The removal of Rhodamine B by H_2O_2 or ClO_2 combined with hydrodynamic cavitation

Kun Wang, Ri-ya Jin, Yi-na Qiao, Zeng-di He, Ying Wang
and Xiao-jian Wang

ABSTRACT

Rhodamine B (RhB), widely used as an industrial dye, is a toxic organic that is hazardous to human health and can cause water pollution. In this study, the removal rate of RhB was investigated by the following methods: hydrodynamic cavitation (HC) operated individually, and HC combined with oxidants H_2O_2 or ClO_2. The effect of different operating parameters including pressure (2–6 bar) and initial pH (2–8) on the extent of degradation was investigated using an orifice plate as the cavitation device to achieve maximum removal of RhB. Under the parameters of HC, the effect of different loadings was investigated: H_2O_2 (n(RhB):n(H_2O_2) was varied from 1:17.60 to 1:211.28) and ClO_2 (n(RhB):n(ClO_2) was varied from 1:8.87 to 1:177.53). A combination of cavitation and H_2O_2 or ClO_2 resulted in degradations of 80.6% and 95.3%. The results indicated that the combination of HC and oxidants was better than the individual HC process for the degradation of RhB. When combining HC with H_2O_2 or ClO_2, the synergistic coefficients of 62.54 and 74.79 were obtained. The combination of HC and ClO_2 was proven to be more effective for the removal of RhB compared to HC alone and the hybrid process of HC and H_2O_2.

Key words | advanced oxidation processes, ClO_2, coalescent methods, hydrodynamic cavitation, Rhodamine B

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INTRODUCTION

Rhodamine B (RhB) is widely used as a typical dye in the printing and dyeing industry. The industry consumes a lot of water, resulting in water pollution. Rhodamine B is difficult to degrade because of its structural stability (Li et al. 2009; Tian et al. 2018). If inhaled and swallowed, it probably irritates the respiratory tract and causes lesions with symptoms of coughing, sore throat, labored breathing, and chest pain (Jain et al. 2007; Khan et al. 2012). Therefore, removing Rhodamine B from the effluents before discharging it to surface waters is imperative for human health and environmental protection.

Dyes have been removed from effluent water by many treatment techniques such as oxidative processes (Jiang et al. 2018), adsorption (Ma et al. 2016), photocatalytic degradation (Li et al. 2017), membrane filtration (An et al. 2016), and microbiological decomposition (Parmar & Shukla 2018). Although adsorption and membrane filtration are effective for removing dye, they do not break down the dye into harmless products, but simply create pollutants requiring further treatments. Photocatalytic degradation can be effective only at a laboratory level, and it is difficult to achieve for large-scale applications. Yet advanced oxidation processes (AOPs) can transform complex macromolecular organics into simple small-molecule organics or directly mineralize them. AOPs include cavitation, photolysis, hydrogen peroxide, Fenton, photo-Fenton, and ozonation, utilized individually or combined with each other (Gogate & Pandit 2004a; Kralj et al. 2007).

Hydrodynamic cavitation (HC) can provide higher degradation efficiency and has a great potential for large scale applications (Badve et al. 2015). HC is a physical phenomenon that occurs by the formation, development, and collapse of microbubbles (Montusiewicz et al. 2018). A cavitation generator is used to limit the flow of water to create local pressure changes. When the pressure of the liquid is reduced below the saturated vapor pressure, the gas core or gas dissolved in the liquid prompts cavitation. As the liquid continues to flow, the bubble grows until it

collapses due to the pressure recovery in the system. Cavitation collapse generates instantaneous high temperature (4,000–6,000 K) and high pressure (1×10^7–5×10^7 Pa) (Suslick *et al.* 1990). The release of powerful energy breaks water molecules into •OH, which act on organic matter, along with several other processes such as mechanical (ZHU *et al.* 2010), pyrolysis (Suslick *et al.* 1990) and supercritical oxidation (Bagal *et al.* 2014). Sivakumar & Pandit (2002) compared the effect of porous plates with different geometric shapes on the removal of Rhodamine B, indicating that turbulent pressure fluctuation frequency can improve cavitation rate by using HC. The results showed that HC had higher cavitational yields than acoustic cavitation.

In addition, the combination of cavitation and other AOPs has been widely studied in sewage treatment applications. Prajapat & Gogate (2016) reported the use of a combination of HC and hydrogen peroxide (H_2O_2), ozone (O_3) or ultraviolet (UV) irradiation process for the treatment of polyacrylamide (PAM) wastewater. These combined methods can depolymerize PAM more effectively than hydraulic cavitation alone. Raut-Jadhav *et al.* (2016) investigated the use of circular venturi as a cavitation device combined with H_2O_2 or ozone to treat pesticide industrial wastewater, and proved that the combined process of HC and H_2O_2 was more cost-effective than the combination of HC and O_3. Boczkaj *et al.* (2018) and Gągol *et al.* (2018a, 2018b) also used ozone and hydrogen peroxide as additional oxidants in combination with cavitation to treat asphalt wastewater and phenolic wastewater. O_3 and H_2O_2, which have strong oxidation properties themselves, with the oxidation potentials of 2.08 V and 1.78 V, respectively (Li *et al.* 2010), combined with cavitation, have been widely studied for the treatment of organic pollutants and proven to be very effective.

Chlorine dioxide, an efficient disinfectant and oxidant, has a high oxidative capacity for removing organics from wastewater, not generating trihalomethanes (THMs) and other organic halides (Hua & Reckhow 2007; Ye *et al.* 2013). The combination of HC and chlorine dioxide has not been reported in the literature for the treatment of wastewater containing Rhodamine B. HC/ClO_2 was compared to HC/H_2O_2 to investigate whether HC/ClO_2 had a better synergistic effect; however, this has not been reported in literature. In this study, the effect of operating parameters while using an orifice plate as the cavitation device for the treatment of Rhodamine B, and HC combined with hydrogen peroxide or chlorine dioxide was also investigated for comparison. The optimum amount of oxidant for the treatment of Rhodamine B and its reaction kinetics were studied in the experiment.

MATERIALS AND METHOD

Chemicals

Rhodamine B (AR grade) was purchased from Tianjin Guangfu Fine Chemical Research Institute, China. Hydrogen peroxide (30%, w/v, AR grade) was obtained from Sinopharm Chemical Reagent Co., Ltd, China. Chlorine dioxide was obtained from chlorine dioxide tablets. Each tablet contains 250 mg of chlorine dioxide (Jin *et al.* 2012) and was prepared in our laboratory.

Experimental facility

In this study, the HC equipment used is shown in Figure 1. The equipment comprises a tank, a booster pump (rated power 2.2 kW, rated flow 2 m^3/h, head 81 m), and regulating valves (V_1, V_2, and V_3). The cavitation generator was fitted in the main pipeline, and the flow rate of the main pipeline was controlled through the bypass pipeline. The tank was designed with a cooled shroud to adjust the temperature of the liquid. Pressure gauges were set to measure the inlet pressure (P1) and fully recovered pressure (P) downstream. A flowmeter was installed on the main pipeline to measure the flow rate. The perforated plate was used as the cavitation generator with a plate thickness of 5 mm, an outside diameter of 45 mm, the number of holes as 22; the diameter of each hole was 1.5 mm. The dimensions of the orifice plate are shown in Figure 2, and the components and functions of the device are listed in Table 1.
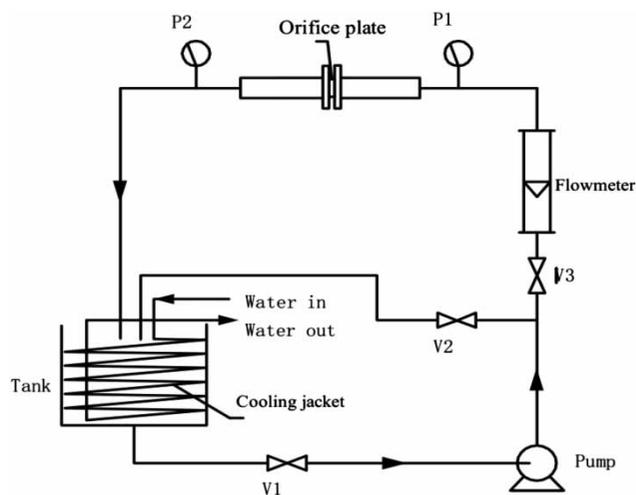

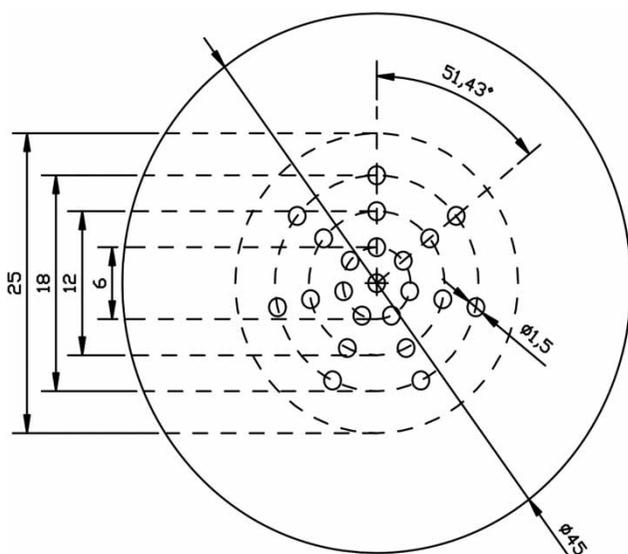**Figure 1** │ Schematic diagram of the HC experimental device.

Figure 2 | Dimensions of the orifice plate.

Table 1 | The composition of the HC device

Device composition	Model and manufacturer
Booster pump	Model: CDLF – 100 (Shanghai Yuquan Pump Co., Ltd)
Water tank	Made of PVC material, dimensions 500 mm × 500 mm × 600 mm, thickness: 5 mm; capacity: 150 L
Condensing tube	Made with rubber hose
Valve	Stainless steel, DN40 ball valve
Pipeline	The main pipeline is made of stainless steel. The bypass pipeline is made of PVC and the pipe diameter is DN40.
Flow meter	Model: LWSY – 25, measuring range 1–10 $m^3 h^{-1}$ (Dongtai Dongxing Instrument Factory)
Pressure gauge	Model: BD – 801 K, Range 0–1.0 MPa (Shanghai Kaixun Technology Co., Ltd)

Experimental methods

Rhodamine B solution at a concentration of 4 mg/L was prepared, and 100 L of the solution was added to the tank. The temperature was kept in the range 35–38 °C by circulating water in the jacketed tank.

The effect of inlet pressure (2–6 bar) and pH (2–8) on the degradation of Rhodamine B was investigated. Hydrogen peroxide (n(RhB):n(H_2O_2)) was varied from 1:17.60 to 1:211.28) and chlorine dioxide (n(RhB):n(ClO_2)) was varied from 1:8.87 to 1:177.53) were used as the additional oxidant of highly reactive radicals to enhance the

degradation. The combination of cavitation and H_2O_2 or ClO_2 was investigated under the optimized operating parameters for the removal of RhB. Based on the calculation of the kinetic rate constants of the single operation and combination processes, the degree of enhancement of the combination methods was obtained by the synergy index.

The solution of RhB was degraded circularly using the HC facility for 100 min. Samples were collected every 20 min to determine the concentration of residual Rhodamine B.

Analysis

The concentration of Rhodamine B was measured using a UV–visible light spectrophotometer (model Lambda 650, PerkinElmer Co., Ltd, USA) at a wavelength of λ of 554 nm. Kinetic analysis of the degradation process was carried out by the integral method. The degradation of Rhodamine B was calculated as follows:

$$\omega_1 = \frac{A_0 - A_1}{A_0 - 0.004} \times 100\% \qquad (1)$$

where A_0 is the initial absorbance of Rhodamine B, and A_1 is the absorbance of Rhodamine B which has been degraded after the set time interval.

The orifice ratio (β) is the ratio of the total flow area of the holes on the porous plate to the cross-sectional area of the upstream pipeline. It is a relative value and is calculated by the formula:

$$\beta = N\left(\frac{d}{D}\right)^2 \qquad (2)$$

where d (mm) is the aperture of the porous plate; D (mm) is the pipe diameter of the pipeline upstream of the porous plate (m); N is the number of holes in the porous plate.

RESULTS AND DISCUSSION

Treatment using HC alone

Effect of inlet pressure on the percentage of Rhodamine B degraded

In order to study the effect of inlet pressure on the degradation rate, the inlet pressure was changed within the range of 2–6 bar at pH 2. The variation in the
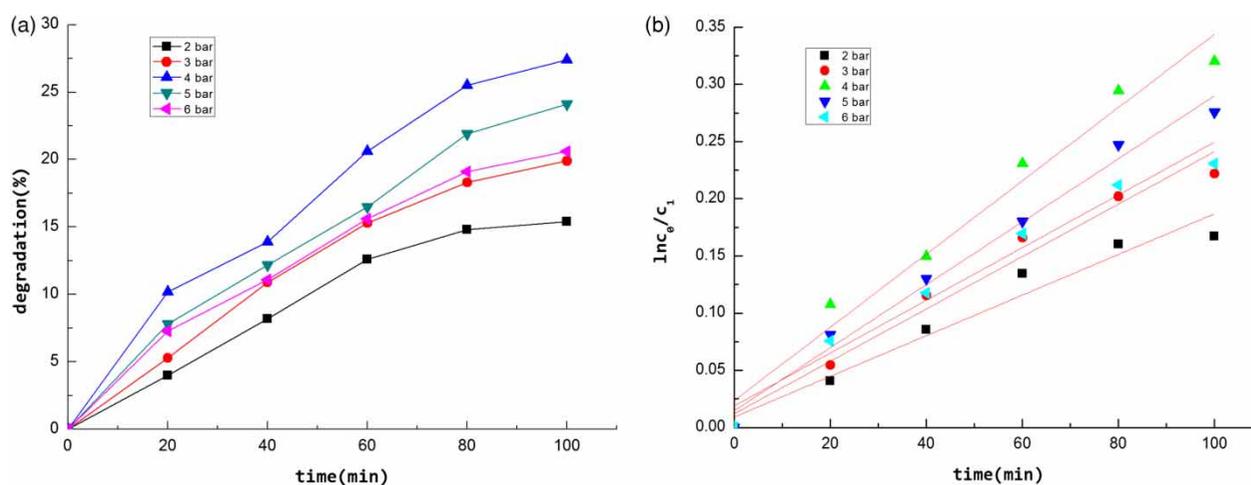
Figure 3 │ (a) Effect of inlet pressure on the degradation rate of Rhodamine B using HC at initial pH = 2. (b) Kinetic rate constant at different initial pressures using HC.

degradation rate is shown in Figure 3(a). The variation in the kinetic rate constant is listed Table 2. Figure 3(b) shows the plot of lnC_{a0}/C_a with time, which is approximately a straight line, indicating that the decomposition of Rhodamine B using HC is the pseudo-first-order reaction. The results showed that the kinetic rate constant and the percentage degradation increased significantly till the most suitable pressure of 4 bar, and then decreased with increasing inlet pressure. The maximum removal was 27.4% at a pressure of 4 bar, and the rate coefficient of this pseudo-first-order reaction was 3.2×10^{-3} min^{-1}.

Initially, with increasing inlet pressure, the degradation rate increased. The results may be attributed to the increasing cavitation intensity. The cavitation number σ can be expressed by the following equation:

$$\sigma = \frac{P_\infty - P_V}{\rho u_\infty^2 / 2} \tag{3}$$

where P_∞ and u_∞ are the inflow pressure and flow rate of the liquid, respectively, ρ is the liquid density, and P_V is the saturated vapor pressure of the liquid at ambient

temperature. According to Equation (3), cavitational intensity depends very much on the inlet pressure (Saharan *et al.* 2011). As the inlet pressure increased, more cavities formed and thus the number of collapsing events also increased, resulting in the generation of more •OH radicals due to the higher number of cavitational events (Gore *et al.* 2014). Therefore, the degradation rate of RhB increased.

Beyond the optimum value of 4 bar, with increasing inlet pressure, the percentage degradation of RhB decreased gradually because of the condition of choked cavitation. The uncontrolled growth of bubbles formed numerous cavities, which coalesced and combined with each other, forming a cavity cloud. Cavity cloud cushioned the collapse of cavities, decreasing the intensity of cavitation. Similar results have been reported on the effect of operating pressure on the decomposition of other organic pollutants. Jawale *et al.* (2014) studied the degradation of potassium ferrocyanide with a perforated plate used as the cavitation generator. Different experiments were carried out at inlet pressures over the range of 3–7 bars and enhanced oxidation with increasing inlet pressure was observed till an optimized pressure of 5 bar, then oxidation decreased with further increases in the pressure. Pradhan & Gogate (2010) studied the removal of *p*-nitrophenol at 3–6 bar pressure. The degree of degradation increased with a rise in inlet pressure due to cavitational activity, which strengthened at higher pressures.

Table 2 │ Kinetic rate constants at different inlet pressures for decomposing Rhodamine B using HC

Inlet pressure (bar)	Pseudo-first-order rate constant ($k \times 10^{-3}$ min^{-1})	R^2	Extent of degradation (%)
2	1.67	0.96	15.4
3	2.22	0.974	19.9
4	3.2	0.973	27.4
5	2.73	0.979	23.9
6	2.31	0.986	20.6

Effect of initial pH on the degradation rate of Rhodamine B

At an inlet pressure of 4 bar, the effect of initial pH in the range 2–8 on the degree of degradation was studied.
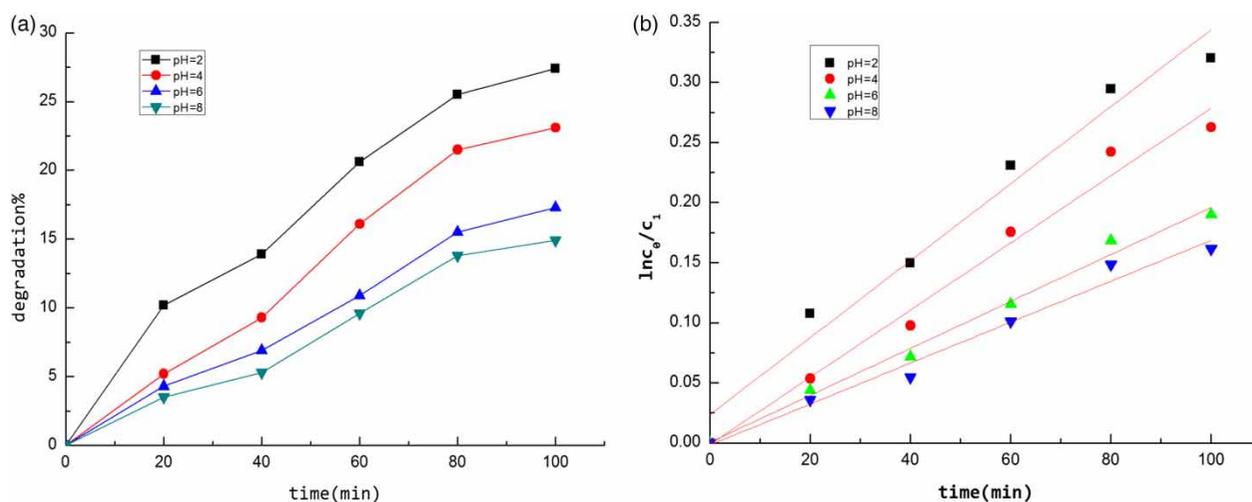
Figure 4 │ (a) Effect of initial pH on the extent of degradation of Rhodamine B using HC at inlet pressure = 4 bar. (b) Kinetic rate constant at different initial pH using HC at inlet pressure = 4 bar.

The effect of pH on the percentage degradation of Rhodamine B and the kinetic rate constant are shown in Figure 4 and Table 3, respectively. The results indicated that the percentage degradation increased from 14.9% to 27.4% with a decrease in the pH from 8 to 2. The maximum percentage degradation of 27.4% was obtained at pH = 2, and the pseudo-first-order kinetic rate constant was 3.2×10^{-3} min^{-1} because under alkaline conditions, scavenger CO_3^- and HCO_3^- reacted with •OH and consumed them.

$$CO_3^{2-} + \bullet OH \rightarrow OH^- + CO_3^{\bullet -} \tag{4}$$

$$\bullet OH + HCO_3^- \rightarrow OH^- + HCO_3^{\bullet} \tag{5}$$

Under acidic conditions CO_3^{2-} and HCO_3^- will be converted into CO_2 and escape solution (Li *et al.* 2010). On the other hand, in an acid reaction medium, RhB is present in the molecular state and it becomes more hydrophobic. RhB molecules can diffuse to the negatively charged hydrophobic interface of liquid–gas cavitation bubbles. At the interface of the cavities, the RhB molecules are directly attacked by OH radicals, and pyrolysis inside the

cavity and shear forces increase the degradation rate. In an alkaline medium, RhB molecules remain in the ionic state and are dispersed evenly in the solution. As only about 10% of the total generated OH radicals diffuse into the solution and the rest recombine to form H_2O_2, the removal rate decreases (Papadopoulos *et al.* 2016; Mukesh *et al.* 2004). Therefore, the degradation rate is higher in acidic conditions than that in neutral or alkaline conditions.

Similar conclusions that acidic conditions were more suitable for cavitation to decompose organic pollutants have been reported previously. Barik & Gogate (2016) investigated the decomposition of 4-chloro-2-aminophenol (4C2AP) at different pH values over the range 3–8 and reported a maximum percentage degradation of 39% at pH 4 using an orifice plate as the cavitation device. It was established that acidic conditions were conducive to the decomposition of 4-chloro-2-aminophenol (4C2AP). Cai *et al.* (2016) reached a similar conclusion for the degradation of the azo dye Orange G (OG) using HC. The results suggested that the decolorization rate of OG was only 12.3% at neutral pH. However, at pH of 2.0, 3.0, and 5.0, the decolorization rates were 98.8%, 93.2%, and 86.1% respectively, indicating that acidic conditions were more conducive to the decolorization of OG.

HC combined with hydrogen peroxide (HC/H$_2$O$_2$)

The combination of n(RhB):n(H$_2$O$_2$) in the range of 1:17.60 to 1:211.28 was investigated at the optimized inlet pressure of 4 bar and pH 2. The obtained results are shown in Figure 5. It can be seen that the percentage degradation
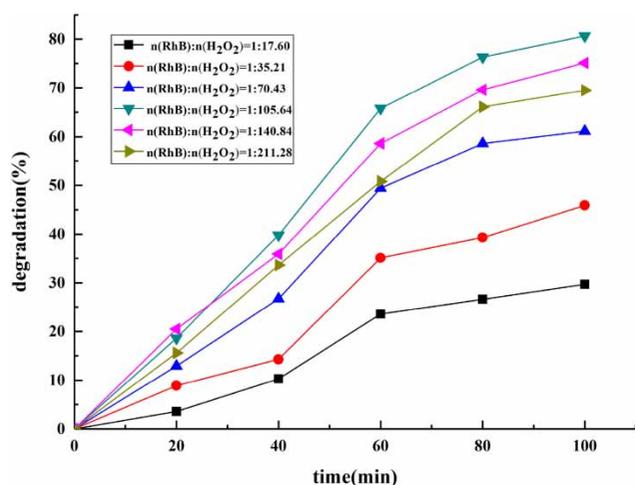
Table 3 │ Kinetic rate constants at different initial pH for degradation of RhB using HC

pH	Pseudo-first-order rate constant (k × 10^{-3} min^{-1})	R^2	Extent of degradation (%)
2	3.2	0.974	27.4
4	2.63	0.984	23.1
6	1.9	0.991	17.3
8	1.61	0.98	14.9

Figure 5 | Effect of H_2O_2 loadings for degradation of Rhodamine B using combined process of HC and H_2O_2 at inlet pressure = 4 bar and pH = 2.

of RhB increased with increasing loadings of H_2O_2 till an optimal loading of $n(RhB):n(H_2O_2) = 1:105.64$. Beyond loadings of $n(RhB):n(H_2O_2) = 1:105.64$, the percentage degradation of Rhodamine B decreased. The maximum percentage degradation was 80.6% at 30 mg/L of H_2O_2. The kinetic studies are shown in Table 4, revealing that the kinetic rate constants increased from 3.52×10^{-3} min^{-1} to 16.39×10^{-3} min^{-1} with increasing loadings of H_2O_2 – $n(RhB):n(H_2O_2)$ from 1:17.60 to 1:105.64. However, kinetic rate constants decreased when at loadings higher than $n(RhB):n(H_2O_2) = 1:105.64$.
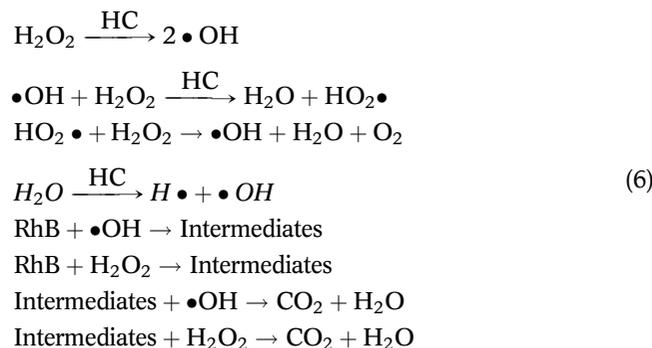
Hydrogen peroxide, as an oxidant in wastewater treatment, is largely dependent on OH radicals produced by the dissociation of H_2O_2. Under conventional stirring, the efficiency of oxidizing the organic pollutant is low because of the small amount of •OH radicals produced when using hydrogen peroxide on its own.

However, in the high temperatures and pressures of HC, H_2O_2 molecules more easily dissociate into •OH radicals due to the extra energy provided by HC. Therefore, to some

Table 4 | Kinetic rate constants at different loadings of H_2O_2 for the degradation of Rhodamine B using the combined process of HC and H_2O_2

$n(RhB):n(H_2O_2)$	Pseudo-first-order rate constant ($k \times 10^3$ min^{-1})	R^2	Extent of degradation (%)
1:17.60	3.52	0.954	29.7
1:35.21	6.14	0.962	45.9
1:70.43	9.44	0.967	61.1
1:105.64	16.39	0.979	80.6
1:140.84	13.91	0.988	75.1
1:211.28	11.87	0.983	69.5

extent, the combination of HC and H_2O_2 can generate more •OH radicals, thus increasing the degree of degradation with increasing H_2O_2 concentration. The following are the main reactions occurring in the process of HC and H_2O_2:

$$H_2O_2 \xrightarrow{\text{HC}} 2 \bullet OH$$

$$\bullet OH + H_2O_2 \xrightarrow{\text{HC}} H_2O + HO_2\bullet$$
$$HO_2 \bullet + H_2O_2 \rightarrow \bullet OH + H_2O + O_2$$

$$H_2O \xrightarrow{\text{HC}} H \bullet + \bullet OH \tag{6}$$
$$RhB + \bullet OH \rightarrow \text{Intermediates}$$
$$RhB + H_2O_2 \rightarrow \text{Intermediates}$$
$$\text{Intermediates} + \bullet OH \rightarrow CO_2 + H_2O$$
$$\text{Intermediates} + H_2O_2 \rightarrow CO_2 + H_2O$$

Beyond the optimal $n(RhB):n(H_2O_2) = 1:105.64$ loading of H_2O_2, the percentage degradation decreased. This result can be ascribed to the excess of H_2O_2 acting as scavengers of •OH radicals and recombining with each other, as indicated by the following reaction:

$$H_2O_2 + OH\bullet \rightarrow \bullet HO_2 + H_2O \tag{7}$$
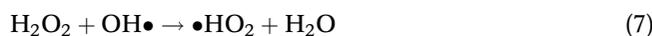
The removal of Rhodamine B was also observed using H_2O_2 alone. The effect of loadings of $n(RhB):n(H_2O_2) = 1:105.64$ on the percentage degradation of Rhodamine B with an initial concentration of 4 mg/L $(0.835 \times 10^{-2}$ mM) was investigated under the optimized pH of 2 and the temperature in the range 35–38 °C for a 100 min treatment time. As listed in Table 5, 25.5% degradation was obtained with a pseudo-first-order kinetic rate constant of 2.94×10^{-3} min^{-1} listed in Table 8 using the oxidizing agent alone.

The synergistic coefficient of 62.54 indicates that a higher efficiency of degradation can be obtained by combining the HC with H_2O_2 than the individual process. The synergistic coefficient can be calculated as follows (Metheniti et al. 2017):

$$
\begin{aligned}
S_1 &= 100 \frac{k_{\text{combined}} - \sum_{1}^{n} k_i}{k_{\text{combined}}} \\
&= 100 \frac{16.39 \times 10^{-3} - (3.2 \times 10^{-3} + 2.94 \times 10^{-3})}{16.39 \times 10^{-3}} \\
&= 62.54
\end{aligned}
\tag{8}
$$

Table 5 | Removal of Rhodamine B using H_2O_2 alone

Time (min)	0	20	40	60	80	100
Extent of degradation (%)	0	5.6	10.3	18.4	23.1	25.5

$n(RhB):n(H_2O_2) = 1:105.64$, pH = 2.

Similar trends have been mentioned in some literature. Gore et al. (2014) investigated the effect of molar ratio of Reactive Orange 4 dye (RO4): H_2O_2 (over the range 1:5–1:50) on the degradation of RO4 using HC combined with H_2O_2. The results showed that the maximum 99.56% degradation was obtained with 1:30 molar ratio of RO4: H_2O_2. The total organic carbon removal of 50.73% was significantly higher than the 22.22% removed using HC alone.

Combination of HC and chlorine dioxide (HC/ClO$_2$)

The chlorine radical (Cl•) is an oxidant with an oxidation potential of 1.57 V. In the case of HC, chlorine dioxide can be dissociated into a large amounts of Cl• and O• radicals, which are highly active in terms of degrading organic pollutant. The concentration of chlorine dioxide plays a critical role in the degradation of Rhodamine B.

Experiments were carried out with different loadings of ClO_2 (n(RhB):n(ClO_2)) was varied from 1:8.87 to 1:177.53), at the optimized inlet pressure of 4 bar, the initial concentration of 4 mg/L, and the initial solution pH of 2. The results are shown in Figure 6. The extent of degradation and reaction rate constants are listed in Table 6.

It can be seen that with increasing concentrations of ClO_2, the removal rate of Rhodamine B increased. At the maximum loading of ClO_2 (n(RhB):n(ClO_2) = 1:177.53), 95.3% removal rate of RhB was obtained, whereas at the minimum loading (n(RhB):n(ClO_2) = 1:8.87), 59.1% removal rate was achieved in a 100 min treatment. The kinetic rate constant increased from 8.94×10^{-3} min^{-1} to 30.58×10^{-3} min^{-1} with increased loading of n(RhB):n(ClO_2) = 1:8.87–1:177.53.
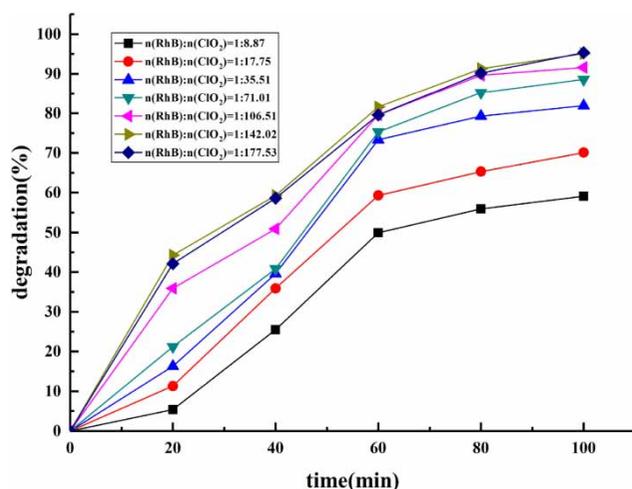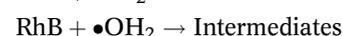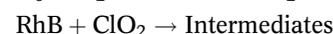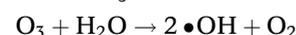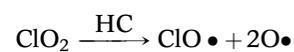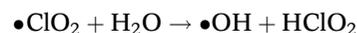

Figure 6 | Effect of ClO$_2$ loadings for degradation of Rhodamine B using combined process of HC and ClO$_2$ at inlet pressure = 4 bar and pH = 2.

Table 6 | Kinetic rate constants at different loadings of ClO$_2$ for degradation of RhB using the combination of HC and ClO$_2$

n(RhB):n(ClO$_2$)	Pseudo-first-order rate constant (k × 10^{-3} min^{-1})	R^2	Extent of degradation (%)
1:8.87	8.94	0.967	59.1
1:17.75	12.73	0.981	70.1
1:35.51	17.09	0.967	81.9
1:71.01	21.72	0.992	88.6
1:106.51	24.77	0.957	91.6
1:142.02	30.16	0.95	95.1
1:177.53	30.58	0.965	95.3

Under the extreme conditions of cavitation, the increase in the extent of degradation can be ascribed to an enhanced number of the oxidizing species (ClO•, O•, Cl_2, $HClO_2$, and •OH), generated by the dissociation of the ClO_2. These oxidizing species cause a series of chain reactions to attack and degrade the Rhodamine B molecules, increasing the degradation rate. The following are the main reactions expected to occur in the degradation of RhB by HC/ClO_2:

$$
\begin{aligned}
&\bullet ClO_2 + H_2O \rightarrow \bullet OH + HClO_2 \\
&ClO_2 \xrightarrow{HC} ClO\bullet + 2O\bullet \\
&O\bullet + H_2O \rightarrow 2\bullet OH \\
&3O\bullet \rightarrow O_3 \\
&O_3 + H_2O \rightarrow 2\bullet OH + O_2 \\
&RhB + ClO_2 \rightarrow Intermediates \\
&RhB + \bullet OH_2 \rightarrow Intermediates \\
&Intermediates + ClO_2 \rightarrow CO_2 + H_2O \\
&Intermediates + \bullet OH \rightarrow CO_2 + H_2O
\end{aligned} \tag{9}
$$

These equations show that under HC conditions, chlorine dioxide can not only cause non-ionic hydrolysis of water to produce primary •OH, but also produce secondary •OH. A large amount of •OH increases the efficiency of HC/ClO_2 for the degradation of RhB.

To study the percentage degradation rate using ClO_2 alone, the effect of a loading of ClO_2 n(RhB):n(ClO_2) = 1:177.53 was investigated under the same operating conditions, with a 95.3% degradation rate. The kinetic rate constants of 3.20×10^{-3} and 4.51×10^{-3} were obtained with HC and ClO_2 alone, respectively, as listed in Table 8. In addition, 36.3% degradation was obtained using ClO_2 alone as listed in Table 7. It reached 30.58×10^{-3} under the process of combining HC with ClO_2. The synergistic

Table 7 | Removal of Rhodamine B by using ClO_2 alone

Time (min)	0	20	40	60	80	100
Extent of degradation (%)	0	7.6	10.3	18.9	27.9	36.3

n(RhB):n(ClO_2) = 1:177.53, pH = 2.
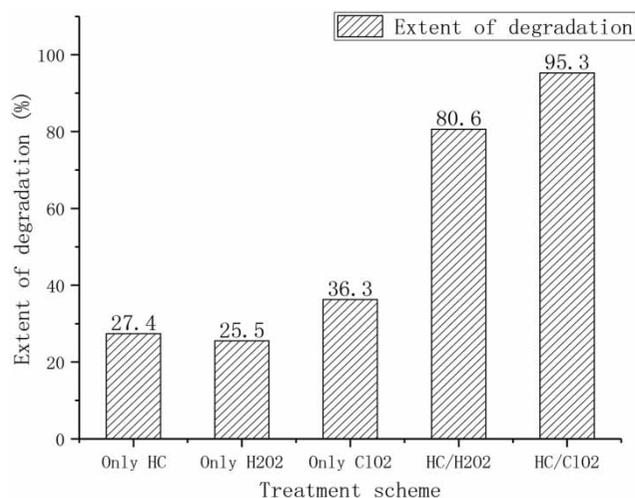
Figure 7 | Extent of degradation from different approaches.

coefficient was calculated by Equation (10) (Metheniti et al. 2017):

$$S_2 = 100 \frac{k_{\text{combined}} - \sum_{1}^{n} k_i}{k_{\text{combined}}}$$

$$= 100 \frac{30.58 \times 10^{-3} - (3.2 \times 10^{-3} + 4.51 \times 10^{-3})}{30.58 \times 10^{-3}}$$

$$= 74.79 \tag{10}$$

The synergistic effect of 74.79 can be ascribed to the HC/ClO_2 process, which can generate more oxidizing species. The water molecule is decomposed by chlorine dioxide through a non-ionic form, and this process produces •OH rather than OH^- due to the extreme conditions of high temperature, pressure, and fluid turbulence created by the HC. In addition, the formation of cavities accelerated due to the presence of dissolved gases and/or solid particles, which act as pre-nuclei (Gągol et al. 2018c). ClO_2 dissolved in solution increases the gas holdup of solution, and can function as the cavitation nuclei to enhance the HC effect (Braeutigam et al. 2010). In the HC/H_2O_2 process, H_2O_2 produced increasing number oxidizing •OH radicals under the cavitation conditions, and thus HC enhanced the removal effect of H_2O_2 on RhB. H_2O_2, however, existed in the wastewater as a liquid, as mentioned above, and thus it could not enhance cavitation; therefore, the synergistic coefficient and the removal rate of Rhodamine B of HC/H_2O_2 are less than that of HC/ClO_2.

The comparison of all the treatments used in this study shows that the best results were observed for HC/ClO_2, as represented in Figure 7. It can be also observed that the removal rate by the combined methods was higher than the uncombined methods. This also suggests that AOPs based on HC can generate more •OH radicals (Gogate & Patil 2015).

The treatment cost of HC with oxidants

The calculations of the cost of the effluent treatment by HC as well as AOPs include treatment time needed for oxidation, cost of oxidants, and electric energy. The operating cost of the treatment at laboratory scale is also listed in Table 8. For a treatment time of 100 min, the treatment cost of HC/H_2O_2 is 1.914 CNY/100 L, and that of HC/ClO_2 is 4.833 CNY/100 L. For individual processes: H_2O_2, ClO_2, and HC, the cost of treatment is 0.081, 3 and 1.833 CNY/100 L, respectively. Although the combined process is more expensive than the single process, considering the comprehensive treatment effect, the combined process is more economical, effective, and more suitable for large-scale industrial operation. The results of the calculations relate only to the laboratory scale.

Table 8 | Comparison of different approaches in terms of extent of degradation, treatment cost for 100 L RhB simulated wastewater in 100 min and synergistic index

Treatment scheme	Extent of degradation (%)	Rate constant (min⁻¹)	R^2	Synergistic Index	Cost (CNY)
Only HC	27.4	3.2×10^{-3}	0.974	——	1.833
Only H_2O_2	25.5	2.94×10^{-3}	0.9854	——	0.081
Only ClO_2	36.3	4.51×10^{-3}	0.966	——	3
HC/ H_2O_2	80.6	16.39×10^{-3}	0.979	62.54	1.914
HC/ClO_2	95.3	30.58×10^{-3}	0.965	74.79	4.833

CONCLUSIONS

In this study, the decomposition of Rhodamine B in water was using HC and its combination with H_2O_2 or ClO_2. The effect of cavitation was more effective in combination with different oxidizing agents when compared to the single process, especially HC/ClO_2. Based on the results obtained, the following conclusions were drawn.

The inlet pressure of 4 bar and acidic conditions (pH 2) were found to be more beneficial for the removal of Rhodamine B using HC alone, and the maximum removal rate was 27.4%. The maximum removal rates of Rhodamine B by HC/H_2O_2 and HC/ClO_2 were 80.6% and 95%, respectively. The combined approaches were found to be synergistic and followed pseudo-first-order kinetics. HC with H_2O_2 treatment gave a synergistic coefficient of 62.54, and the HC with ClO_2 approach proved to be better, with a higher synergetic coefficient of 74.79.

HC/ClO_2 is more effective than HC/H_2O_2 for the removal of Rhodamine B, although the oxidation potential of H_2O_2 is higher than that of ClO_2.

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