Enhancement of chloroform degradation by the combination of hydrodynamic and acoustic cavitation

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Abstract

The decomposition of chloroform by the combination of hydrodynamic and acoustic cavitation (Hydrodynamic–Acoustic-Cavitation/HAC) has been investigated. The flow rate and the hole diameter of the orifice plate remarkably affect the conversion of chloroform in the combined system. The conversion increases with increasing fluid velocity without any restriction. With a 2.8 mm orifice plate the conversion reaches an optimal value. A synergistic effect has been obtained by the hybrid method of acoustic and hydrodynamic cavitation. The total synergistic effect achieves 17% and 73% per pass, respectively. The analysis of the energy efficiencies shows different results. Due to high optimization potential, this hybrid method can be visualized as a new step for wastewater treatment.

1. Introduction

Cavitation is able to induce and enhance various chemical and physical effects. Application of cavitation includes, for example, the acceleration of chemical reactions [1,2], the cleaning of surfaces [3,4], the formation of emulsions [5], and the production of amorphous nanoparticles [6]. In the field of wastewater treatment, the positive effects of cavitation have been investigated [7].

There are four general methods for generating cavitation which differ in their manner of energy input (acoustic, hydrodynamic, particle induced and optical) [8]. The most widely used form is the generation with ultrasound (acoustic cavitation). Ultrasonic waves were generated by using different transducers (piezoelectric/magnetostrictive). The formation and the continuous growth of cavitation nuclei take place, due to change in expansion and compression (rectified diffusion) [9]. When the bubbles reach a critical size, they finally collapse.

However, some problems limit the applications of acoustic cavitation. On one hand, it is difficult to scale up an ultrasonic device due to variation in the acoustic field and the difficulty to calculate it [10]. On the other hand, there exist various opinions about the energy efficiencies both of hydrodynamic and acoustic cavitation.

The working group of Pandit has published that hydrodynamic cavitation is more energy efficient than acoustic cavitation [11]. The results of other working groups lead to inverse conclusions [12,13]. Thus it is difficult to make an overall statement about the energy efficiencies or the maximum of the conversion or yield because they are heavily dependent on different factors like frequency, intensity and reactor geometry.

To solve these problems another type for creating cavitation bubbles, hydrodynamic cavitation, was increasingly investigated in the last two decades. Thereby, cavities are created by an increase of the fluid velocity and the ensuing decrease in the static pressure. This principle can be described with the Bernoulli Equation (Eq. (1)) [14]:

\[
p_{\text{stat}} + p_{\text{dyn}} = \text{const} = p_{\text{stat}} + \frac{1}{2} \rho v^2
\]

where \(p_{\text{stat}}\) is the static and \(p_{\text{dyn}}\) is the dynamic pressure, \(\rho\) is the density of the liquid and \(v\) is the velocity of the fluid. The Bernoulli Equation indicates that the sum of dynamic and static pressure is constant. If the fluid velocity increases, the dynamic pressure increases too, and consequently the static pressure decreases. If the static pressure reaches the cavitation threshold of the solvent (in general the vapor pressure of the solvent) cavities are formed. Usually, moderate conditions are sufficient to produce cavitation [14].

An increasing fluid velocity can be achieved with a rejuvenation in a pipe (e.g. venturi, valves and orifice plate), through homogenizers, or by devices, which use the rotor–stator principle [15].

Characteristic numbers describing the hydrodynamic cavitation setup have been proposed, thus the dimensioning of hydraulic...
streams is simple [16]. Therefore, the pressure conditions in the system play an important role.

The Cavitation number ($C_v$) (Eq. (2)) is a dimensionless number and describes the cavitation in hydraulic systems [17]

$$C_v = \frac{p_d - p_v}{0.5 \rho v^2}$$

where $p_d$ (downstream pressure) corresponds to the fully recovered pressure in the downstream of the restriction and $p_v$ to the vapor pressure of the solution.

The formation of cavities starts with a cavitation number of $C_v < 1$. With a decrease in the cavitation number, the number of collapsing bubbles per unit time increases and simultaneously, the intensity of the collapse decreases [18]. Other parameters ($\alpha$ and $\beta_0$) used to describe the restriction properties have already been explained and investigated elsewhere [18].

The applications of hydrodynamic cavitation include the degradation of organics [13,19], the destruction of the cell walls of microorganisms [11], hydrolysis of fatty acids [20] and the preparation of biodiesel [21].

In comparison with acoustic cavitation, hydrodynamic cavitation is easier to scale up [22]. Furthermore the investment costs are low leading to an economic benefit. Unfortunately, like acoustic cavitation, the collapse intensities (reached collapse-temperatures and -pressures) of the bubbles, generated with hydrodynamic cavitation are low [23].

In the past, many individual methods of advanced oxidation processes (AOP) have been combined to create hybrid methods [24]. It was mentioned that the combination of acoustic and hydrodynamic cavitation has a great potential [10,24–25]. Till today, there exists only one investigation for that hybrid system [26].

The aim of this work is to combine both methods (acoustic and hydrodynamic cavitation) most effectively, joining the positive properties of the individual applications and optimizing the parameters affecting the system to perform. More cavitation nuclei are created in the hydrodynamic device (advantage of hydrodynamic cavitation) and procured to the acoustic field. Due to acoustic cavitation the nuclei undergo more violent collapses (advantage of acoustic cavitation). Another benefit of hydrodynamic cavitation is the scale up, because of characteristic numbers, describing the hydraulic system. As a result a practicable usage for the hybrid method (HAC) will be possible in the future. Another point is that with this hybrid method it is necessary to work in a continuous flow system, which is also a benefit for industrial applications.

2. Material and methods

2.1. Chemicals

Chloroform (CHCl₃, CAS-Nr.: 67–66-3, Riedel-de-Haehn, 99%) and deionised water (CAS-Nr.: 7732–18-5) were used as received.

2.2. Experimental setup

The experimental setup is shown in Fig. 1. The device consists of a pump (SGY-028/II-LL-LA, centrifugal pump, 1.1 kW, 2800 min⁻¹, SPECK Pumpen GmbH & Co. KG, Roth, Germany) with an Advanced Operation Panel, with the possibility to adjust the fluid velocity while using the same orifice plate. The used pipes (stainless steel, 316/316L) have an inner diameter of 10 mm and an external diameter of 12 mm. The fittings, angles, tees and pressure gauges are also made of stainless steel and were purchased from SWAGELOK (Swagelok Leipzig, Germany). A device for fixing the orifice plate was set before the ultrasonic reactor which was self-manufactured at the Friedrich-Schiller-University.

The ultrasonic double-walled glass reactor (500 mL, MEINHARDT Ultrasonic Technology, Leipzig, Germany), which was connected with a cryostat (FP50-NC, JULABO Labortechnik GmbH, Seelbach, Germany), was linked with an piezoelectric ultrasonic transducer (E/805/T, MEINHARDT Ultrasonic Technology) and an ultrasonic generator (Ultrasonic Power Generator K8, MEINHARDT Ultrasonic Technology, 850 kHz, 120 W electrical power, 40 W acoustic power/calorimetrical measurement). To measure the flow velocity in the system, a flow meter (DRS-9250/4L4420, 2–40 min⁻¹, Pmax: 200 bar, KOBOld Messring GmbH, Hofheim, Germany) with matching display (AUF-1000Y) was used.

A self-made reservoir (500 mL) in front of the suction side of the pump was connected with a cryostat, to adjust and control the temperature of the solution.

2.3. Experimental procedure

Chloroform solution (1.5 L) of 1 mM was prepared. The investigated orifice plate was set into the device and fixed. Afterwards the system was filled with the reaction solution. After reservoir and ultrasonic reactor were closed, the pump could be switched on. Dependent on the experiment, the ultrasound generator was set on the maximum power input (120 W electrical power, 40 W acoustic power and 2 W cm⁻² acoustic power density).

During the experiments, the solution temperature was kept constantly at 25 °C. The reaction time was 30 min and the
The degradation mechanism is shown. For the optimization, the conversion of chloroform was chosen as a model reaction. In Eqs. (3)–(9) a part of the radical-induced degradation mechanism is shown.

$$\begin{align*}
\text{H}_2\text{O} & \rightarrow \text{H} + \text{OH} & (3) \\
\text{CHCl}_3 & \rightarrow \text{H} + ^\ast \text{CCl}_3 & (4) \\
\text{CHCl}_3 & \rightarrow \text{Cl} + ^\ast \text{CHCl}_2 & (5) \\
^\ast \text{H} + \text{CHCl}_3 & \rightarrow \text{H}_2 + ^\ast \text{CCl}_3 & (6) \\
^\ast \text{H} + \text{CHCl}_3 & \rightarrow \text{HCl} + ^\ast \text{CHCl}_2 & (7) \\
^\ast \text{Cl} + \text{CHCl}_3 & \rightarrow \text{HCl} + ^\ast \text{CCl}_3 & (8) \\
^\ast \text{OH} + \text{CHCl}_3 & \rightarrow \text{H}_2\text{O} + ^\ast \text{CCl}_3 & (9)
\end{align*}$$

Due to formation of hydrochloric acid (product), an increase in the conductivity was observed. At the same time a decrease in the chloroform concentration (educt) was measured (GC). From Fig. 2 it can be seen that a linear relationship between the conductivity of the solution and the conversion of chloroform exists. For the least square line (Fig. 2), aliquots (2 × 10 mL) of the processed solution were periodically extracted from the reaction system by graduated pipette. The concentration of chloroform in aqueous solution was detected by headspace/GC/FID. In the following work the conversion of chloroform was measured by HS-GC on the one hand, and by the conductivity on the other hand.

The correlation between the conversion and the conductivity is given by Eq. (10)

$$X = \left(1 - \frac{c_t}{c_0}\right) \times 100\% = (\lambda_t - \lambda_0) \times 0.2183$$

where X is the conversion, $c_0$ is the initial concentration (1 mM), $c_t$ is the concentration after the treatment for the time t, $\lambda_t$ is the conductivity after the treatment time t and $\lambda_0$ is the initial conductivity. The factor 0.2183 is the slope of Fig. 2.

From the peaks in the chromatograms and the corresponding conductivities the least square line could be created.

### 3. Results and discussion

For the optimization, the conversion of chloroform was chosen as a model reaction. In Eqs. (3)–(9) a part of the radical-induced degradation mechanism is shown.

The results of these experiments are very important, as a minimum fluid velocity must exist to create hydrodynamic cavitation [29]. However, the conversion per pass decreases with an increasing fluid velocity. This result is not surprising, because the residence time per pass in the ultrasonic field is much lower with a high fluid velocity. In contrast the number of passes increases and overall the conversion of chloroform after 30 min increases, too. But, changing the flow conditions through the use of an orifice plate could have a negative influence on the bubbles and the acoustic field.

### 3.1. Influence of the fluid velocity on the acoustic field

The influence of the fluid velocity on the conversion of chloroform in the acoustic field of the ultrasonic reactor was investigated.

A 10 mm orifice plate having a hole diameter equal to the inside pipe diameter was fixed in the holder. Thus, there was no formation of hydrodynamic cavitation. The flow was regulated with the pump. The investigated results are shown in Fig. 3.

It is observed that with an increasing fluid velocity, the conductivity and thus the conversion of chloroform increases by trend within 30 min. The acoustic cavities accumulate worse at high fluid velocities and do not form clusters because of the reduced secondary Bjerkess force [27,28]. Thus, more bubbles are available for collapse and the conversion increases.

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![Fig. 2. Correlation between conductivity and chloroform conversion, 30 min, 0.5 L 1 mM CHCl3, 40 W acoustic power, 850 kHz, 25 °C.](image)
Orifice plates with various hole diameter were fixed in the appropriate holder. The ratio between the hole area of the restriction and the pipe area can be described with $b_0 (b_0 = \frac{A_r}{A_p} = \frac{n\pi r_L^2}{n\pi r_R^2})$, where $A_r$ is the hole area of the orifice plate, $A_p$ the pipe area, $n$ is the number of the holes, $r_L$ is the hole radius in the orifice plate and $r_R$ is the radius of the pipe. In Table 1 the investigated orifice plates are listed with their corresponding parameters. Fig. 4 shows the results for the different orifice plates in combination with acoustic cavitation (hybrid method) or without (hydrodynamic cavitation).

### Table 1
Investigated orifice plates.

<table>
<thead>
<tr>
<th>Orifice plate number</th>
<th>Diameter (mm)</th>
<th>Hole area (mm$^2$)</th>
<th>$b_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.43</td>
<td>1.61</td>
<td>0.021</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>3.14</td>
<td>0.04</td>
</tr>
<tr>
<td>3</td>
<td>2.8</td>
<td>6.16</td>
<td>0.0784</td>
</tr>
<tr>
<td>4</td>
<td>3.2</td>
<td>8.04</td>
<td>0.102</td>
</tr>
<tr>
<td>5</td>
<td>5.09</td>
<td>20.35</td>
<td>0.239</td>
</tr>
<tr>
<td>6</td>
<td>10$^a$</td>
<td>78.54</td>
<td>1</td>
</tr>
</tbody>
</table>

$^a$ No hydrodynamic cavitation is emerging.

It is clear that the conversion with an orifice plate diameter of 2.8 mm ($b_0 = 0.0784$) reaches the best conversions in both cases. This optimum was already established by using hydrodynamic cavitation [29]. Enlargement or reduction of the restriction diameter reduces the conversion of chloroform. Accordingly, the 2.8 mm orifice plate can be assumed optimal for the degradation of chloroform with the experimental setup used here. Furthermore it can be seen that the conversion with the individual application of hydrodynamic cavitation is really low in comparison with the hybrid method.

In Fig. 5, considering the chloroform conversion per pass, a clearly different result for the hybrid method is shown, while the results for hydrodynamic cavitation have the same structure. For the hybrid system an increasing hole diameter leads to a decrease in the conversion. This result can be explained as follows, the total fluid velocity in the system increases with larger diameter of the restrictions and as a consequence the residence time in the ultrasonic reactor decreases. Thus, the acoustic irradiation time per pass, and the conversion decreases, because the ultrasonic irradiation has the dominant influence on the degradation of chloroform.

Due to high flow velocity, the number of passes per unit time increases and that's why the total chloroform conversion after 30 min has an optimum at a restriction diameter of 2.8 mm as shown in Fig. 5.
3.3. Comparison of the individual methods and the hybrid method

Investigations were performed with hydrodynamic, acoustic or the hybrid cavitation system. In the case of hydrodynamic cavitation, ultrasound was not used, and an orifice plate with a diameter of 2.8 mm was applied. For the individual method of ultrasound, a 10 mm orifice plate (equivalent to the pipe diameter) was used.

In the case of the hybrid method a 2.8 mm orifice plate was fixed in the corresponding holder and ultrasound was also used. In Fig. 6 the total conversions after 30 min and the conversions per pass, by using the individual and the hybrid methods, are shown. The best results could be obtained by combining acoustic and hydrodynamic cavitation which leads to 90% and 0.5%, respectively. The treatment with ultrasound achieves a conversion of 70% and 0.25%, while the hydrodynamic cavitation only achieves a conversion of about 7%, 0.04%, respectively.

With the above mentioned values the synergistic effect can be calculated with Eq. (11)

\[
\text{Synergistic effect} = \left( \frac{X_{\text{HC+US}}}{X_{\text{HC}} + X_{\text{US}}} \right) \times 100\% \quad (11)
\]

where \(X_{\text{HC+US}}\) is the conversion with the hybrid method, \(X_{\text{HC}}\) and \(X_{\text{US}}\) are the conversions with the individual methods.

It was calculated that the synergistic effect is about 17% with regard to an experimental time of 30 min. For the synergistic effect per pass a much better result of 73% was obtained. This means that the hybrid method is 73% better than the sum of the individual methods per pass.

To investigate whether the hybrid method of acoustic and hydrodynamic cavitation or the individual methods are energetically most favorable, the energy efficiency (EE) was calculated and compared. The EE provides information of how much chloroform is converted per kJ. There exists two different point of views:

![Fig. 5. Chloroform conversion per pass with different hole diameter of the orifice plates for the hybrid method (●) and the hydrodynamic system (■), 1.5 L 1 mM CHCl₃ solution, 40 W acoustic power, 850 kHz, 25 °C.](image1)

![Fig. 6. Comparison of chloroform conversion with the 2 individual methods and the hybrid method after 30 min and per pass, 1.5 L 1 mM CHCl₃ solution, 25 °C; HC (hydrodynamic cavitation): 2.8 mm orifice plate, no ultrasound; US (ultrasonic cavitation): 10 mm orifice plate, 40 W acoustic power, 850 kHz; HC + US (hybrid method): 2.8 mm orifice plate, 40 W acoustic power, 850 kHz.](image2)
for the EE. On the one hand, EE I which refer to the actual energy that is extracted from the power supply system, on the other hand, EE II which refer to the truly transferred energy in the system as computation base. Both values (EE I and EE II) are connected over the degree of efficiency (Eqs. (12)–(14))

\[
EE\ I = \frac{X}{E_{el}} \quad (12)
\]

\[
EE\ II = \frac{X}{\eta E_{el}} \quad (13)
\]

\[
EE\ II = \eta \times EE\ I \quad (14)
\]

where \(X\) is the conversion of chloroform in \(\mu\text{mol}\), \(E_{el}\) the measured electrical energy, which was taken from the power strip, \(\eta\) the degree of efficiency of the setup. The degree of efficiency for the ultrasound transducer was determined calorimetrically (Eq. (15)) and for the pump it was calculated by using Eq. (16) [13]

\[
E_{\text{input,}\ I} = mc_p \frac{dT}{dt} + H \rho g vt \quad (15)
\]

\[
E_{\text{input,}\ II} = H \rho g vt \quad (16)
\]

where \(m\) is the mass of water used, \(c_p\) is the heat capacity, \(dT/dt\) is the temperature difference, \(dt\) is the time difference, 1 is the pressure altitude, \(g\) the acceleration due to gravity \((9.81 \text{ m s}^{-2})\), \(v\) is the fluid velocity and \(t\) the test duration.

In Fig. 7, the EE I and EE II are shown. Considering EE I, it is clear that the individual method of acoustic cavitation reaches the best value and is very efficiency. The EE I of the hybrid method reaches a lower value and for the individual application of hydrodynamic cavitation it remarkably decreases. Comparing these values with the EE II, the order is changed. The hybrid method is the most efficient method and the individual application of ultrasound is less efficient. For hydrodynamic cavitation, EE II is still the lowest value. The low EE I of the hybrid method and the individual hydrodynamic cavitation can be explained with the smaller hole diameter (2.8 mm) in contrast to the single application of ultrasound, where a 10 mm diameter plate was used. With a smaller plate, the pump consumes more energy. As a result, the energy efficiency drops because the losses increase due to friction and heat from the pump impellers.

These losses are not considered in the EE II, only the energy which is transferred into the liquid. That is why EE II is higher for the hybrid method (HAC) than for the individual applications.

4. Conclusions

In this study, hydrodynamic cavitation, acoustic cavitation and the combination of these individual methods (HAC) have been investigated and optimized. Therefore an experimental setup was designed and built. All experiments were performed with a 1 mM chloroform solution as a model pollutant. It was able to correlate the conversion of chloroform with an increase in the conductivity of the reaction solution. The conversion rate increases with an increasing flow in the ultrasonic system without any restriction. It is likely that an optimum value for the maximum fluid velocity exists. An optimal hole diameter was found (2.8 mm, \(\eta_0 = 0.0784\)) in the hybrid system.

Finally, the hybrid method was compared with the individual methods, synergy and energy efficiency were evaluated. The combination achieved the best conversion rates, and synergies of 17% for a treatment after 30 min and 73% for a single pass were obtained.

The individual application of ultrasound has the lowest energy requirement for EE I. The value of the EE I slightly decreases for the hybrid method and remarkably for the individual method of hydrodynamic cavitation. The EE II demonstrates, however, that the hybrid method uses the energy, which was actually introduced into the system best. Losses due to friction and heat are neglected and the degree of efficiency is considered in this case. It should be mentioned that this hybrid method is a new step into the future for the combination and optimization of advanced oxidation processes. Especially in the purification of wastewater contaminated with organic pollutants, this hybrid method of two AOP’s represent an effective alternative to the common methods.

To improve the hybrid method and to increase the conversion of the contaminant more investigation should follow, such as the distance between the orifice plate and acoustic field (sonotrode).

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