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Synergistic Degradation of Methylene Blue by Hydrodynamic Cavitation Combined with Hydrogen Peroxide/Vitamin C System

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ABSTRACT: In this study, a new combined process of hydrodynamic cavitation (HC) and a hydrogen peroxide/vitamin C (H_2O_2/Vc) system was proposed for the degradation of methylene blue (MB) in wastewater. An impact-jet hydraulic cavitator was used as the cavitation generation equipment, and H_2O_2/Vc was selected as a homogeneous oxidation system. The degradation characteristics of MB were investigated. The results showed that the degradation effect of HC in combination with the H_2O_2/Vc system was more effective than that of the individual HC or H_2O_2/Vc system. A maximum degradation rate of 87.8% was achieved under the following conditions: H_2O_2 concentration of 0.03 mol/L, Vc concentration of 0.021 mol/L, inlet pressure of 0.3 MPa, initial solution concentration of 4 μmol/L, solution volume of 150 mL, and reaction time of 10 min. The synergy index was 1.615, indicating a synergistic effect between the HC and H_2O_2/Vc system. The data of the hydroxyl radical ($\cdot$OH) yield under the conditions of HC, the H_2O_2/Vc system, and the HC + H_2O_2/Vc system were fitted and analyzed. A correlation equation for $\cdot$OH yield was established, further revealing the synergistic mechanism of the HC and H_2O_2/Vc system. The intermediate products of MB degradation were detected based on LC-MS, and three possible degradation pathways of MB degradation were proposed. The combined process of HC and H_2O_2/Vc systems exhibited relatively low energy efficiency and operating cost, indicating that it was in line with the development direction of wastewater treatment.
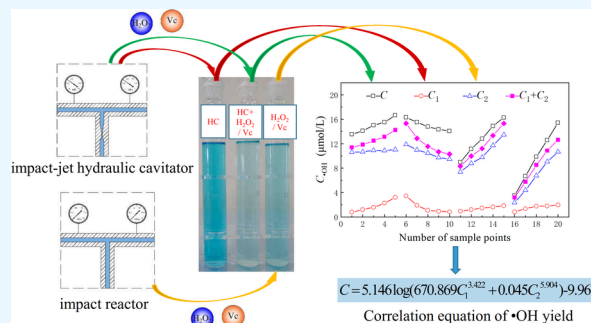
1. INTRODUCTION

Methylene blue (MB) is an organic alkaline dye in printing and dyeing wastewater and poses significant harm to the environment and human health. Traditional methods for dye removal include chemical coagulation,[1] adsorption,[2] biochemical oxidation,[3] etc. However, these methods have problems, such as high cost, long degradation cycle, and susceptibility to secondary pollution. In recent years, advanced oxidation processes (AOPs) applied to eliminate harmful substances in wastewater have become popular. It involves the production of hydroxyl radicals ($\cdot$OH) with high oxidation activity, which oxidize organic matter into H_2O, CO_2, and some small molecules to achieve efficient degradation of dye wastewater. AOPs have the advantages of high efficiency, low environmental impact, and low cost in decomposing toxic pollutants. It is regarded as a green and powerful treatment technology for dye degradation. AOPs include electrochemical oxidation,[4] Fenton and Fenton-like oxidation,[5,6] photocatalytic oxidation,[7] and cavitation,[8] etc. In addition, microbial degradation[9] was also recognized as a promising method, which utilized random mutagenesis for the bioremediation of dyes, leading to dye degradation. The combination of two AOPs or one AOP with other methods has attracted the attention of many researchers due to its higher efficiency compared to a single method.[10−12]

Hydrodynamic cavitation (HC) is considered as one of the AOPs. In the process of HC, pressure changes cause the growth, contraction, and collapse of cavitation bubbles, resulting in a strong chemical effect (free radical effect) and mechanical effect.[13] Since HC has the advantages of low cost, low energy consumption, and no secondary contamination problems, it is favored by researchers and has been widely used in wastewater treatment,[14] biodiesel synthesis,[15] preparation of nanoemulsion,[16] sterilization,[17] polymer degradation,[18] etc. HC is regarded as a very promising technology for the degradation of water pollutants.[19] Many researchers have studied the degradation of organic compounds in wastewater by HC technology. Rajoriya et al.[20] studied the degradation mechanism of Rhodamine 6G under the action of HC using two types of cavitation devices, slit and circular venturi, and pointed out that $\cdot$OH was the main factor affecting the degradation effect. Dhanke et al.[21] utilized an HC reactor to
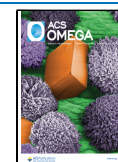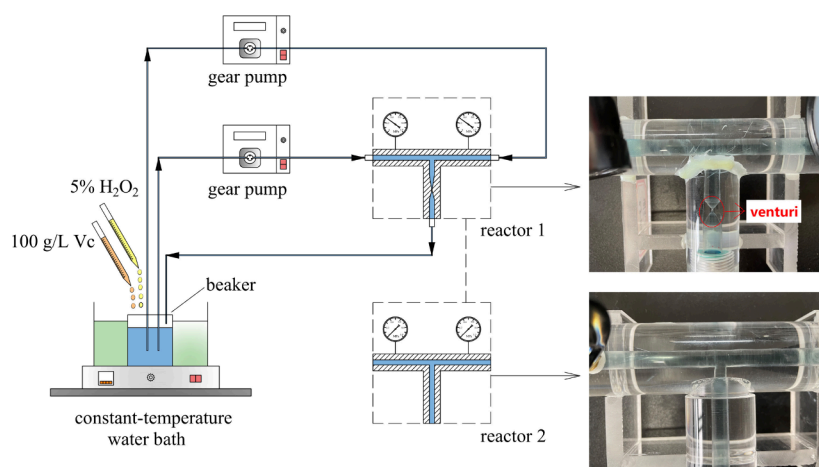
Figure 1. Schematic diagram of experimental setup (Photograph courtesy of Yan Cao).

treat fish processing wastewater. The biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), odor, and color of this wastewater have been reduced promisingly. It was pointed out that this wastewater can be degraded effectively by HC. Although HC has unique advantages in wastewater treatment, the use of HC alone poses problems such as insufficient cavitation intensity and low degradation efficiency of organic matter.

H_2O_2 has strong oxidizing properties and can decompose to produce ·OH.[22] However, in the absence of a catalyst, the rate of H_2O_2 decomposition to produce ·OH is very slow. Generally, H_2O_2 is combined with Fe^{2+} to form a Fenton reagent. Under the catalysis of Fe^{2+}, H_2O_2 can rapidly decompose to produce highly active ·OH, greatly accelerating the reaction rate. The Fenton process is one of the AOPs. It was reported that the combination of HC and AOPs can significantly improve the degradation efficiency of organic matter,[23] and the combination of HC and Fenton has been widely studied. Rajoriya et al.[24] reported four combined processes (HC + air, HC + O_2, HC + O_3, HC + Fenton) for the treatment of textile dyeing industry effluent. It was pointed out that the combination of HC and Fenton was the most effective for the treatment of this wastewater, resulting in a 48% reduction in TOC and a 38% reduction in COD. Askarniya et al.[25] investigated the decolorization of Congo red using the hybrid process of HC with H_2O_2, $FeSO_4$, and Fenton. It was pointed out that the combination of HC and Fenton can achieve a maximum decolorization rate of 70% within 60 min, and the hybrid process has a more effective decolorization effect than the individual process. However, a major drawback with the use of Fenton reagents was the generation of a large amount of sludge during the process of treating wastewater, resulting in new pollution issues.[26]

Vitamin C (Vc), also known as ʟ-ascorbic acid, is an acidic polyhydroxy compound containing 6 carbon atoms, mainly derived from fresh fruits and vegetables. It is an essential nutrient for higher primates and a few other organisms and has strong reducibility. In the presence of Vc, H_2O_2 can easily decompose to produce ·OH. Yan et al.[27] pointed out that the degradation mechanism of Vc and H_2O_2 was similar to that of Fe^{2+} and H_2O_2 in Fenton's reagent. The combination reagent $(H_2O_2 + Vc)$ was considered as one of Fenton's reagents. Both Vc and Fe^{2+} tended to promote the decomposition of H_2O_2 to generate ·OH,[28] thereby leading to the degradation of organic

compounds. The H_2O_2 + Vc composite reagent is an environmentally friendly redox reaction system, and its use will not cause secondary pollution. Currently, this composite reagent is commonly used for the degradation of polysaccharides in food. Li et al.[29] reported the degradation of polysaccharides from Passiflora edulis peel by the Vc-H_2O_2 system. After degradation, the molecular weight and intrinsic viscosity of the Passiflora edulis peel were significantly reduced. It was pointed out that the Vc-H_2O_2 system was effective in the degradation of Passiflora fruit peel. Yan et al.[27] studied the degradation of codium cylindricum polysaccharides by combined processes of H_2O_2 + Vc + ultrasonic and H_2O_2 + Fe^{2+} + ultrasonic. It was pointed out that many ·OH that affected positive antioxidant activity were produced in both processes. The combined process of H_2O_2 + Fe^{2+} + ultrasound has stronger antioxidant activity, while the combined process of H_2O_2 + Vc + ultrasound had a mild reaction and higher recovery rate. In addition, the application of the H_2O_2–Vc composite reagent has been extended to the field of wastewater treatment. Li et al.[30] used the H_2O_2–Vc system to treat azo dye wastewater which contained a high concentration of methyl orange. The results showed that this system can effectively degrade methyl orange with a decolorization rate of over 98%. However, there is currently no research on the use of H_2O_2–Vc composite reagent for the treatment of MB in wastewater.

This paper proposed a new combined process of the HC and H_2O_2/Vc system, both of which were green and environmentally friendly AOPs. In the present work, the degradation characteristics of MB by the combined process of the HC and H_2O_2/Vc system were investigated. First, the effects of various factors on the degradation rate of MB and the yield of ·OH were studied. In addition, the synergistic effect of HC and H_2O_2/Vc and the degradation mechanism of MB were explored. This study attempts to explore a new green method for the efficient degradation of MB in wastewater.

2. EXPERIMENTAL SECTION

2.1. Materials. Methylene blue (AR grade) was obtained from Tianjin Zhiyuan Chemical Reagent Co., Ltd., Tianjin, China. Hydrogen peroxide (30%, AR grade) and ʟ-ascorbic acid (AR grade) were provided by Xilong Scientific Co., Ltd., Shantou, China. All of the solutions were prepared with pure
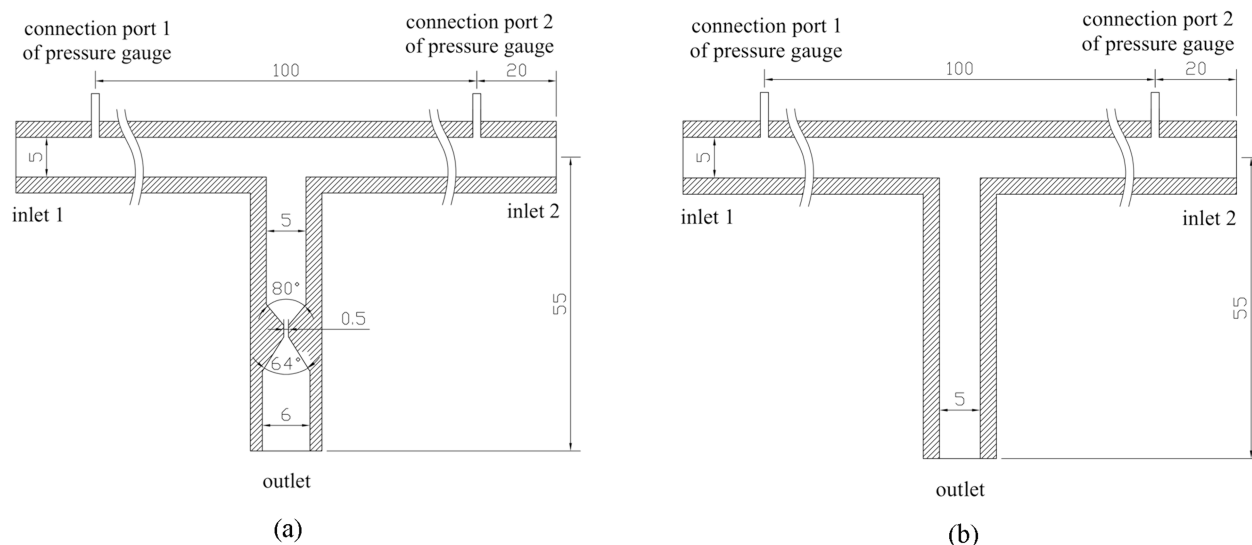
Figure 2. Structures of the reactors used in this study: (a) reactor 1, (b) reactor 2.

water produced by a Milli-Q system (Millipore Co., Ltd., Billerica, MA, USA).

2.2. Experimental Process Parameters. The MB solution was preheated to a reaction temperature of 30 °C before carrying out the experiment. Appropriate amounts of H_2O_2 and Vc were added sequentially to the MB solution. Two gear pumps were started simultaneously, and the flow rate could be controlled by adjusting the speed of the pumps. When the reaction was complete, sampling and analysis were carried out immediately. The parameters and conditions selected in the experiments were as follows: H_2O_2 concentration, 0.01−0.05 mol/L; Vc concentration, 0−0.035 mol/L; inlet pressure, 0.1−0.5 MPa; initial concentration of MB solution, 4−20 μmol/L; volume of solution, 120−240 mL; time, 2.5−12.5 min. In all experiments, the pH of the simulated MB wastewater was maintained at 6.23, and the reaction temperature was set at 30 °C.

2.3. Experimental Setup. The schematic diagram of the experimental setup is shown in Figure 1. The setup included a constant-temperature water bath (DF-101S, Gongyi Yuhua Instrument Co., Ltd., Zhengzhou, China), a beaker, two gear pumps (WT3000-1JB, Longer Precision Pump Co., Ltd., Baoding, China), and a reactor. These devices were connected by silicone tubes to form a circulation loop. The pressure gauges (Y-40Z, Hongqi Instrument Co., Ltd., Leqing, China) were installed in the two inlet sections of the reactor to display the real-time pressure. Two types of reactors were used in this experiment. Reactor 1 and reactor 2 were the devices with and without venturi on the outlet, respectively.

The structures of reactors 1 and 2 are shown in Figure 2. The reactor 1 was an impact-jet hydraulic cavitator, which had two inlets and one outlet. The inner diameters of the inlet and outlet were 5 and 6 mm, respectively. A venturi with a throat diameter of 0.5 mm was placed in the outlet section. The inlet cone angle and outlet cone angle of the venturi were 40 and 32°, respectively. The reactor 2 was an impact reactor, which had the same structure as the reactor 1, except for the absence of a venturi in the outlet section. The reactor 1 was used to study the degradation of MB under two conditions, HC alone and HC in combination with the HC + H_2O_2/Vc system. The effect of the H_2O_2/Vc system alone on MB degradation was

investigated using reactor 2, in which the influence of cavitation on MB degradation can be eliminated.

2.4. Experimental Analysis. An ultraviolet−visible spectrometer (UV-2600, Shimadzu Co., Ltd., Suzhou, China) was used to measure the absorbance of the MB solution. The absorption spectrum of the MB solution was acquired within the wavelength range of 400−800 nm, as shown in Figure 3.
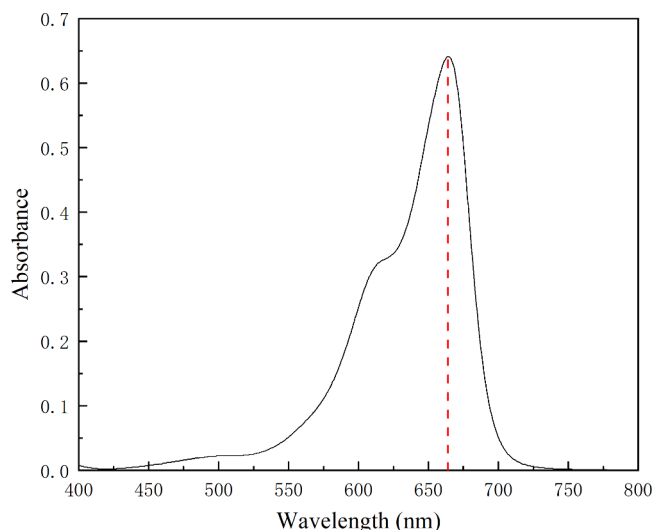

Figure 3. Absorption spectrum of the MB solution.

The maximum absorption peak was observed at a wavelength of 664 nm. Therefore, the absorbance of the MB solution in this study was measured at a maximum wavelength of 664 nm. The concentration of MB can be determined based on the MB standard curve, as shown in Figure 4, obtained from Beer−Lambert Law. The degradation products of MB were detected with liquid chromatography−mass spectrometry (LC-MS, Agilent LC1290-QQQ-6470, USA). The mass spectrometric conditions included positive ion acquisition mode, a dry gas temperature of 150 °C, a dry gas flow rate of 12 L/min, an atomized gas pressure of 30 Psi, a capillary voltage of 3500 V, and a quality detection range set to m/z from 50 to 400. The chromatographic conditions consisted of a flow rate of 0.35
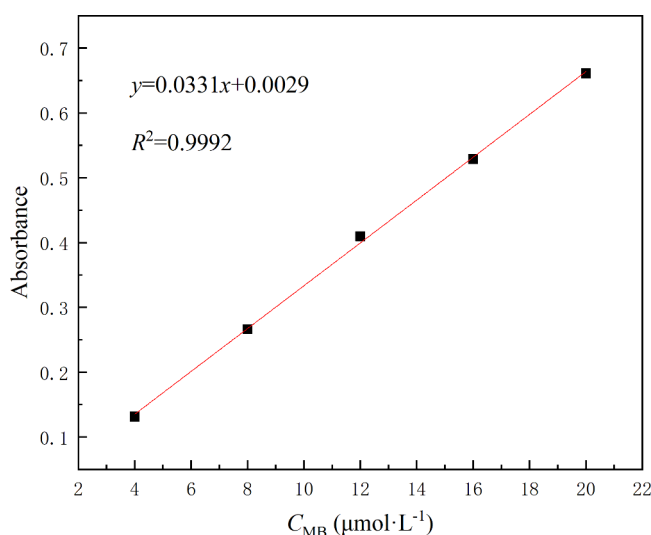
Figure 4. Standard curve of the MB solution.

mL/min and a mobile phase composed of acetonitrile and 0.1% formic acid. The TOC was measured by using a TOC analyzer (Elementar vario TOC, Germany).

In order to reduce the influence of experimental errors on the experimental results, each experiment was repeated three times. The experimental data in the figures were expressed as the mean or mean ± standard deviation.

3. RESULTS AND DISCUSSION

In this study, ·OH was mainly derived from the HC process and the reaction between H_2O_2 and Vc. In the process of HC, when the fluid passed through a constriction (such as orifice plate, venture, etc.), cavitation bubbles underwent the process of formation, growth, and collapses due to pressure changes. At the moment when the cavitation bubble collapsed, an extreme environment of high temperature (500−15,000 K) and high pressure (100−5000 bar) was generated. In this extreme environment, water molecules were decomposed into species with high oxidative activity, such as ·OH, ·OOH, etc. The energy required for dissociation of the OH bond in H_2O_2 was 388 kJ/mol.[31] The presence of catalysts (such as Fe^{2+}, Vc, etc.) reduced the energy barrier for H_2O_2 decomposition and promoted the cleavage of the OH bond.

·OH reacts with MB to generate various degradation products, and the reaction process can be described as follows:

$$n·OH + MB \rightarrow \text{products (intermediates, } CO_2, \ H_2O,$$

$$\text{etc.)} \tag{1}$$
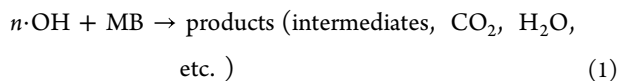
Under the attack of a large number of ·OH, a series of reactions occur, such as demethylation, hydroxylation, bond cleavage, etc. Hydroxylation is the process of introducing ·OH into a molecular structure to form compounds with hydroxyl groups. However, the degradation pathways of MB are usually more than one, and the degree of hydroxylation of intermediate products varies in different degradation pathways. It was found in various degradation pathways reported in the literature[32−34] that in most cases intermediate products containing one hydroxyl radical were usually formed. Similar findings were found in our study (as shown in Section 3.4). There are three possible pathways for MB degradation. The intermediate products containing one hydroxyl radical were

formed in pathways 1 and 2, while polyhydroxy compounds were only formed in pathway 3. Therefore, in order to achieve quantitative analysis of the yield of ·OH captured, the degradation process of MB has been simplified, and a hypothesis was proposed that the hydroxyl radical reacted equimolarly with MB ($n = 1$ in eq 1). A similar method for obtaining the yield of· OH was reported by Zhang et al.[35] Therefore, the concentration of ·OH captured can be calculated as follows:

$$C_{·OH} = C_{MB,o} - C_{MB} \tag{2}$$

Where $C_{MB,o}$ and C_{MB} are the concentrations before and after MB degradation, respectively.

The degree of MB degradation is reflected by the degradation rate (η),[36] which can be calculated as follows:

$$\eta = \frac{C_{MB,o} - C_{MB}}{C_{MB,o}} \times 100\% \tag{3}$$

In HC devices, the degradation of MB was closely related to the cavitation intensity, which can be evaluated by the cavitation number (C_v). Generally, cavitation occurs when $C_v \leq 1$. A smaller C_v value indicates a higher cavitation intensity. C_v is a dimensionless parameter,[37] which can be defined as follows:

$$C_v = \frac{P_r - P_v}{(1/2)\rho v^2} \tag{4}$$

Where P_r denotes the outlet pressure of the hydraulic cavitator, P_v denotes the vapor pressure of the liquid, ρ denotes the density of liquid, and v denotes the average velocity of the liquid at the venturi throat.

3.1. Effect of H_2O_2 Concentration on Degradation of MB by the HC + H_2O_2/Vc System. In the process of synergistic degradation of MB by HC and the H_2O_2/Vc system, H_2O_2 was the main source of ·OH. The amount of H_2O_2 had a significant impact on the production of ·OH, which further affected the degradation efficiency of MB. In this experiment, the influence of H_2O_2 concentration on the degradation of MB was studied using reactor 1. The results are shown in Figure 5.

With the increase in H_2O_2 concentration from 0.01 to 0.05 mol/L (corresponding to a molar ratio of H_2O_2/MB ranging from 500 to 2500), the degradation rate of MB gradually

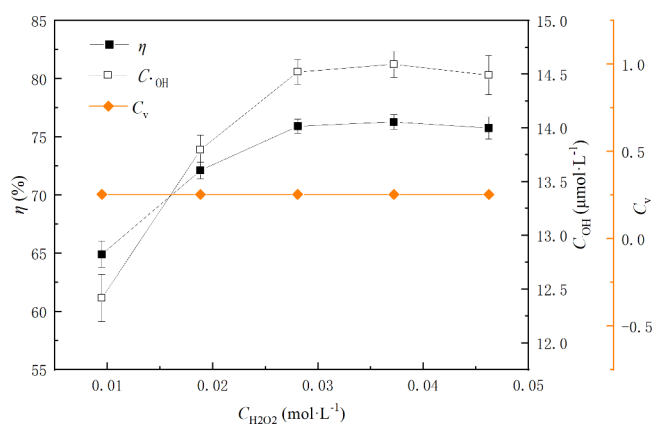**Figure 5.** Effect of H_2O_2 concentration on degradation of MB by the HC + H_2O_2/Vc system (conditions: P_{in} = 0.3 MPa, $C_{MB,o}$ = 20 μmol/L, t = 10 min, V = 150 mL, C_{Vc} = 0.021 mol/L).

increased, reached a plateau, and then slightly decreased. The C_v did not change with the variation of the H_2O_2 concentration, and its value was 0.210. A constant C_v indicated that the amount of ·OH generated by HC remained unchanged, and the change in the ·OH yield was mainly contributed by the reaction between H_2O_2 and Vc. The increase in H_2O_2 concentration led to an increase in the ·OH yield, thereby accelerating the degradation rate of MB. However, when there is an excess of H_2O_2, the excess H_2O_2 can react with ·OH, leading to a slight decrease in the ·OH yield.[38] Consequently, the degradation rate of MB also slightly decreased. Excess H_2O_2 not only hindered the degradation of MB but also posed a risk of damage to the reaction equipment.[39] Therefore, it was necessary to control the amount of H_2O_2 added at the appropriate level. It was considered that the appropriate H_2O_2 concentration was 0.03 mol/L, with a molar ratio of H_2O_2/MB at 1500.

3.2. Effect of Vc Concentration on Degradation of MB by the HC + H_2O_2/Vc System.

Vc exhibited strong reducibility and can form a strong redox system with H_2O_2. Vc can accelerate the decomposition of H_2O_2 to produce ·OH. The amount of Vc added had a significant impact on the production of ·OH in the system, which affected the degradation of MB.

Figure 6 shows the influence of Vc concentration on the degradation of MB. When the Vc concentration increased from
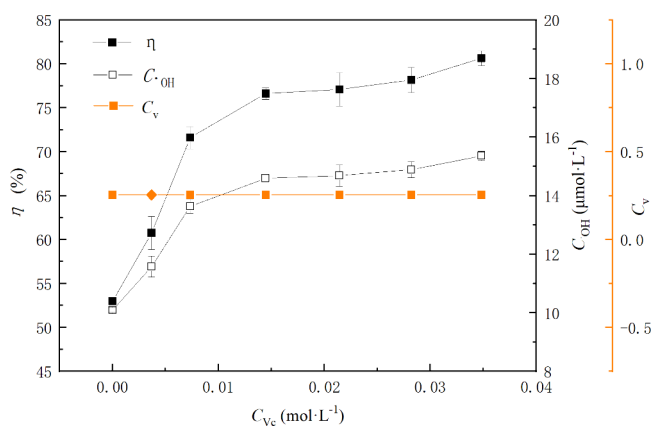

Figure 6. Effect of Vc concentration on degradation of MB by the HC + H_2O_2/Vc system (conditions: P_{in} = 0.3 MPa, $C_{MB,o}$ = 20 μmol/L, t = 10 min, V = 150 mL, C_{H2O2} = 0.03 mol/L).

0 to 0.014 mol/L, the degradation rate of MB increased significantly from 53.0 to 76.6%. However, the degradation rate of MB only increased by about 4% with the increase of the Vc concentration from 0.014 to 0.035 mol/L. The larger the amount of Vc added in the system, the more ·OH generated by the reaction between H_2O_2 and Vc, which can significantly improve the degradation rate of MB. The change in Vc concentration did not cause a change in cavitation intensity. A constant C_v indicated that the change in the ·OH yield was mainly contributed by the reaction between H_2O_2 and Vc. The ·OH was mainly derived from the decomposition of H_2O_2. In this experiment, the amount of H_2O_2 was constant, so the amount of Vc required in the redox reaction should also be constant. Excess Vc cannot generate more ·OH in the system. Thus, it was taken into consideration of a cost saving, the appropriate Vc concentration was 0.021 mol/L.

3.3. Synergistic Effect of HC and H_2O_2/Vc System.

In Sections 3.1 and 3.2, the concentrations of H_2O_2 and Vc were determined to be 0.03 and 0.021 mol/L, respectively. In this study, in order to obtain the synergistic mechanism of HC and H_2O_2/Vc system on the degradation of MB, the influence of various factors (inlet pressure, initial solution concentration, solution volume, and time) on the degradation rate of MB was investigated under different conditions, namely HC alone, H_2O_2/Vc system alone, and combined process of HC + H_2O_2/Vc system.

3.3.1. Effect of Inlet Pressure on Degradation of MB. The change in the inlet pressure can cause a change in the fluid velocity. According to eq 4, changes in fluid velocity can lead to changes in C_v. Thus, the inlet pressure was an important factor affecting the cavitation intensity. In this study, the influence of the inlet pressure or pump speeds on the degradation of MB was studied. The results are shown in Figure 7.

The degradation rate of MB increased with the increase of inlet pressure under the conditions of individual HC and the HC combined with the H_2O_2/Vc system. As the inlet pressure increased from 0.1 to 0.5 MPa, the C_v value decreased from 0.829 to 0.109, indicating an enhanced cavitation effect.[40] Therefore, more ·OH could be generated. In addition, the fluid velocity increased with an increase in inlet pressure. The increase in fluid velocity can result in an increase in the number of passes of fluids ($N = Qt/V$)[41] through the hydraulic cavitator within the same cavitation time. Thus, more opportunities to generate ·OH can be obtained. Wang et al.[26] pointed out that pressure not only affected cavitation behavior but also affected the number of passes of fluids. Higher inlet pressure contributed to the degradation of the organic matter.

Figure 7 shows that in the individual H_2O_2/Vc system, the degradation rate of MB increased with the increase of pump speed, but the trend of increase was very slow, only rising from 53.3 to 55.5%. An increase in the pump speed can increase the collision velocity and the number of collisions of the two fluids. The mixing of H_2O_2 and Vc was enhanced, leading to the generation of more ·OH. However, the effect of improving the impact velocity of fluids to enhance the degradation rate of MB was not very significant.

When the inlet pressure was 0.3 MPa, the degradation rates of MB under the conditions of HC, H_2O_2/Vc system, and HC + H_2O_2/Vc system were 7.9, 54.9, and 74.2%, respectively. The decolorization effect of MB is shown in Figure 8. The degradation rate of MB by the H_2O_2/Vc system was significantly higher than that by HC alone, indicating that the ·OH generated by the decomposition of H_2O_2 mainly contributed to the degradation of MB. On the basis of the H_2O_2/Vc system, the utilization of HC can significantly improve the degradation rate of MB, which is mainly due to the combined effects of free radical effect and mechanical effect generated during the process of HC. In the process of HC, the strong shock wave and high-speed microjet flow generated by the collapse of cavitation bubbles can greatly enhance the mixing of H_2O_2 and Vc. The reaction process between Vc and H_2O_2 was strengthened, leading to the production of more ·OH. Therefore, the degradation rate of MB could be improved. It can be seen that the method of the HC-assisted H_2O_2/Vc system was a promising method for the degradation of MB. In consideration of energy saving and safety, an inlet pressure of 0.3 MPa was selected for the following research.
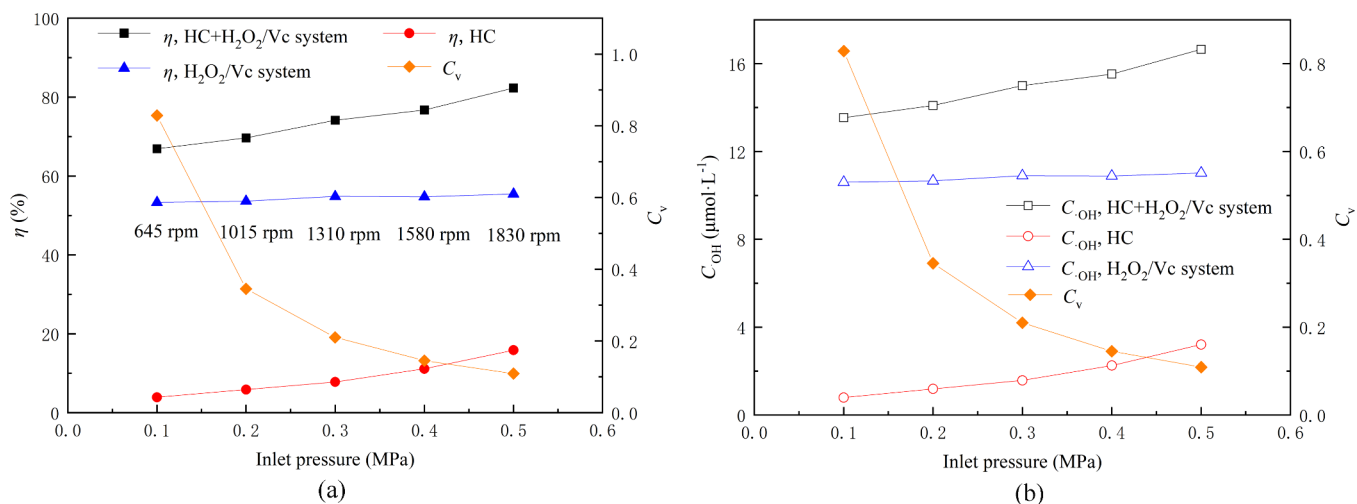
Figure 7. Effect of the inlet pressure on the degradation of MB. (a) Degradation rate of MB; (b) ·OH yield (conditions: t = 10 min, $C_{MB,o}$ = 20 μmol/L, V = 150 mL).
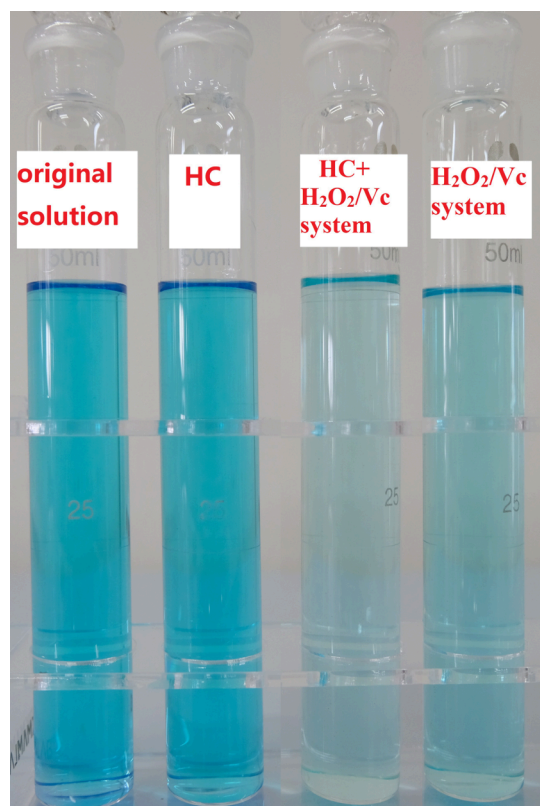

Figure 8. Image of MB decolorization effect (Photograph courtesy of Yan Cao).

3.3.2. Effect of Initial Solution Concentration on Degradation of MB.

The initial concentration of organic matter in the solution was an important factor affecting its degradation rate. It can be seen from Figure 9 that with the increase of the initial concentration of MB, the degradation rate of MB decreased while the yield of ·OH increased. Since the HC conditions and the amounts of H_2O_2 and Vc added were constant, the yield of ·OH in the system would be constant. However, the total amount of MB increased with the increase of the initial concentration of MB, so more ·OH will be captured by MB.[14,42] The maximum amount of ·OH was

generated under the conditions of the HC + H_2O_2/Vc system compared with that of HC alone and the H_2O_2/Vc system alone. As the concentration of organic matter in the solution increased, the probability of ·OH being captured was higher. Therefore, under the condition of the HC + H_2O_2/Vc system, the increased amount of ·OH was the largest, which was 11.913 μmol/L. However, due to the fact that the increase in the number of ·OH captured was less than the increase in the number of MB, the degradation rate of MB decreased. This result was similar to that obtained by Wang et al.[43] using swirling jet-induced cavitation combined with H_2O_2 to degrade rhodamine B in aqueous solution.

3.3.3. Effect of Solution Volume on Degradation of MB.

In our previous research, it was found that the solution volume had a significant impact on the generation of ·OH.[44] Therefore, the influence of solution volume on the degradation of MB was studied in this study. The results are shown in Figure 10.

Under the conditions of HC, H_2O_2/Vc system, and HC + H_2O_2/Vc system, the degradation rate of MB decreased with the increase of solution volume, and HC in combination with the H_2O_2/Vc system maintained the best degradation effect. Although a change in solution volume did not cause a change in cavitation intensity, it can lead to a change in the number of passes of fluids. The larger the solution volume, the smaller the number of passes of fluids, and the less ·OH can be generated. Moreover, the total amount of organic matter in the solution increased with increasing the solution volume. Therefore, the degradation rate of MB would inevitably decreased. Similarly, the number of cyclic impacts decreased with a decrease in solution volume. The reaction between Vc and H_2O_2 was weakened, and the yield of ·OH decreased.

3.3.4. Effect of Time on Degradation of MB and Synergistic Factor.

The effect of time on the degradation of MB was investigated in this study under the conditions of the HC, H_2O_2/Vc system, and HC + H_2O_2/Vc system. Furthermore, the kinetic constants under these three conditions were determined by measuring the concentration of MB at different times. The kinetic rate constant (k)[45] can be calculated as follows:
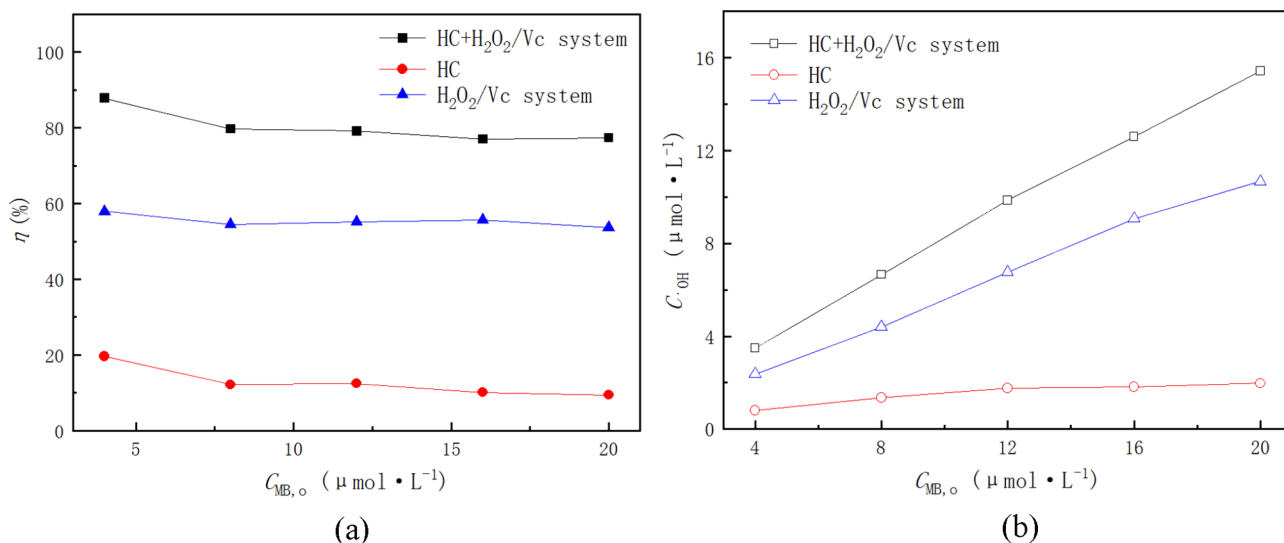
$$\ln\left(\frac{C_{MB,0}}{C_{MB}}\right) = kt + c$$

(5)

Figure 9. Effect of initial solution concentration on degradation of MB and ·OH yield. (a) Degradation rate of MB; (b) ·OH yield (conditions: P_{in} = 0.3 MPa, t = 10 min, V = 150 mL).

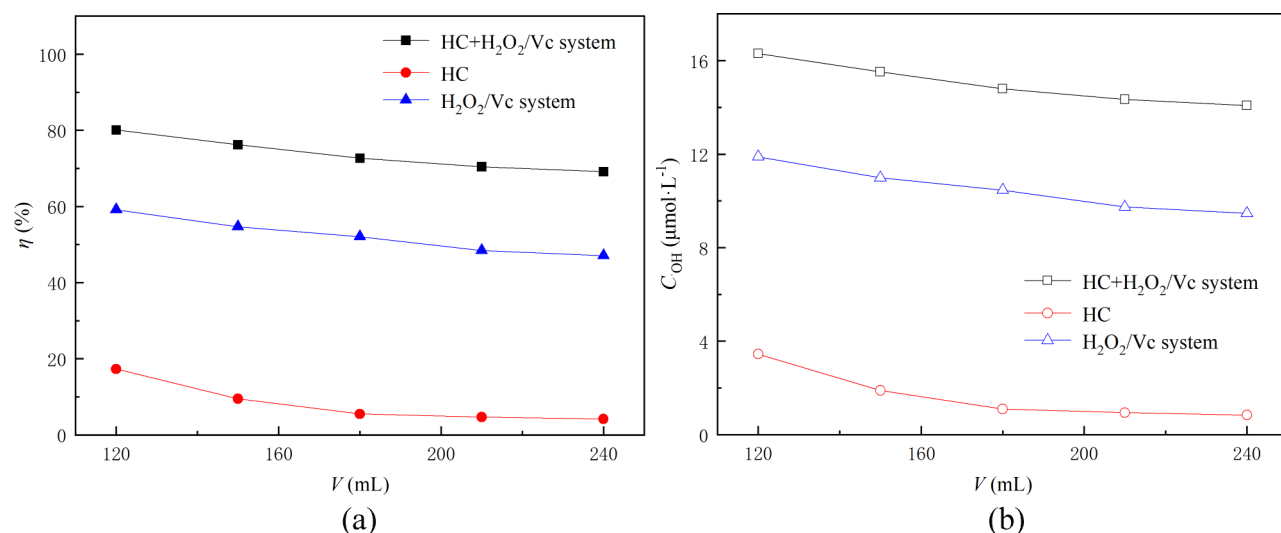**Figure 10.** Effect of the solution volume on the degradation of MB. (a) Degradation rate of MB; (b) ·OH yield (conditions: P_{in} = 0.3 MPa, t = 10 min, $C_{MB,o}$ = 20 μmol/L).

Where t is the degradation time, and c is a constant.

Figure 11a illustrates that the degradation rate of MB increased with the increase of time under the conditions of HC, H_2O_2/Vc system, and HC + H_2O_2/Vc system. Although the increase in time did not cause a change in cavitation intensity, a longer time meant that the more times the fluid underwent cavitation and impact, and the more ·OH was generated.[46] Consequently, the degradation rate of MB increased. It can be seen from Figure 11b that $\ln(C_{MB,0}/C_{MB})$ versus time showed reasonable linearity, which indicated that the degradation of MB conformed to first-order kinetics. The kinetic rate constants under the conditions of HC, H_2O_2/Vc system, and HC + H_2O_2/Vc system were 0.005, 0.0646, and 0.1124 $\min^{-1}$, respectively. This result indicated that MB had the fastest degradation rate under HC in combination with the H_2O_2/Vc system.

In order to explore the synergistic effect between HC and H_2O_2/Vc system, the synergy index SI was introduced, and it can be calculated according to the following equation[47]:

$$SI = \frac{k_{(HC+H_2O_2/Vc)}}{k_{HC} + k_{H_2O_2/Vc}}$$

(6)

Where k_{HC}, $k_{H2O2/Vc}$, and $k_{HC+H2O2/Vc}$ were the kinetic rate constants under the conditions of HC alone, H_2O_2/Vc system alone, and HC in combination with H_2O_2/Vc system, respectively. Usually, an SI value greater than 1 indicates the presence of synergistic effects in the studied system or process.

In this study, the value of SI calculated was 1.615, which was greater than 1, indicating a synergistic effect between HC and the H_2O_2/Vc system. This also confirmed that the combination of the HC and H_2O_2/Vc system was an effective method for improving the degradation of MB.

3.3.5. Correlation Equation of ·OH. ·OH was a significant free radical for the degradation of MB. The yield of ·OH was closely related to the effect of MB degradation. Therefore, research on the yield of ·OH was of great significance. According to the discussion in Section 3.3.4, it was known that there was a synergistic effect between the HC and H_2O_2/Vc
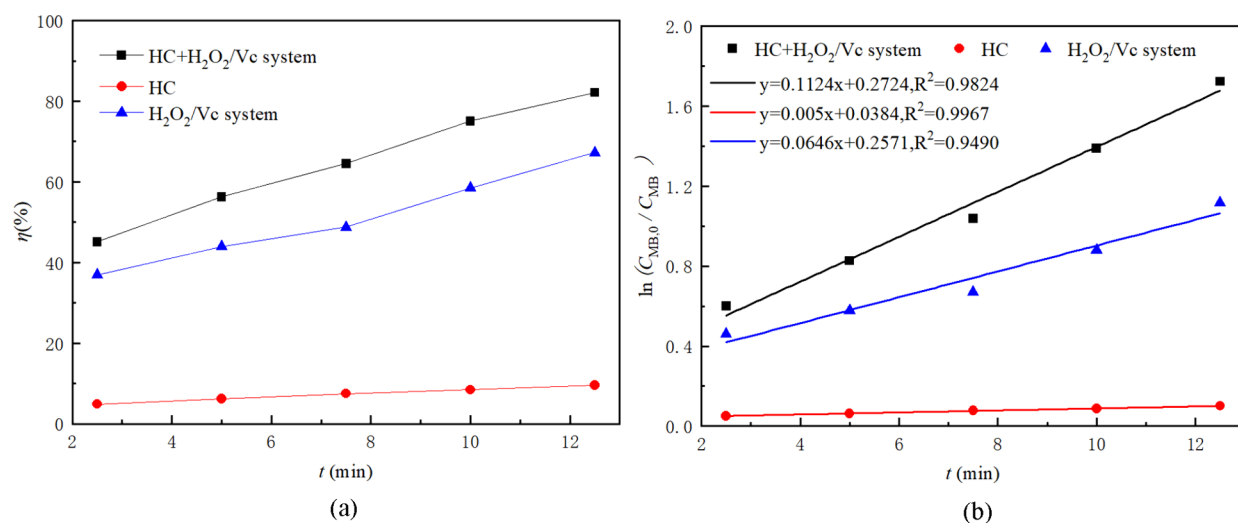
Figure 11. Effect of time on degradation of MB and first-order kinetic fitting of MB degradation. (a) Degradation rate of MB; (b) degradation kinetics curve (conditions: P_{in} = 0.3 MPa, $C_{MB,o}$ = 20 μmol/L, V = 150 mL).

system. This synergistic relationship can be reflected by a certain correlation between the concentrations of ·OH under different conditions.

In order to further investigate the synergistic effect between HC and the H_2O_2/Vc system, the yield of ·OH under different conditions was investigated, as shown in Figure 12.
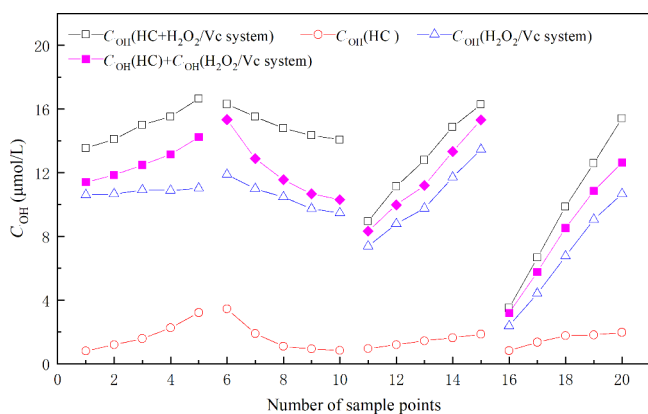

Figure 12. Yield of ·OH under different conditions (experimental points: 1−5 for inlet pressure, 0.1−0.5 MPa; 6−10 for solution volume, 120−240 mL; 11−15 for time, 2.5−12.5 min; 16−20 for initial solution concentration, 4−20 μmol/L).

It can be seen from Figure 12 that the order of ·OH yield was $C_{·OH}$ (HC + H_2O_2/Vc system) > $C_{·OH}$ (H_2O_2/Vc system) > $C_{·OH}$ (HC), and the ·OH yield of HC + H_2O_2/Vc system was greater than the sum of the ·OH yield of HC alone and ·OH yield of H_2O_2/Vc system alone. This further confirmed

the synergistic effect between HC and the H_2O_2/Vc system. During the process of HC, an extreme environment of high temperature and pressure was formed, along with a strong shock wave and high-speed microjet flow. The ability of H_2O_2 decomposition to produce ·OH can be enhanced in the high-temperature and high-pressure environments.[11] In addition, the reaction between H_2O_2 and Vc was enhanced under the conditions of a strong shock wave and high-speed microjet flow. It was the synergistic effect between HC and the oxidant system that led to the generation of more ·OH.

Zhang et al.[35] proposed a correlation equation between collapse pressure (P_c) and the concentration of ·OH based on data fitting and pointed out that P_c was an exponential function of the concentration of ·OH. A correlation equation used to describe the effect of independent variables on the residence time of the liquid in the rotor-stator cavity was established by Wang et al.[48] This correlation equation was obtained by the Levenberg−Marquardt algorithm. Similarly, three models of ·OH yield were proposed based on the ·OH yield data obtained in this study, as shown in Table 1. The parameters and correlation coefficient R^2 of these three models were obtained by the optimization method of Levenberg−Marquardt and Universal Global Optimization in the software 1stOpt 1.5. Table 1 shows that the R^2 value of the regression equation obtained in model 3 was the maximum, with a value of 0.9549, which indicated that the correlation between the concentrations of ·OH was the best in this model.

The experimental values of ·OH yield were compared with the theoretical values of ·OH yield calculated by these three models, and the results are shown in Figure 13. It can be seen that almost all data points in model 3 were within ±10%

Table 1. Models of ·OH Yield[a]

model	correlation equation	parameters	R^2	relative deviation
model 1	$C = a(C_1 + C_2)$	$a = 1.171$	0.9282	±15%
model 2	$C = aC_1 + bC_2$	$a = 0.569, b = 1.272$	0.9413	±12%
model 3	$C = k\log(aC_1^b + cC_2^d) + h$	$k = 5.146, a = 670.869$ $b = 3.422, c = 0.045$ $d = 5.904, h = -9.960$	0.9549	±10%

[a]C, C_1, and C_2 denoted the yield of ·OH generated in the HC + H_2O_2/Vc system, HC alone, and H_2O_2/Vc system alone, respectively.
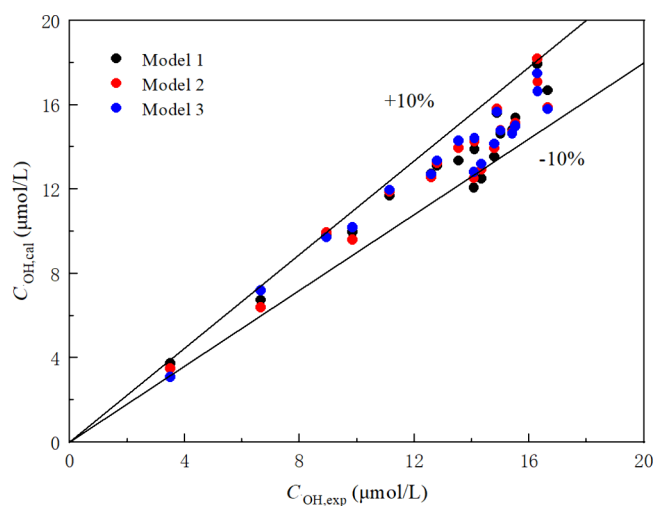
Figure 13. Comparison of experimental and calculated values for ·OH yield.

deviation lines. The relative deviations of model 1, model 2, and model 3 were ±15, ± 12, and ±10%, respectively. The model 3 had the smallest relative deviation, which indicated that it was more reasonable to use this model to reflect the intrinsic correlation of ·OH yield under the conditions of the HC, H_2O_2/Vc system, and HC + H_2O_2/Vc system in the range of the present study. Therefore, the correlation equation for ·OH yield established in this study was as follows:

$$C = 5.146 \log(670.869 C_1^{3.422} + 0.045 C_2^{5.904}) - 9.96 \tag{7}$$

The model 3 represented a complex exponential and logarithmic relationship among C, C_1, and C_2, rather than the simple multiple and additive relationships shown in model 1 or model 2. It was indicated that there were complex interactions between HC and the H_2O_2/Vc system. In model 3, the coefficient of C_2 at 0.045 was much smaller than the coefficient of C_1 at 670.869. However, the value of C_2 was much larger than that of C_1, and the exponent of C_2 was greater than that of C_1. Consequently, the calculation result of $0.045 C_2^{5.904}$ was greater than that of $670.869 C_1^{3.422}$. It was indicated that compared with HC, the H_2O_2/Vc system contributed more to the production of ·OH in the synergistic

process. This was consistent with the experimental results. Therefore, the construction of model 3 was reasonable.

3.4. Degradation Pathways of MB. LC-MS technology was used to identify the intermediate products of MB degradation under the condition of HC combined with the H_2O_2/Vc system. Multiple peaks of different intensities are observed in Figure 14a, indicating the destruction of the MB molecule and the production of intermediate products with diverse compositions and concentrations. These intermediates were usually formed through processes such as hydroxylation and demethylation.[49] Due to their similar structures, they exhibited similar polarity, resulting in the elution of multiple intermediates within a narrow time range (2.0−2.5 min). From Figure 14b, it can be seen that some fragment peaks appeared at m/z = 366, 350, 333, 301, 285, 270, 262, 242, 218, 197, 169, 132, 104, and 91. By studying the mass of the eluted intermediates and their cracking law, it can be concluded that 14 main intermediate products were generated. On the m/z values detected with LC-MS, the molecular structure of the main intermediates can be confirmed. Therefore, three possible degradation pathways of MB were proposed, as shown in Figure15.

In path 1, some MB molecules were isomerized to form the intermediate product M_1. The methyl group connected to N was easily attacked by ·OH, and the strong shock wave in the process of HC contributed to the detachment of the methyl group.[50] Under the action of ·OH and a strong shock wave, product M_2 was formed. Under the same action, some M_2 continued to demethylate (two CH_2-) to form product M_3, while others were isomerized and demethylated (one CH_2-) to form product M_4. The main chromophore of MB was $-CH_3$ on the $N-CH_3$ bond. Therefore, the main reason for MB decolorization was demethylation.[51] Due to the weak binding force of the C−S bond in intermediate products, they were easily attacked and broken by ·OH, leading to ring opening.[52] Furthermore, during the process of HC, the collapse of cavitation bubbles would generate an instantaneous high temperature and pressure. This extreme environment can lead to a series of reactions, such as bond breakage, hydroxylation, demethylation, etc., ultimately forming the product M_6. Our findings were similar to those reported by Wang et al.[53] Subsequently, ·OH further attacked the benzene ring, causing its structure to be destroyed and resulting in the formation of products M_{12}, M_{13}, and M_{14}. Ultimately, these products were
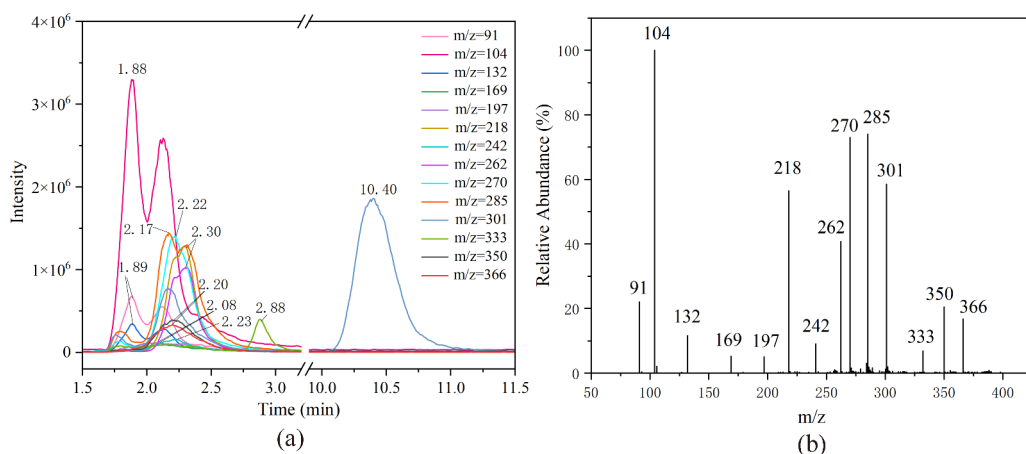

Figure 14. LC-MS of intermediate products of MB degradation. (a) LC chromatogram. (b) MS spectrum.
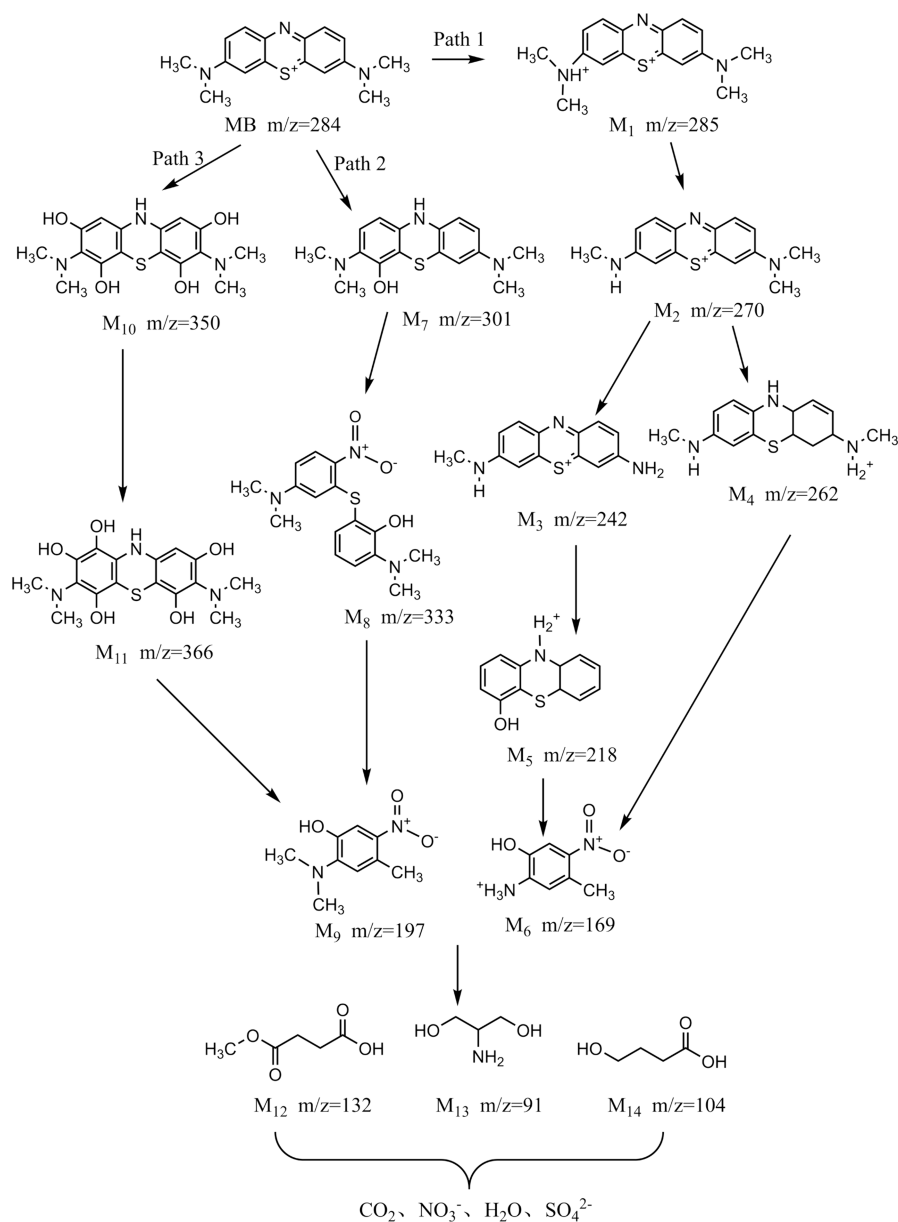
Figure 15. Degradation path of MB by HC combined with the H_2O_2/Vc system.

mineralized to form simple inorganic molecules, such as CO_2, NO_3^-, H_2O, and SO_4^{2-}.

Due to the synergistic effect of the HC and H_2O_2/Vc system, a large number of ·OH were instantly generated, which fiercely attacked MB molecules. As a result, MB molecules were highly hydroxylated and produced various polyhydroxy compounds such as products M_{10} and M_{11} in Path 3. Wang et al.[53] reported a similar finding that a polyhydroxy compound with $m/z = 364$ was obtained in the degradation of MB. Furthermore, under the continuous action of ·OH, the C−S bonds were destroyed, and the intermediate products would undergo nitration and demethylation, ultimately forming the product M_6 or M_9. These products were further destroyed by ·OH, and their rings were opened to form low molecular weight organic compounds, which were ultimately decomposed into simple inorganic molecules, as obtained in Path 1.

In order to further understand the mineralization degree of MB, a TOC analysis was carried out. The mineralization degree of MB can be reflected by the mineralization efficiency

$(\eta_{(TOC)})$, which was calculated according to the following equation[52]:

$$\eta_{(TOC)} = \frac{TOC_0 - TOC_1}{TOC_0} \times 100\% \tag{8}$$

where TOC_0 and TOC_1 were the organic carbon content of the initial and degraded MB solution, respectively. Based on the measured TOC data, the $\eta_{(TOC)}$ was 76.13% under the conditions of inlet pressure of 0.3 MPa, initial solution concentration of 20 μmol/L, solution volume of 150 mL, and reaction time of 10 min. Under the same conditions, the degradation rate of MB was 77.30%, which was close to the mineralization efficiency value. Therefore, it was proved that MB molecules were degraded and effectively mineralized.

3.5. Energy Efficiency. Energy efficiency (E_f) is the energy required to treat 1 L of wastewater, and it can be calculated as follows:

Table 2. Comparison of the Different Treatment Methods for MB

method	conditions	degradation rate (%)	$k \times 10^3$ (min^{-1})	cavitation yield (mg/J)	energy efficiency (kWh/L)	operating cost (CNY/L)	ref
NPV-HC (orifce plate)	pressure: 5 bar; time: 150 min	28.13		4.15×10^{-6}	0.66	0.37	45,52
HC (venturi)	pressure: 5 bar; time: 120 min	32.32	3.41	3.08×10^{-6}	1.1	0.61	54
HC + photocatalytic	pressure: 5 bar; time: 120 min; catalyst: 200 mg/L	64.58	8.62				54
HC + H$_2$O$_2$	pressure: 3 bar; time: 60 min; [H$_2$O$_2$]:0.1 g/L	94.64	42.91	5.99×10^{-6}			54
HC + H$_2$O$_2$/Vc	pressure: 3 bar; time: 10 min; [H$_2$O$_2$]:0.9 g/L	87.8	112.40	4.11×10^{-6}	0.43	0.22	our study

$$E_f = \frac{319.85 C_{MB,o}}{\varepsilon \times 3.6 \times 10^9} \tag{9}$$

Where ε is the cavitation yield, mg/J. Cavitation yield (ε) can reflect the change of the treatment effect per unit of energy consumed in the wastewater treatment process. It can be expressed as follows[39]:

$$\varepsilon = \frac{319.85 \times (C_{MB,o} - C_{MB})}{1000 P_m t/V} \tag{10}$$

Where P_m is the power of the pump, t is the treatment time, and V is the solution volume.

In this study, the pumps were the main source of energy dissipation, with a total power of 300 W. Under the specific conditions: the treatment time was 10 min, the solution volume was 150 mL, and the initial solution concentration was 20 μmol/L; the cavitation yield and energy efficiency were calculated to be 4.11×10^{-6} mg/J and 0.43 kWh/L, respectively. Furthermore, the cost estimation for wastewater treatment using the HC combined with the H$_2$O$_2$/Vc system was completed. The electricity price per kilowatt-hour was 0.50 CNY in China. Therefore, the operating cost was 0.22 CNY/L (0.03 USD/L).

MB in wastewater can be effectively degraded by various methods. Our work has been compared with other methods in terms of degradation rate, energy efficiency, cost, etc., as shown in Table 2. It can be inferred that the combination of two methods exhibited a higher extraction rate and lower operating cost than a single method. The combination process of the HC + H$_2$O$_2$/Vc system exhibited the maximum k value of 0.1124 min^{-1}, indicating that this method had a faster reaction rate compared to other methods. Additionally, this method exhibited a relatively low energy efficiency and operating cost. This indicated that the combined process of the HC and H$_2$O$_2$/Vc system conformed to the development direction of wastewater treatment.

4. CONCLUSIONS

A new combined process of HC and the H$_2$O$_2$/Vc system was proposed for the degradation of MB in wastewater. This study focused on investigating the degradation characteristics of MB using this new combined process. The effects of various parameters, such as H$_2$O$_2$ concentration, Vc concentration, inlet pressure, initial solution concentration, solution volume, and reaction time, on the degradation rate of MB were investigated. The intrinsic correlation of ·OH yield under the conditions of the HC, H$_2$O$_2$/Vc system, and HC + H$_2$O$_2$/Vc system was explored. The degradation pathways of MB were discussed. The main conclusions were as follows:

1. The increase in inlet pressure and time, the decrease in initial solution concentration and solution volume were beneficial for improving the degradation rate of MB. A maximum degradation rate of 87.8% was achieved under the following conditions: H$_2$O$_2$ concentration of 0.03 mol/L, Vc concentration of 0.021 mol/L, inlet pressure of 0.3 MPa, initial solution concentration of 4 μmol/L, solution volume of 150 mL, and reaction time of 10 min.

2. The degradation effects of the combination process of the HC + H$_2$O$_2$/Vc system can be greatly improved compared to only HC or only H$_2$O$_2$/Vc system. The synergy index was 1.615, indicating a synergistic effect between HC and H$_2$O$_2$/Vc system.

3. The order of ·OH yield was $C_{·OH}$ (HC + H$_2$O$_2$/Vc system) > $C_{·OH}$ (H$_2$O$_2$/Vc system) > $C_{·OH}$ (HC). A correlation equation for ·OH yield was established as follows:

$$C = 5.146 \log(670.869 C_1^{3.422} + 0.045 C_2^{5.904}) - 9.96$$

The value of the correlation coefficient R^2 was 0.9549. The relative deviations between the experimental and calculated values of the ·OH yield were basically within 10% of the yield by this model.

4. Based on LC-MS, the molecular structure of 14 main intermediates was confirmed, and three possible degradation pathways of MB were proposed. It was demonstrated that the action of ·OH and strong shock wave acted together on MB molecules, which ultimately decomposed into simple inorganic molecules. A mineralization efficiency of 76.13%, indicating that MB molecules were degraded and effectively mineralized.

5. The combined process of the HC and H$_2$O$_2$/Vc system exhibited a relatively low energy efficiency of 0.43 kWh/L and a relatively low operating cost of 0.03 USD/L. The method of HC-assisted H$_2$O$_2$/Vc system was a promising method for the degradation of MB.

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Notes

The authors declare no competing financial interest.

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