseudo-first-order kinetics plot of MB degradation adding various CCl₄ concentration (conditions: initial pH: 1.95; MB initial concentration: 40 mg/L; temperature: 30 °C; power intensity: 5000 W/L).

Hamdaoui, 2009). As can been seen from the Fig. 5b, -In (C/C_0) is plotted against reaction time, which indicates that degradation of MB corresponds with the character of the pseudo-first-order reaction in kinetics $(-In(C/C_0) = kt, k is)$ apparent rate constant (min⁻¹), C₀ is the initial concentration, C is the instant concentration at time t). Wang et al. (Wang et al., 2007) have reported the similar finding in the case of sonochemical degradation of methylene orange by adding CCl₄. The apparent rate constant k increases with the CCl₄ concentration, 0.0159 min⁻¹ for 0% CCl₄, 0.0279 min⁻¹ for 0.025% CCl₄, 0.0486 min⁻¹ for 0.05% CCl₄, 0.0711 min⁻¹ for 0.075% CCl₄, 0.0804 min⁻¹ for 0.1% CCl₄, 0.0918 min⁻¹ for 0.5% CCl₄, respectively. The rate constant k at a CCl₄ concentration of 0.5% is about six times higher than that of 0%CCl₄, which is much higher than the rate constant of sonocatalytic degradation (ZnO/graphene/TiO2 nanocomposite as the sonocatalyst) of MB reported by Nuengmatcha et al. (Nuengmatcha et al., 2016). When CCl₄ is used as an additive, the sonochemical degradation rate of MB ascends significantly, which is associated with the sonolysis of CCl₄. There is no residual CCl₄ can be observed at the bottom of the reactor after degradation. The CCl₄ is completely degraded into chloride and carbon dioxide in a relatively short irradiation time (Ayyildiz et al., 2005; Bejarano-Pérez and Suárez-Herrera, 2008; Lim et al., 2007; Mahamuni and Pandit, 2006), and the Cl radicals act as an intermediate to form oxidizing substances such as Cl₂ and HClO, as shown in following reactions ((5)–(8)) (Bhatnagar and Cheung, 1994; Chendke and Fogler, 1983; Francony and Pétrier, 1996; Hua and Hoffmann, 1996). Besides, in the case of CCl₄ as a hydrogen atom scavenger, the concentration of strongly oxidizing 'OH radicals increases (Luo et al., 2007; Wang et al., 2007; Zheng et al., 2005). Strong oxidizing species such as 'OH, Cl₂ and HClO attack the MB molecules and cause its rapidly degrade than without CCl₄.

$$CCl_4 \xrightarrow{)))} \cdot CCl_3 + \cdot Cl$$
 (5)

$$\cdot CCl_3 \xrightarrow{)))} \cdot CCl_2 + \cdot Cl \tag{6}$$

$$\cdot Cl + \cdot Cl \to Cl_2 \tag{7}$$

$$Cl_2 + H_2O \rightarrow HClO + HCl$$
 (8)

The pH of the solution gradually decreased during the degradation process because the generation of mineral acid, such as HCl when CCl_4 was present. The similar result has been reported by Ghodbane and Hamdaoui (Ghodbane and Hamdaoui, 2009). The decreases of pH are also observed in the absence of CCl_4 due to the formation of mineral acid by MB degraded.

3.4. Effect of temperature

The effect of aqueous temperature on MB degradation was examined in the range of 20-50 °C in the presence of CCl₄. As shown in Fig. 6, increasing aqueous temperature will slow



Fig. 6 Effect of aqueous temperature on the sonechemical degradation of MB (conditions: CCl_4 concentration: 0.5%; initial pH: 5.45; power intensity: 600 W/L; MB initial concentration: 40 mg/L).

down the degradation of MB, because the rise of temperature will decrease the liquid tensile stress and cause the occurrence of cavitation bubbles easily. Nevertheless, the rise in the vapor pressure of the solution arose by the temperature rise makes the cavitation strength decrease (Ghodbane and Hamdaoui, 2009; Hamdaoui and Naffrechoux, 2007). To sum up, high temperature has a detrimental effect on degradation.

3.5. Effect of pH value

It can be seen from Fig. 2a that after adding HCl, the degradation rate increases sharply, so the pH value of the solution is the crucial parameter to the sonochemical degradation of MB. As shown in Fig. 7, the effect of initial pH on MB degradation was examined in the range of 1.95–11.05. With the increase of pH, the degradation rate of MB decreases because the oxidizing substances attacking MB molecules are more



Fig. 7 (a) Effect of initial pH on MB degradation and spectra of the solution after ultrasonic irradiation for different time at (b) pH 1.95, (c) pH 8.16 and (d) pH 11.05 (conditions: CCl₄ concentration: 0.5%; power: 600 W/L; MB initial concentration: 40 mg/L; temperature: 30 °C).



Fig. 8 Effect of ultrasonic power on MB degradation (conditions: CCl_4 concentration: 0.5%; initial pH: 1.95; MB initial concentration: 40 mg/L; temperature: 30 °C).

active at low pH. For example, the standard potential of OH radical in acidic medium relative to ordinary hydrogen electrode (NHE) is 2.8 V, but in alkaline medium is 1.55 V relative to NHE (Pera-Titus et al., 2004; Wang and Xu, 2012). HClO, which is prevalent in acidic solution, is converted to ClO⁻ in alkaline solutions (Rajkumar et al., 2007; Shi et al., 2005; Szpyrkowicz et al., 2000). Furthermore, the oxidation potential of HClO (1.49 V) is higher than that of ClO⁻ (0.94 V). In addition, partial degradation products of MB and CCl₄ exist in the alkaline solution in the form of CO_3^{2-} , which can be used as a scavenger of OH radicals (Alaton et al., 2002; Song et al., 2007).

According to the UV–Vis spectra, when the initial pH values are 1.95 and 8.16, the absorption peak shifts from 665 to 679 nm after 10 min of ultrasonic degradation (Fig. 7b and c). But when the pH value is 11.05, the absorption peak shifts



Fig. 9 (a) Effect of *tert*-butanol on the sonochemical degradation of MB, and (b) spectra of MB solutions in the presence of CCl₄ and *tert*-butyl alcohol during degradation (conditions: MB initial concentration: 40 mg/L; initial pH: 1.95; temperature: 30 °C; power intensity: 5000 W/L; *tert*-butyl alcohol concentration: 0.5%; CCl₄ concentration: 0.5%).

to 679 nm (Fig. 7d) after 35 min of irradiation. And during the entire degradation process, the pH of the solution drops from the initial 11.05 to 2.79, initial 8.16 to 2.67, initial 5.45 to 2.55, initial 3.27 to 2.38, and initial 1.95 to 1.88, respectively. When the solution is alkaline, the absorption peak at the initial stage of degradation does not shift, indicating that the rate of HClO formation is slow. After a period of degradation, part of the OH^- is neutralized by the HCl generated by the sonolysis of CCl_4 , which causes the decrease of pH, the increase of generation rate of HClO, the increase of solution oxidizability and the red-shift of absorption peak. Accordingly, the MB degradation rate in alkaline media is significantly lower than that in acidic media.

In this study, the MB acoustic degradation process with CCl_4 as an additive is composed by three stages. In the initial reaction stage, the degradation rate slowly increases because CCl_4 gradually decomposes and oxidative substances begin to be generated and accumulated. Besides, with the gradual decrease of pH, the concentration of HClO gradually increases, and the oxidizability of the solution gradually increases. In the second stage of the reaction, MB is rapidly degraded under the action of sufficient H₂O and CCl₄ oxidative sonication products. Ultimately, with the decrease of the MB content, the degradation rate gradually decreases at the end of the reaction.

3.6. Effect of ultrasonic power intensity

The effect of ultrasonic power intensity on the degradation of MB was investigated with powers intensity of 60, 600, 3000, and 5000 W/L. Fig. 8 illustrates that the degradation rates at

60 and 600 W/L are similar, and the degradation rates at 3000 and 5000 W/L are similar. Additionally, the degradation rate of the latter is slightly faster than the former. The intensity of cavitation effect positively related to the acoustic amplitude, and the acoustic amplitude increases with the rise of the ultrasonic power. Accordingly, increasing the ultrasonic power will increase the cavitation effect and accelerate the degradation of MB, H₂O and CCl₄ (Brotchie et al., 2009; Monnier et al., 1999).

3.7. Effect of tert-butyl alcohol

The effect of tert-butyl alcohol on the sonolytic degradation of MB was investigated (Fig. 9a). When *tert*-butyl alcohol was added to the solution without CCl₄, the MB was almost not degraded after 30 min of ultrasonic irradiation. Ke et al. (Ke et al., 2014) have reported the MB can be oxidized by 'OH. Consequently, weak degradation can owe that tert-butanol molecules enter the cavity of the cavitation bubbles to remove the OH. When CCl₄ and tert-butanol were added simultaneously, the MB degradation rate apparently increased. But it is still lower than the degradation rate of MB in the absence of CCl₄ and tert-butyl alcohol. Pétrier and Francony (Pétrier and Francony, 1997) proves that the presence of tert-butanol does not affect the sonochemical decomposition of CCl₄. And most of the oxidizing species formed by the sonolysis of CCl₄ such as HClO, Cl₂ and chlorine-containing free radicals (Cl, CCl₃ and CCl₂) also seem to be scavenged by *tert*butyl alcohol. This inference can be confirmed from the spectra. The spectrum only slightly shifts after 30 min, which proves that HClO can be consumed by tert-butanol (Fig. 9b). Accordingly, tert-butyl alcohol removes oxidizing



Fig. 10 Degradation pathways of methylene blue.

species in the sonolysis products of H_2O and CCl_4 , which causes the MB degradation rate is lower than that does not exist CCl_4 and *tert*-butyl alcohol. From these results, we can infer the mechanism of MB degradation. Partial MB is oxidized by OH radicals and ultrasonic irradiation hardly destroys the chemical bonds in MB molecules. In the presence of CCl_4 , the reason for the acceleration of MB degradation rate is the increase in the concentration of OH radicals in the solution and the generation of chlorine-containing radicals and other oxidizing species such as HCIO and Cl_2 .

The analysis of the intermediate products by LC-MS proved that the main degradation site of initial substrate MB (the molecular ion peak $[M]^+$ at m/z = 284 of the cation part obtained by ionization in electrospray mass spectrometry) occurs on the C-N bonds and S atoms of the dimethylamino groups in the molecular structure when the degradation reaction begins. There are three main degradation reaction pathways (Fig. 10). The first degradation reaction channel is the oxidation of S atoms to obtain sulfoxide-type $((R_1R_2)$ S = O) oxidation product (m/z = 300), and continuous oxidation to obtain (($\mathbf{R}_1\mathbf{R}_2$)S = O₂) oxidation product (m/z = 316). The same intermediates were detected by Cohen et al. when they degrade MB using the OH producing by Fenton process (Cohen et al.). The second and third reaction channels are different from the reaction channel of Fenton degradation. The second degradation reaction channel is represented by the continuous and separate removal of methyl (Me) groups at different positions by the rupture of the Csp3-N bonds in MB to sequentially obtain different products with the same mass number, such as m/z = 270, 256, and 242. The above intermediates are converted into the continuous chlorination of aromatic rings to obtain monochlorinated and polychlorinated products such as m/z = 304, 338, 371, 405 and bromo (bromine-containing impurities from carbon tetrachloride) products at m/z = 382; 290, 324, 358, 382; 276, 310, 344, 378 and re-oxidation product at m/z = 396. The third degradation reaction channel is represented by the chlorination of methylene blue to obtain the corresponding products at m/z318, m/z 352, m/z 386 and its chlorinated oxidation hydroxylation products at m/z = 336, 370. The further degradation of the above products is manifested by the oxidative ring opening, which degrades the ring to produce small molecules of carboxylic acid, amine, and amide compounds, and finally resolves to H_2O , CO_3^{2-} , NO_3^{-} , Cl^- , NH_4^+ , SO_4^{2-} , etc.

The group –Cl, which contains n electron, has no chromogenic function, but when it is connected to the chromogenic group, the p- π conjugation effect will increase the electron cloud density on the double bonds and further reduce the energy difference of the π - π * transition, enhance the colorgenerating ability of the chromophore, and cause the redshift of absorption peak.

3.8. Practical consideration

For the consideration of costs in practical applications, the sonochemical degradation of MB at smaller ultrasonic power and lower concentration of CCl_4 was examined. The degradation rate of MB by 60 W/L ultrasonic irradiated 35 min with 0.05% CCl_4 is similar to that by 5000 W/L ultrasonic with 0.5% CCl_4 , as shown in Fig. 11a. Consequently, the high-



Fig. 11 (a) Effect of low addition of CCl_4 and low power on MB degradation, (b) composition of inorganic chlorine in the solution after complete degradation, (c) the source and concentration of Cl^- and (d) content of TOC before and after degradation (conditions: MB initial concentration: 40 mg/L; pH: 1.95; temperature: 30 °C).

efficiency sonochemical degradation can be achieved at low ultrasonic power and low ${\rm CCl}_4$ concentration.

 CCl_4 is considered as a pollutant. High concentration Cl^- discharging into environment will deteriorate the water quality, damage the aquaculture industry, and corrode the water

distribution system. Therefore, the ClO⁻, Cl⁻ and TOC contents were measured and the source of Cl⁻ was calculated in the solution after MB was completely degraded under the conditions of low power (60 W/L) and low CCl₄ concentration (0.05%) (Fig. 11b-d). Within the solution the Cl⁻ and ClO⁻ concentrations produced by the decomposition of CCl₄ are 0.3 and 0.7 mmol/L, respectively. Additionally, the TOC content in the solution after degradation is 0.046 mmol accounting for 3.2% of initial TOC content. As a result, CCl₄ was almost completely degraded simultaneously. Both TOC content and Cl⁻ concentration meet the industrial wastewater discharge standards. Consequently, when sonochemical degrade industrial wastewater containing MB, adding a smaller amount of CCl₄ will not cause new pollution.

4. Conclusion

CCl₄ significantly enhances the sonochemical degradation of MB, because it can intensify the ultrasound AOP and its acoustic decomposition will produce strong chlorinecontaining oxidation radicals, HClO and Cl₂. The concentration of CCl₄ and the initial pH exhibit obvious influences on the degradation of MB. Under the optimal experimental conditions: pH 1.95, power intensity of 5000 W/L, CCl₄ concentration of 0.5%, and temperature of 30 °C, a 200 mL solution with an initial MB concentration of 40 mg/L can be virtually completely degraded after ultrasonic irradiation for 30 min. But when without CCl₄, the degradation rate of MB is only 36.75%. The CCl₄ addition and ultrasound power can be optimized to 0.05% and 60 W/L respectively. It is also calculated that the concentration of Cl⁻ from CCl₄ is 0.3 mmol/L and TOC content decreases by 96.8% after degradation, which reaches the standard of discharging and will not cause secondary pollution. Three degradation pathways and intermediates of MB was identified by LC-MS. Comparing pathways and intermediates in present study with that of methylene blue degradation by Fenton reaction, the addition of CCl₄ provides new pathways and forms new intermediates. Since the group -Cl is connected to the chromophore groups, the red-shift of MB spectrum was noticed during the degradation process.

CRediT authorship contribution statement

Qi Li: Conceptualization, Investigation, Methodology, Writing - original draft. Yongfeng Chang: Supervision, Project administration, Funding acquisition, Writing - review & editing. Feng Xie: Supervision, Project administration, Funding acquisition, Writing - review & editing. Wei Wang: .: Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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