The removal of Rhodamine B by H₂O₂ or ClO₂ 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 H₂O₂ or ClO₂. 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: H₂O₂ (n(RhB):n(H₂O₂) was varied from 1:17.60 to 1:211.28) and ClO₂ (n(RhB):n(ClO₂) was varied from 1:8.87 to 1:177.53). A combination of cavitation and H₂O₂ or ClO₂ 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 H₂O₂ or ClO₂, the synergistic coefficients of 62.54 and 74.79 were obtained. The combination of HC and ClO₂ was proven to be more effective for the removal of RhB compared to HC alone and the hybrid process of HC and H₂O₂.

Key words | advanced oxidation processes, ClO₂, coalescent methods, hydrodynamic cavitation, Rhodamine B

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 \( \cdot \text{OH} \), 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\(_2\)O\(_2\)), 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\(_2\)O\(_2\) or ozone to treat pesticide industrial wastewater, and proved that the combined process of HC and H\(_2\)O\(_2\) was more cost-effective than the combination of HC and O\(_3\). Boczkaj et al. (2018) and Gaślągol 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\(_2\)O\(_2\), 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\(_2\)O\(_2\) 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 (P\(_1\)) 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.
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(H₂O₂) was varied from 1:17.60 to 1:211.28) and chlorine dioxide (n(RhB):n(ClO₂) 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 H₂O₂ or ClO₂ 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:

$$\omega = \frac{A_0 - A_1}{A_0 - 0.004} \times 100\%$$  (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 ($\beta$) 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:

$$\beta = \frac{N(d)}{D}$$  (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
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 ln(Ca0/Ca) 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:

\[
\sigma = \frac{P_\infty - P_V}{\rho u_\infty^2 / 2}
\]  

(3)

where \(P_\infty\) and \(u_\infty\) are the inflow pressure and flow rate of the liquid, respectively, \(\rho\) 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 \(\bullet \text{OH}\) 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. (2017) 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>
<thead>
<tr>
<th>Inlet pressure (bar)</th>
<th>Pseudo-first-order rate constant ( \times 10^{-3} \text{ min}^{-1} )</th>
<th>( R^2 )</th>
<th>Extent of degradation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.67</td>
<td>0.96</td>
<td>15.4</td>
</tr>
<tr>
<td>3</td>
<td>2.22</td>
<td>0.974</td>
<td>19.9</td>
</tr>
<tr>
<td>4</td>
<td>3.2</td>
<td>0.973</td>
<td>27.4</td>
</tr>
<tr>
<td>5</td>
<td>2.75</td>
<td>0.979</td>
<td>23.9</td>
</tr>
<tr>
<td>6</td>
<td>2.31</td>
<td>0.986</td>
<td>20.6</td>
</tr>
</tbody>
</table>

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

**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.
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 $3.2 \times 10^{-3}$ min$^{-1}$ because under alkaline conditions, scavenger CO$_3$$^-$/HCO$_3$$^-$/OH and consumed them.

$$\text{CO}_2^2^- + \bullet\text{OH} \rightarrow \text{OH}^- + \text{CO}_3$$

$$\text{OH} + \text{HCO}_3^- \rightarrow \text{OH}^- + \text{HCO}_3$$

Under acidic conditions CO$_3$$^-$/HCO$_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$_2$O$_2$, 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%, 95.2%, and 86.1%, respectively, indicating that acidic conditions were more conducive to the decolorization of OG.

| Table 3 | Kinetic rate constants at different initial pH for degradation of RhB using HC |
|---|---|---|---|
| pH | Pseudo-first-order rate constant ($k \times 10^{-2}$ 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 |

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
of RhB increased with increasing loadings of H₂O₂ till an optimal loading of n(RhB):n(H₂O₂) = 1:105.64. Beyond loadings of n(RhB):n(H₂O₂) = 1:105.64, the percentage degradation of Rhodamine B decreased. The maximum percentage degradation was 80.6% at 30 mg/L of H₂O₂. 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 H₂O₂ at loadings higher than n(RhB):n(H₂O₂) = 1:105.64. However, kinetic rate constants decreased when at loadings higher than n(RhB):n(H₂O₂) = 1:70.43.

Hydrogen peroxide, as an oxidant in wastewater treatment, is largely dependent on OH radicals produced by the dissociation of H₂O₂. 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, H₂O₂ molecules more easily dissociate into •OH radicals due to the extra energy provided by HC. Therefore, to some extent, the combination of HC and H₂O₂ can generate more •OH radicals, thus increasing the degree of degradation with increasing H₂O₂ concentration. The following are the main reactions occurring in the process of HC and H₂O₂:

\[
\begin{align*}
H₂O₂ & \xrightarrow{HC} 2 \bullet OH \\
•OH + H₂O₂ & \xrightarrow{HC} H₂O + HO₂• \\
HO₂• + H₂O₂ & \rightarrow •OH + H₂O + O₂
\end{align*}
\]

Beyond the optimal n(RhB):n(H₂O₂) = 1:105.64 loading of H₂O₂, the percentage degradation decreased. This result can be ascribed to the excess of H₂O₂ acting as scavengers of •OH radicals and recombining with each other, as indicated by the following reaction:

\[
H₂O₂ + OH• \rightarrow •HO₂ + H₂O
\]

The removal of Rhodamine B was also observed using H₂O₂ alone. The effect of loadings of n(RhB):n(H₂O₂) = 1:105.64 on the percentage degradation of Rhodamine B with an initial concentration of 4 mg/L (0.835 × 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 H₂O₂ than the individual process. The synergistic coefficient can be calculated as follows (Metheniti et al. 2017):

\[
S_1 = 100 \frac{k_{combined} - \sum \frac{k_i}{k_{combined}}}{16.39 \times 10^{-3} - (3.2 \times 10^{-3} + 2.94 \times 10^{-5})} = 62.54
\]

Table 4 | Kinetic rate constants at different loadings of H₂O₂ for the degradation of Rhodamine B using the combined process of HC and H₂O₂

<table>
<thead>
<tr>
<th>n(RhB):n(H₂O₂)</th>
<th>Pseudo-first-order rate constant (k, × 10⁻³ min⁻¹)</th>
<th>R²</th>
<th>Extent of degradation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:17.60</td>
<td>3.52</td>
<td>0.954</td>
<td>29.7</td>
</tr>
<tr>
<td>1:35.21</td>
<td>6.14</td>
<td>0.962</td>
<td>45.9</td>
</tr>
<tr>
<td>1:70.43</td>
<td>9.44</td>
<td>0.967</td>
<td>61.1</td>
</tr>
<tr>
<td>1:105.64</td>
<td>16.39</td>
<td>0.979</td>
<td>80.6</td>
</tr>
<tr>
<td>1:140.84</td>
<td>13.91</td>
<td>0.988</td>
<td>75.1</td>
</tr>
<tr>
<td>1:211.28</td>
<td>11.87</td>
<td>0.983</td>
<td>69.5</td>
</tr>
</tbody>
</table>

Table 5 | Removal of Rhodamine B using H₂O₂ alone

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extent of degradation (%)</td>
<td>0</td>
<td>5.6</td>
<td>10.3</td>
<td>18.4</td>
<td>23.1</td>
<td>25.5</td>
</tr>
</tbody>
</table>

n(RhB):n(H₂O₂) = 1:105.64, pH = 2.
Similar trends have been mentioned in some literature. Gore et al. (2013) investigated the effect of molar ratio of Reactive Orange 4 dye (RO4): H₂O₂ (over the range 1:5–1:50) on the degradation of RO4 using HC combined with H₂O₂. The results showed that the maximum 99.56% degradation was obtained with 1:30 molar ratio of RO4: H₂O₂. 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/ClO₂)

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 ClO₂ (n(RhB):n(ClO₂) 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.

Table 6 | Kinetic rate constants at different loadings of ClO₂ for degradation of RhB using the combination of HC and ClO₂

<table>
<thead>
<tr>
<th>n(RhB):n(ClO₂)</th>
<th>Pseudo-first-order rate constant (k × 10⁻³ min⁻¹)</th>
<th>R²</th>
<th>Extent of degradation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:8.87</td>
<td>8.94</td>
<td>0.967</td>
<td>59.1</td>
</tr>
<tr>
<td>1:17.75</td>
<td>12.73</td>
<td>0.981</td>
<td>70.1</td>
</tr>
<tr>
<td>1:35.51</td>
<td>17.09</td>
<td>0.967</td>
<td>81.9</td>
</tr>
<tr>
<td>1:71.01</td>
<td>21.72</td>
<td>0.992</td>
<td>88.6</td>
</tr>
<tr>
<td>1:106.51</td>
<td>24.77</td>
<td>0.957</td>
<td>91.6</td>
</tr>
<tr>
<td>1:142.02</td>
<td>30.16</td>
<td>0.95</td>
<td>95.1</td>
</tr>
<tr>
<td>1:177.53</td>
<td>30.58</td>
<td>0.965</td>
<td>95.3</td>
</tr>
</tbody>
</table>

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•, Cl₂, HClO₂, and •OH), generated by the dissociation of the ClO₂. 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/ClO₂:

\[
\begin{align*}
\text{ClO}_2 + \text{H}_2\text{O} & \rightarrow \text{•OH} + \text{HClO}_2 \\
\text{ClO}_2 & \xrightarrow{\text{HC}} \text{Cl}• + 2\text{O•} \\
\text{O•} + \text{H}_2\text{O} & \rightarrow 2 \text{•OH} \\
3\text{O•} & \rightarrow \text{O}_3 \\
\text{O}_3 + \text{H}_2\text{O} & \rightarrow 2 \text{•OH} + \text{O}_2 \\
\text{RhB} + \text{ClO}_2 & \rightarrow \text{Intermediates} \\
\text{RhB} + \text{•OH}_2 & \rightarrow \text{Intermediates} \\
\text{Intermediates} + \text{ClO}_2 & \rightarrow \text{CO}_2 + \text{H}_2\text{O} \\
\text{Intermediates} + \text{•OH} & \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\end{align*}
\]

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/ClO₂ for the degradation of RhB.

To study the percentage degradation rate using ClO₂ alone, the effect of a loading of ClO₂ n(RhB):n(ClO₂) = 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 ClO₂ alone, respectively, as listed in Table 8. In addition, 36.5% degradation was obtained using ClO₂ alone as listed in Table 7. It reached 30.58 × 10⁻³ under the process of combining HC with ClO₂. The synergistic...
The synergistic coefficient was calculated by Equation (10) (Metheniti et al. 2017):

\[
S_2 = 100 \frac{k_{\text{combined}} - \sum \frac{n}{1} 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
\quad (10)

The synergistic effect of 74.79 can be ascribed to the HC/ClO₂ 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 (Gagol et al. 2018c). ClO₂ 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/H₂O₂ process, H₂O₂ produced increasing number oxidizing •OH radicals under the cavitation conditions, and thus HC enhanced the removal effect of H₂O₂ on RhB. H₂O₂, 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/H₂O₂ are less than that of HC/ClO₂.

The comparison of all the treatments used in this study shows that the best results were observed for HC/ClO₂, 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/H₂O₂ is 1.914 CNY/100 L, and that of HC/ClO₂ is 4.833 CNY/100 L. For individual processes: H₂O₂, ClO₂, 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 7 | Removal of Rhodamine B by using ClO₂ alone

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extent of degradation (%)</td>
<td>0</td>
<td>7.6</td>
<td>10.3</td>
<td>18.9</td>
<td>27.9</td>
<td>36.3</td>
</tr>
</tbody>
</table>

n(RhB):n(ClO₂) = 1:177.53, pH = 2.
CONCLUSIONS

In this study, the decomposition of Rhodamine B in water was using HC and its combination with H₂O₂ or ClO₂. The effect of cavitation was more effective in combination with different oxidizing agents when compared to the single process, especially HC/ClO₂. 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/H₂O₂ and HC/ClO₂ were 80.6% and 95%, respectively. The combined approaches were found to be synergistic and followed pseudo-first-order kinetics. HC with H₂O₂ treatment gave a synergistic coefficient of 62.54, and the HC with ClO₂ approach proved to be better, with a higher synergetic coefficient of 74.79.

HC/ClO₂ is more effective than HC/H₂O₂ for the removal of Rhodamine B, although the oxidation potential of H₂O₂ is higher than that of ClO₂.

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