Chapter 6
Treatment of the Pesticide Industry Effluent using Hydrodynamic Cavitation and its combination with Process Intensifying Additives
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6.1 Introduction

Contamination of surface and groundwater resources by the pesticides is mainly due to industrial discharges and agricultural activities (Mahamoodi et al., 2007). Wastewater generated from the pesticide manufacturing industries poses significant pollution problems due to the high values of chemical oxygen demand (COD) and reduced biodegradability (Chen et al., 2007). Most of the pesticide compounds are very toxic and hazardous in nature, even at low concentrations.

Although conventional biological treatments are widely used for the degradation of organic pollutants in wastewater, biorefractory compounds are not effectively removed by these methods (Oller et al., 2011). Since last decade, advanced oxidation processes (AOPs) have proved to be very effective in improving the overall degradation efficiency of biorefractory compounds such as pesticides (Tamimi et al., 2008; Xiong et al., 2011). The degradation mechanism of AOPs is primarily based on the generation of highly reactive and nonselective hydroxyl radicals (OH•) and its subsequent attack on the organic pollutant to convert them into CO2, water and inorganic ions (Zapata et al., 2009). However, the application of AOPs is not very cost-effective if they are applied individually to obtain mineralization of recalcitrant compounds in wastewater. Hence, instead of replacing the cost-effective biological processes with AOPs, the effective and proper combination of both systems is very essential (Cesaro et al., 2013). AOPs such as Fenton, ozonation, cavitation etc. can be used for pre-treatment of industrial wastewater to improve its biodegradability index (BOD5: COD ratio) and thus enhancing the probability of degradation using microbial action (Mahamuni and Adewuyi, 2010).

Hydrodynamic cavitation has been reported to be the most cost effective and efficient way of inducing the cavitation (Gogate and Patil, 2015). The degradation of pollutants using hydrodynamic cavitation occurs through the pyrolysis/thermal decomposition of the pollutant molecules entrapped inside the cavity and the oxidation of pollutant molecule using OH• radicals at cavity water interface (Saharan
et al., 2011). Hydrodynamic cavitation has attracted the attention of many researchers since it can be easily scaled up (Gore et al., 2014). However, it has a serious limitation of low degradation or mineralization rates when applied individually for the treatment of complex wastewater (Bagal and Gogate, 2014). The efficacy of hydrodynamic cavitation can be enhanced by using the process intensifying additives such as hydrogen peroxide and ozone since all such processes have a similar degradation mechanism, i.e. the generation and subsequent attack of OH• radicals on the pollutant molecule (Jyoti and Pandit, 2003).

The work done so far on the application of a combination of hydrodynamic cavitation and other AOPs is primarily based on the degradation of synthetic wastewater containing single pollutant and the reports on the treatment of real industrial effluent are very few. Chakinala et al. (2008a) have explored the combined process of hydrodynamic cavitation (HC) and advanced Fenton process for the treatment of real industrial wastewater and reported that HC is very effective as a pre-treatment to biological oxidation. Padoley et al. (2012) have also reported the improvement in the biodegradability index (BI) of complex biomethanated distillery wastewater (B-DWW) by using the hydrodynamic cavitation.

The combined application of hydrodynamic cavitation and the process intensifying additives for the degradation of real pesticide industry effluent is not yet reported in the literature to the best of our knowledge. The objective of the present work is to reduce the toxicity and increase the biodegradability of actual pesticide industry effluent by the application of hydrodynamic cavitation in combination with process intensifying additives such as hydrogen peroxide (H₂O₂) and ozone (O₃). The change in the toxicity of pesticide industry effluent after treatment has been evaluated by measuring the COD, BOD and TOC values of the effluent. H₂O₂ use was found to interfere with COD analysis by consuming certain amount of potassium dichromate and thus leading to overestimation of the COD values (Kang et al., 1999; Kuo, 1992 and Talinli and Anderson, 1992). Due to this, the interference of H₂O₂ on COD estimation during HC+ H₂O₂ was also evaluated to obtain the corrected COD values. In addition to this, the cost estimation of HC, HC+ H₂O₂ and HC + Ozone processes is also included in the present work to obtain the most effective and economical process for the treatment of pesticide industry effluent.
6.2. Materials and methods

6.2.1 Materials

Hydrogen peroxide (30 % w/v) and sodium hydroxide (NaOH) both of AR grade were obtained from S D Fine Chemicals Ltd., Mumbai, India. All chemicals were used as received from the supplier. A sample of pesticide industry effluent was collected from the pesticide manufacturing industry in Mumbai, India. The effluent collected was filtered before use to remove any suspended solids. The obtained supernatant was used in the degradation study after the desired dilution and pH adjustment. The characteristics of the effluent are summarized in Table 6.1.

Table 6.1

Characteristics of pesticide industry effluent

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>0.3-0.5</td>
</tr>
<tr>
<td>Total suspended solids</td>
<td>106 mg/L</td>
</tr>
<tr>
<td>Total dissolved solids</td>
<td>1,08,500 mg/L</td>
</tr>
<tr>
<td>Biological oxygen demand</td>
<td>2100-2200 mg/L</td>
</tr>
<tr>
<td>Chemical oxygen demand</td>
<td>17000-18000 mg/L</td>
</tr>
<tr>
<td>Ratio of BOD&lt;sub&gt;5&lt;/sub&gt;/COD</td>
<td>0.123</td>
</tr>
</tbody>
</table>

6.2.2 Experimental set-up

Hydrodynamic cavitation set-up used in the present system and for the degradation of imidacloprid/ methomyl is identical. The details of the experimental set-up are already explained in chapter 3 (Section 3.2.2; Figure 3.1). The only modification made in the earlier set-up is that, an external UV source was not kept in the holding tank and provision was made for the introduction of the ozone at the throat of the venturi. The geometric specifications of the circular venturi and the insertion point of ozone are already provided in the chapter 4 (section 4.2.2, Fig.4.1).

6.2.3 Experimental methodology

All the experiments were performed for the duration of 120 min (unless specified otherwise) by using 6 L of pesticide industry effluent with pH adjusted to 7
by adding 1N NaOH. Initially, the holding tank was filled with the effluent to be treated and then the reciprocating pump was started so that effluent will get re-circulated continuously in the experimental set-up. The control valve in the bypass line was used to adjust the desired inlet pressure to the cavitating device by controlling the flow in the main line. The samples were collected after regular interval of time to determine the COD, BOD and TOC values of the samples. Initially, during HC pretreatment the effect of dilution of effluent on COD reduction was studied by using effluent without any dilution and with 5 and 10 times dilution with pH adjusted to 7. The inlet pressure to the cavitating device was 6 bar in all the experiments.

The experiments of pretreatment using a combined process of hydrodynamic cavitation and H$_2$O$_2$ were performed by using various concentrations of H$_2$O$_2$ such as 2, 5 and 10 g/L. All such experiments were performed using 6 bar inlet pressure, 5 times dilution and pH adjusted to 7. The decomposition of H$_2$O$_2$ during these experiments was also evaluated by measuring the concentration of unreacted H$_2$O$_2$ in the effluent by using the DMP method. The experiments of studying the interference of H$_2$O$_2$ on standard COD estimation were carried out by using the various loadings of H$_2$O$_2$ such as 2, 5, 7 and 10 g/L. First the effluent was diluted to different proportions and the COD was measured using a standard method. The COD measured was in the range of 1200 to 6000 mg/L. Keeping the identical dilutions of the effluent, later the COD was measured immediately after adding the fixed quantity of H$_2$O$_2$. The average increase in the COD estimation for various loadings of H$_2$O$_2$ (2, 5, 7 and 10 g/L) was obtained to determine the correlation of COD overestimation.

The effect of loading of ozone on the performance of combined process of hydrodynamic cavitation and ozone was also studied by varying loading of ozone from 0.5 to 3 g/h (0.5, 0.75, 1 and 3 g/h). The flow rate ratios of diluted effluent to ozone corresponding to the loadings of 0.5, 0.75, 1 and 3 g/h of ozone are 0.0000525, 0.000787, 0.001050 and 0.00315 respectively. These values are based on the liquid flow rate of 445 LPH at the chosen inlet pressure of 6 bar to the cavitator. Ozonator with a capacity of 180 W (make- Eltech Engineers, India) was used for generating ozone with a maximum ozone producing capacity of 10 g/h. Oxygen generator (capacity – 420 W and oxygen output - 1–5 LPM) was used to produce the oxygen (94% purity) since it is a feed to the ozonator for producing the ozone. The generated ozone was then constantly injected at the throat of the venturi.
6.2.4 Analysis

The samples withdrawn after pretreatment were centrifuged at 4500 rpm (5660 g relative centrifugal force) to remove the solid particles and supernatant was subjected to the further physico-chemical analysis. The COD and BOD analysis were carried out as per the standard methods (APHA, 1998). The degree of mineralization of industrial effluent into end products (such as CO₂ and H₂O) was analyzed using a total organic carbon analyzer (make-Shimadzu Corporation, Japan) at various optimum conditions. The concentration of H₂O₂ was determined by the spectrophotometric method (λ<sub>max</sub> of Cu(DMP)<sup>2+</sup> complex- 454 nm) using copper (II) ion and DMP (2,9-Dimethyl-1,10-phenanthroline) (Kosaka et al., 1998). The calibration chart prepared for the determination of concentration of H₂O₂ is illustrated in Fig. 6.1.

![Calibration chart for the determination of H₂O₂ using DMP method](image)

Fig. 6.1 Calibration chart for the determination of H₂O₂ using DMP method

6.3 Results and discussion

6.3.1 Effect of dilution on COD reduction using hydrodynamic cavitation (HC)

The effect of dilution of wastewater effluent on the rate and extent of COD reduction has been studied by utilizing different dilutions of the effluent viz. no dilution, 1:5 dilution and 1:10 dilution for the pre-treatment using hydrodynamic
cavitation. All the experiments were carried out for the duration of 90 minutes using 6 L of the effluent with desired dilution and by keeping the inlet pressure to the venturi as 6 bar. The initial pH of the effluent was adjusted to 7 (by adding 5 N NaOH) in order to neutralize the effect of chloride ions present in the effluent which may cause corrosion of the experimental setup (Zhao et al, 2008). The COD analysis was performed using the standard method for the samples withdrawn at the regular interval of time during these experiments. The results obtained have been depicted in the Fig. 6.2 which indicated that the rate of COD reduction obtained using pre-treatment of hydrodynamic cavitation follows first order kinetics for all the dilutions studied.

![Fig. 6.2 Effect of dilution on the mineralization of pesticide industry effluent (Subjected to: treatment volume- 6L, inlet pressure- 6 bar, pH-7)](image)

It has been observed that, with an increase in the extent of dilution, the rate of COD removal is also increasing monotonically with the maximum COD reduction of 21% obtained using 1:10 dilution of industrial effluent. However, an increase in the extent of dilution has shown a negative impact on the actual moles of pollutant degraded (based on COD values). The rate constant of COD removal (k), extent of COD reduction and moles of pollutant degraded at various dilutions of effluent have been summarized in Table 6.2.
Table 6.2
Rate constant of COD removal (k), extent of COD reduction and moles of pollutant degraded at various dilutions of effluent.

<table>
<thead>
<tr>
<th>Process</th>
<th>Rate constant of COD removal, ( k \times 10^3 ) min(^{-1} )</th>
<th>Percent COD reduction after 2 h</th>
<th>( C_{A0} ), based on COD, moles/L</th>
<th>( C_{A0} - C_{A} ), based on COD, moles/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC, No dilution</td>
<td>1.09</td>
<td>8.98</td>
<td>0.386</td>
<td>0.0473</td>
</tr>
<tr>
<td>HC, 1:5 dilution</td>
<td>1.38</td>
<td>14.77</td>
<td>0.0825</td>
<td>0.0126</td>
</tr>
<tr>
<td>HC, 1:10 dilution</td>
<td>2.63</td>
<td>21.42</td>
<td>0.035</td>
<td>0.0095</td>
</tr>
</tbody>
</table>

It can be seen that, with an increase in the extent of dilution, although the extent of COD reduction is increasing, effective number of moles of pollutant degraded have reduced. Hence, the use of much diluted effluent for the pre-treatment using hydrodynamic cavitation is not a promising option for effective treatment of pesticide industry effluent. The results obtained are consistent with the earlier reports indicating that, the rate of removal of pollutants under cavitating conditions is inversely proportional to the initial concentration of the pollutant.

Chakinala et al. (2008a) have studied the effect of dilution of industrial wastewater effluent on the extent of COD and TOC removal. The extent of COD removal in 150 min of treatment time was 42 %, 62 % and 73 % for a dilution ratio of 10, 25 and 50 respectively. It was clearly observed that the extent of COD reduction does increase appreciably with an increase in the extent of dilution, but not the actual moles of the effluent. Padoley et al. (2012) have also studied the effect of dilution on mineralization of distillery wastewater. The original wastewater (34,000 mg/L COD) was diluted to 25% and 50% concentration (%) using tap water and was treated using hydrodynamic cavitation. It was observed that the dilution has no significant effect on the mineralization of distillery wastewater, since the COD and TOC reduction was lower at 25 % and 50 % dilution as compared to undiluted wastewater. It is also important to note here that, an increase in the dilution of the effluent will increase the total amount of wastewater to be treated and hence will increase the cost of treatment as well. Keeping this in mind, all further experiments were performed using only 5 times diluted effluent.
6.3.2 Effect of loading of ozone on the mineralization of the effluent using HC+Ozone

Ozonation process has attracted the attention of many researchers since it is capable of oxidizing the organic pollutants due to its high oxidation potential of 2.08 eV. However, during the conventional ozonation process, the rate of reaction of ozone with pollutant molecule is not very significant due to high mass transfer resistances in aqueous solutions (Zhang et al., 2006). The combination of HC and ozone can enhance the rate of reaction of ozone with pollutant molecules since local turbulence created by cavitation can increase the mass transfer of ozone from gas phase to the bulk liquid phase (Wu et al., 2011). In addition to this, highly reactive hydroxyl radicals are generated by the reaction of water molecule and the atomic oxygen (O) generated by the dissociation of ozone molecule in the presence of cavitation (Gore et al., 2014). Hence the combination of hydrodynamic cavitation and ozone can be a promising option for the treatment of wastewater. With this background, the effect of loading of ozone on the extent of mineralization of pesticide industry effluent has been evaluated by applying HC + Ozone process and by varying the loading of ozone from 0.5 to 3 g/h. All the experiments have been carried at an inlet pressure of 6 bar and pH of 7 and the samples withdrawn at regular interval of time were subjected to COD and TOC analysis. It can be seen from the Fig. 6.3 and Fig. 6.4 that, with an increase in the loading of ozone, the rate of COD as well as TOC reduction increases.

The rate constant (k), extent of COD and TOC reduction and the moles of pollutant degraded at various loadings of O$_3$ are summarized in Table 6.3. The rate and the extent of COD reduction of $1.38 \times 10^{-3}$ min$^{-1}$ and 14.77 % obtained by using individual hydrodynamic cavitation have enhanced significantly (approximately by 80%) to $2.47 \times 10^{-3}$ min$^{-1}$ and 25.69 % by using HC in combination with 0.75 g/h of ozone. A similar trend has also obtained in case of the effect of other loadings of ozone on the rate and extent of TOC reduction. Although, efficacy of HC has increased noticeably in the presence of ozone, increasing the loading of ozone beyond 0.75 g/h (Ozone to liquid flow rate ratio as 0.000787) has shown only marginal increase in the rate of COD and TOC reduction. Similarly, the moles of effluent degraded have also not increased very significantly by increasing the loading of ozone beyond 0.75 g/h. Hence, an optimal loading of ozone should be used in the combined process of HC and ozone, for the effective and economical treatment of industrial wastewater effluent.
Fig. 6.3 Effect of loading of ozone on the COD reduction of pesticide industry effluent (Subjected to: treatment volume- 6L, inlet pressure- 6 bar, pH-7)

Fig. 6.4 Effect of loading of ozone on the TOC mineralization of pesticide industry effluent (Subjected to: treatment volume-6L, inlet pressure-6 bar, pH-7)

The treatment of actual pesticide industry effluent using combination of HC and ozone is studied in the present research work for the first time to the best of our knowledge. However, the combined process of cavitation and ozone has been studied
in the past for the treatment of synthetic wastewater containing single organic pollutant and has observed to be more effective than the individual processes. Gore et al. (2014) have observed that the efficiency of HC for the degradation of reactive orange 4 dye (RO₄) enhances significantly by combining it with ozone. TOC reduction of 14.67% obtained in case of HC has increased to 76.25% when HC was coupled with ozone. Similarly, Wu et al. (2011) have also demonstrated the enhanced effect of suction-cavitation on the ozonation of phenol using orifice as a cavitator.

Table 6.3
Rate constant (k), extent of COD and TOC reduction and moles of pollutant degraded at various loadings of O₃

<table>
<thead>
<tr>
<th>Process</th>
<th>Rate constant for COD removal in k × 10⁻³ min⁻¹</th>
<th>Rate constant for TOC removal in k × 10⁻³ min⁻¹</th>
<th>% COD reduction after 2 h</th>
<th>% TOC reduction after 2 h</th>
<th>Cₐ₀-Cₐ based on COD, moles/ L</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC</td>
<td>1.38</td>
<td>0.56</td>
<td>14.77</td>
<td>6.58</td>
<td>0.0126</td>
</tr>
<tr>
<td>HC+ Ozone, 0.5 g/h</td>
<td>1.66</td>
<td>1.01</td>
<td>19.08</td>
<td>10.92</td>
<td>0.0146</td>
</tr>
<tr>
<td>HC+ Ozone, 0.75 g/h</td>
<td>2.47</td>
<td>1.5</td>
<td>25.69</td>
<td>16.63</td>
<td>0.0203</td>
</tr>
<tr>
<td>HC+ Ozone, 1.0 g/h</td>
<td>2.94</td>
<td>1.89</td>
<td>29.98</td>
<td>19.36</td>
<td>0.0238</td>
</tr>
<tr>
<td>HC+ Ozone, 3.0 g/h</td>
<td>3.45</td>
<td>2.48</td>
<td>36.26</td>
<td>26.204</td>
<td>0.0272</td>
</tr>
</tbody>
</table>

6.3.3 Effect of HC and HC + Ozone processes on the biodegradability index

Biodegradability index (BI), a ratio of BOD₅: COD is a measure of the extent to which a wastewater is amenable to biodegradation (Padoley et al., 2012). A minimum BI of 0.3–0.4 is needed for an effective treatment of wastewater using microbial action (Metcalf & Eddy, 2nd ed., 1979). Wastewater effluent pre-treatment using hydrodynamic cavitation or its combination with ozone can reduce the toxicity of wastewater and thus can enhance its biodegradability. The biodegradability index of the pesticide industry effluent has been evaluated after the pre-treatment of HC or HC + Ozone processes and the results obtained have been summarized in Table 6.4. It
has been observed that pre-treatment of HC for either diluted or non-diluted effluent could lead to only marginal enhancement in the BI even after 120 min of treatment time. However, the pre-treatment of combination of HC and ozone process has shown significant impact on the biodegradability of the wastewater effluent. The BI of the effluent has substantially increased from 0.121 to 0.324 after pre-treatment of HC + Ozone (3 g/h) over the treatment duration of 120 min.

Table 6.4
Effect of HC and HC+ Ozone processes on biodegradability index

<table>
<thead>
<tr>
<th>Process</th>
<th>Time in minutes</th>
<th>Number of passes</th>
<th>COD mg/L</th>
<th>BOD mg/L</th>
<th>BOD/COD</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC, No dilution</td>
<td>0</td>
<td>0</td>
<td>12360</td>
<td>1490</td>
<td>0.121</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>108</td>
<td>11490</td>
<td>1740</td>
<td>0.151</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>216</td>
<td>11250</td>
<td>1805</td>
<td>0.160</td>
</tr>
<tr>
<td>HC, 1:5 dilution</td>
<td>0</td>
<td>0</td>
<td>2640</td>
<td>325</td>
<td>0.123</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>108</td>
<td>2420</td>
<td>375</td>
<td>0.155</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>216</td>
<td>2250</td>
<td>400</td>
<td>0.178</td>
</tr>
<tr>
<td>HC+ Ozone, Ozone-1.0 g/h</td>
<td>0</td>
<td>0</td>
<td>2560</td>
<td>320</td>
<td>0.125</td>
</tr>
<tr>
<td>1:5 dilution</td>
<td>60</td>
<td>108</td>
<td>2070</td>
<td>460</td>
<td>0.222</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>216</td>
<td>1794</td>
<td>510</td>
<td>0.284</td>
</tr>
<tr>
<td>HC+ Ozone, Ozone-3.0 g/h</td>
<td>0</td>
<td>0</td>
<td>2570</td>
<td>322</td>
<td>0.125</td>
</tr>
<tr>
<td>1:5 dilution</td>
<td>60</td>
<td>108</td>
<td>2097</td>
<td>470</td>
<td>0.224</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>216</td>
<td>1638</td>
<td>530</td>
<td>0.324</td>
</tr>
</tbody>
</table>

Similar observation has been reported by Padoley et al. (2012) while studying the effect of HC pre-treatment for distillery wastewater. It was observed that, the HC treatment of distillery wastewater (with 25 % dilution) at an inlet pressure of 13 bar results into an increase in the BI from 0.14 to 0.32 after 50 min. It was reported that, HC pre-treatment results in an increase in the efficiency of the conventional biological process by almost 6 times in terms of COD removal and biogas formation. Bis et al. (2015) have also observed that the application of HC can enhance the biodegradability index of the mature landfill leachate. The orifice plate having three holes of 10 mm
diameter and cavitation number of 0.033 was observed to be the most favourable for enhancing the biodegradability index of mature leachate. Using this configuration and maintaining 30 recirculation passes through the cavitation zone at an inlet pressure of 7 bar, the highest increase of biodegradability index (BI) was observed. The results obtained were attributed to the physical and chemical effects of cavitation.

Overall, it has been observed that HC in combination with ozone can effectively be utilized for reducing the toxicity and thereby enhancing the biodegradability index of the pesticide wastewater effluent. The combined process of HC and ozone can be used as a pre-treatment tool since an increase in the BI of the wastewater makes it suitable for further treatment by the conventional biological processes.

6.3.4 Effect of loading of H$_2$O$_2$ on the TOC reduction using HC + H$_2$O$_2$ process

Hydrogen peroxide being a potential oxidant can be used for enhancing the efficacy of hydrodynamic cavitation since it dissociates easily in the presence of cavitation providing additional highly reactive hydroxyl radicals (Saharan et al., 2012). The effect of loading of H$_2$O$_2$ on the TOC reduction has been evaluated by using the various loadings of H$_2$O$_2$ viz. 2, 5 and 10 g/L for the treatment of pesticide industry effluent (5 times diluted) with pH adjusted to 7. The results obtained have been depicted in Fig. 6.5, which indicated that the effect of H$_2$O$_2$ on the TOC values of the effluent during the combined process of HC and H$_2$O$_2$ followed first order kinetics.

Table 6.5 summarizes the values of rate constant (k) and extent of TOC reduction and moles of the effluent degraded (based on TOC) after 120 min of operation. The results obtained have clearly shown that the rate and extent of TOC reduction increases with an increase in the loading of H$_2$O$_2$. The combined process of HC and H$_2$O$_2$ was observed to more efficient than HC operated individually, since the rate constant of $0.56 \times 10^{-3}$ min$^{-1}$ (TOC reduction- 6.58%) obtained using only HC was significantly enhanced to $2.42 \times 10^{-3}$ min$^{-1}$ (TOC reduction- 22.85%) by using HC in combination with 2 g/L of H$_2$O$_2$. Similarly, degraded moles of the pollutant from pesticide industry effluent ($C_{A0}$-$C_A$ based on TOC) in case of individual HC ($4.614 \times 10^3$ moles) has also increased appreciably by using HC in combination with 2 g/L of H$_2$O$_2$ ($1.749 \times 10^2$ moles).
Fig. 6.5 Effect of loading of H$_2$O$_2$ on the TOC mineralization of pesticide industry effluent (SubJECTED to: treatment volume- 6L, inlet pressure- 6 bar, pH-7)

However, further increase in the loading of H$_2$O$_2$ has shown a monotonic increase in the TOC reduction, even though loading of H$_2$O$_2$ increases even by 5 times i.e. from 2 g/L to 10 g/L. Hence, optimized loading of H$_2$O$_2$ should be used for effective mineralization of pesticide effluent. The results obtained are attributed to the fact that at very high loading of H$_2$O$_2$ the detrimental effects are observed due to recombination/ scavenging of OH$^\cdot$ radicals by H$_2$O$_2$ present. In a similar study of treatment of actual industrial wastewater effluent, Chakinala et al. (2008a) have also observed that the efficacy of hydrodynamic cavitation enhances appreciably by using it in combination with H$_2$O$_2$. It was found that the extent of TOC reduction increases with an increase in the loading of H$_2$O$_2$ although enhancement in the TOC reduction was marginal at higher loading of H$_2$O$_2$. 
Table 6.5
Rate constant (k) and extent of TOC reduction and moles of pollutant degraded at various loadings of H$_2$O$_2$

<table>
<thead>
<tr>
<th>Process</th>
<th>Rate constant for TOC removal, k ×10$^{-3}$ min$^{-1}$</th>
<th>% TOC reduction</th>
<th>$C_{A_0}$ based on TOC moles/L</th>
<th>$C_{A_0} - C_A$ based on TOC moles/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC</td>
<td>0.56</td>
<td>6.58</td>
<td>0.071</td>
<td>4.614E-03</td>
</tr>
<tr>
<td>HC + H$_2$O$_2$, 2 g/L</td>
<td>2.42</td>
<td>22.85</td>
<td>0.0694</td>
<td>1.749E-02</td>
</tr>
<tr>
<td>HC + H$_2$O$_2$, 5 g/L</td>
<td>3.86</td>
<td>37.66</td>
<td>0.07177</td>
<td>2.661E-02</td>
</tr>
<tr>
<td>HC + H$_2$O$_2$, 10 g/L</td>
<td>6.02</td>
<td>54.87</td>
<td>0.07551</td>
<td>3.884E-02</td>
</tr>
</tbody>
</table>

6.3.5 Influence of H$_2$O$_2$ on the standard COD estimation of the effluent

While studying the effect of H$_2$O$_2$ on the COD reduction it was observed that the COD values of the effluent samples were increasing rather than decreasing after the pretreatment using combined process of HC and H$_2$O$_2$. These abnormal results were due to the interference by H$_2$O$_2$ since COD overestimation was not observed during pretreatment with combined process of HC and ozone. To confirm the existence and extent of H$_2$O$_2$ interference on the COD estimation, COD analysis was performed using different loadings of H$_2$O$_2$ viz. 2, 5, 7 and 10 g/L. The samples were prepared by using the various dilutions of the effluent and COD analysis was carried out immediately after adding fixed quantity of H$_2$O$_2$. The COD analysis of the effluent was also carried out without addition of H$_2$O$_2$ keeping extent of dilutions identical. Later, the COD overestimation was obtained by determining the increase in the COD values due to the addition H$_2$O$_2$. The COD overestimation of the effluent due addition of 2, 5, 7 and 10 g/L of H$_2$O$_2$ is as shown in Fig 6.6.
Fig. 6.6 COD overestimation due to addition of various loading of H$_2$O$_2$

It was confirmed that the presence of hydrogen peroxide leads to an overestimation of the COD values and the extent of COD overestimation was found to
be directly proportional to the concentration of H₂O₂ used. The average increase in the COD values was estimated for various loadings H₂O₂ to determine the correlation of COD overestimation. Fig. 6.7 establishes the correlation of COD overestimation as a function of concentration of H₂O₂. It has been observed that the average COD overestimation of pesticide wastewater effluent is 0.441 mg/L for 1 mg/L of H₂O₂. Many other previous reports have also confirmed the interference of H₂O₂ on the COD estimation (Kang et al., 1999; Kuo, 1992 and Lee et al., 2011). Hydrogen peroxide leads to the COD overestimation since it gets consumed during COD analysis as per the oxidation reaction given in Eq. 6.1 (Talinli and Anderson, 1992) leading to more utilization of potassium dichromate and higher COD values.

\[
K_2Cr_2O_7 + 3H_2O_2 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3O_2 \quad (6.1)
\]

Lee et al. (2011) have reported that based on Eq. 6.1 theoretical COD value of 1 mg/L of H₂O₂ is 0.470 mg/L. The COD overestimation of 0.441 mg/L for 1 mg/L of H₂O₂ obtained in the present work is marginally lower than the theoretical one, since some fraction of H₂O₂ might have got consumed in the oxidation of effluent even though COD analysis was carried out immediately after the addition of H₂O₂. Thus, in short the results shown in Fig. 6.7 indicating the linearity between COD overestimation and the loading of H₂O₂, imply that the extent of COD overestimation during oxidation can be determined by correlating COD values with the H₂O₂ concentration, although the exact COD overestimation correlation is dependent on the type of the wastewater under question.

### 6.3.6 Effect of loading of H₂O₂ on the rate of COD reduction using HC + H₂O₂ process (based on corrected COD values)

For studying the effect of loading of H₂O₂ on the rate of COD reduction, the determination of residual concentration of H₂O₂ and corrected COD values is very essential. Fig. 6.8 shows the change in the residual concentration of H₂O₂ during the combined process of HC and H₂O₂. It was observed that the residual concentration of H₂O₂ is decreasing with time for all the loadings of H₂O₂ during HC + H₂O₂ process. The results obtained have clearly indicated that very high loading of H₂O₂ is not very beneficial, since the rate of decomposition of H₂O₂ was decreasing with an increase in the initial loading of H₂O₂. The values of residual concentration of H₂O₂ have been
used to obtain the extent of COD overestimation, which is further used for estimating the true/corrected values of COD as below.

Extent of COD overestimation in mg/L = residual conc. of H$_2$O$_2$ in mg/L × 0.441
True/ Corrected COD in mg/L = measured COD value - extent of COD overestimation

The corrected COD values obtained have been used further to study the effect of loading of H$_2$O$_2$ on the rate of COD reduction at various loadings of H$_2$O$_2$ viz. 2, 5 and 10 g/L. The results obtained have been illustrated in Fig. 6.9.

**Fig. 6.8 First order rate of decomposition of H$_2$O$_2$ during HC + H$_2$O$_2$ Process**

Trends of the results obtained while studying the effect of loading of H$_2$O$_2$ on the rate of TOC and COD reduction are very similar, which indicated that the combined process of HC and H$_2$O$_2$ is more efficient than HC alone for reducing the toxicity of wastewater effluent. The details of the rate constant (k) and extent of COD reduction and moles of effluent degraded at various loadings of H$_2$O$_2$ are summarized in Table 6.6. It has been observed that rate and extent of COD reduction increases monotonically with an increase in the loading of H$_2$O$_2$, since the rate of COD reduction obtained in case of 2 g/L of H$_2$O$_2$ has not increased significantly even after increasing the loading of H$_2$O$_2$ by 5 times i.e. to 10 g/L.
Fig. 6.9 Effect of loading of H$_2$O$_2$ on the COD reduction of pesticide industry effluent (Based on corrected COD values)

Table 6.6
Rate constant (k) and extent of COD reduction and moles of pollutant degraded at various loadings of H$_2$O$_2$

<table>
<thead>
<tr>
<th>Process</th>
<th>k × 10$^{-3}$ min$^{-1}$</th>
<th>% COD reduction after 120 min.</th>
<th>C$_{A0}$ moles/L</th>
<th>C$<em>{A0}$-C$</em>{A}$ moles/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC</td>
<td>1.382</td>
<td>14.77</td>
<td>0.0825</td>
<td>0.012607504</td>
</tr>
<tr>
<td>HC + H$_2$O$_2$, 2 g/L</td>
<td>2.676</td>
<td>28.8</td>
<td>0.0806</td>
<td>0.022144768</td>
</tr>
<tr>
<td>HC + H$_2$O$_2$, 5 g/L</td>
<td>4.547</td>
<td>42.36</td>
<td>0.0801</td>
<td>0.033642336</td>
</tr>
<tr>
<td>HC + H$_2$O$_2$, 10 g/L</td>
<td>7.259</td>
<td>60.21</td>
<td>0.0818</td>
<td>0.047610368</td>
</tr>
</tbody>
</table>

Similarly, moles of the pollutant degraded based on COD values have not enhanced proportionately with an increase in the loading of H$_2$O$_2$. Hence, based on the rate of decomposition of residual H$_2$O$_2$ and the rate of COD reduction it has been concluded that even though the efficacy of hydrodynamic cavitation greatly enhances in the presence of H$_2$O$_2$ the use of very high loading of H$_2$O$_2$ should be avoided for...
the sake of any apparent increased rate of COD reduction. In the multivariate analysis of mineralization of phenol using hydrodynamic cavitation, Chakinala et al. (2008b) have also indicated that an optimum loading of H\textsubscript{2}O\textsubscript{2} must be used for enhancing the efficacy of HC, since an excess amount acts as a scavenger of hydroxyl radicals and also contribute to the excess COD of the pollutant.

6.3.7 Comparison of energy efficiency and cost effectiveness

The energy efficiency of cavitation based processes can be expressed in terms of cavitational yield, which is defined as the ratio of quantifiable effects of cavitation per unit energy supplied to the system (Sivakumar and Pandit, 2002). In the present study, the cavitational effects have been measured on the basis of number of moles of wastewater pollutant degraded, whereas the power consumption (KWh/m\textsuperscript{3}) and the cost of electricity (Rs/m\textsuperscript{3}) have been evaluated on the basis of treatment time required for obtaining the 60 \% COD reduction. Table 6.7 provides the comparison of energy efficiency and cost effectiveness of various processes such as HC and its combination with various loadings of H\textsubscript{2}O\textsubscript{2} or ozone.

Table 6.7
Comparison of cavitational yield and cost effectiveness of various processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Cavitational yield, moles effluent degraded/J</th>
<th>Rate constant, k (based on COD) \textsuperscript{min\textsuperscript{-1}}</th>
<th>Treatment time in h to achieve the 60% COD reduction</th>
<th>Power consumption in KWh/m\textsuperscript{3}</th>
<th>Cost of electricity Rs./m\textsuperscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC (1:5 dilution)</td>
<td>1.589E-09</td>
<td>1.38E-03</td>
<td>11.050</td>
<td>2025.89</td>
<td>10250.99</td>
</tr>
<tr>
<td>HC + H\textsubscript{2}O\textsubscript{2}, 2 g/L</td>
<td>2.796E-09</td>
<td>2.68E-03</td>
<td>5.707</td>
<td>1046.26</td>
<td>5294.05</td>
</tr>
<tr>
<td>HC + H\textsubscript{2}O\textsubscript{2}, 5 g/L</td>
<td>4.248E-09</td>
<td>4.55E-03</td>
<td>3.359</td>
<td>615.74</td>
<td>3115.65</td>
</tr>
<tr>
<td>HC + H\textsubscript{2}O\textsubscript{2}, 10 g/L</td>
<td>6.011E-09</td>
<td>7.26E-03</td>
<td>2.104</td>
<td>385.70</td>
<td>1951.63</td>
</tr>
<tr>
<td>HC+ Ozone, 0.75 g/h</td>
<td>1.658E-09</td>
<td>2.47E-03</td>
<td>6.183</td>
<td>1751.79</td>
<td>8864.07</td>
</tr>
<tr>
<td>HC+ Ozone, 1.0 g/h</td>
<td>1.943E-09</td>
<td>2.94E-03</td>
<td>5.194</td>
<td>1471.74</td>
<td>7447.03</td>
</tr>
<tr>
<td>HC+ Ozone, 3.0 g/h</td>
<td>2.224E-09</td>
<td>3.45E-03</td>
<td>4.427</td>
<td>1254.18</td>
<td>6346.16</td>
</tr>
</tbody>
</table>
The major fraction of the operating cost of these processes is typically utilized for supplying the electrical energy to the system, since the cost of reagents such as H₂O₂ is very nominal as compared to the cost of electrical energy (Weng et al., 2013). Due to this, the cost of reagents is neglected in the present study, while determining the cost effectiveness of various processes. It has been observed that the energy efficiency of individual hydrodynamic cavitation notably enhances by combining it with H₂O₂. The cavitational yield of 1.589×10⁻⁹ moles/J obtained in the case HC has approximately enhanced by 2, 3 and 4 times as a result of combining it with 2, 5 and 10 g/L of H₂O₂ respectively. It has also been observed that the power consumption of individual hydrodynamic cavitation is very high due to the low rate of COD reduction leading to high treatment time. This makes the application of only HC a non-feasible and expensive option for the treatment of industrial wastewater effluent. However, the operating cost of the HC can be reduced if the wastewater effluent is available at considerable hydrostatic heads or pressures. In that case treatment cost of HC can be reduced by designing the pressure reduction devices in such a way that they will work in a hydrodynamic cavitation mode, without a supply of any additional energy (Jyoti and Pandit, 2004).

A marginal enhancement in the energy efficiency and cost effectiveness was observed by combining HC with ozone. This is because additional energy (ozonator-180W and oxygen concentrator -420W) supplied to generate the ozone has not shown significant enhancement in the rate of COD reduction. Due to this, the combined application HC and ozone is not very economically attractive if applied for the treatment of pesticide industry wastewater effluent under question. However, it can be used as a pretreatment tool for increasing the BI, which can be further treated with simple biological means. Another option for reducing the treatment cost of HC is to use it in combination with the optimum loading of H₂O₂. It was observed that moles of pollutant degraded in case of HC has increased substantially by using HC in combination with H₂O₂, even though energy supplied to both processes is identical. The combination of HC with H₂O₂ is found to be a relatively cost-effective option; since it has significantly reduced the treatment time required for obtaining a desired COD reduction leading to less power consumption. The electrical cost of 10250.99 Rs./m³ incurred during HC has drastically reduced to 1951.63 Rs/m³ (i.e. almost by 4 times) when HC was combined with 10 g/L of H₂O₂. The results obtained are attributed to the fact that hydrogen peroxide can easily dissociate in presence of
hydrodynamic cavitation leading to increased generation of hydroxyl radicals resulting into higher rate of COD reduction. Although, cost of electricity has appreciably reduced due to the combination of HC and H₂O₂, even the reduced cost is excessive and cannot be observed by a pesticide manufacturing unit and hence additional optimization is needed. However, this work has indicated the direction of the future effort needed.

6.4. Conclusions

The treatment of actual pesticide industry effluent using HC and its combination with H₂O₂ and ozone has established the following important conclusions:

- The efficacy of hydrodynamic cavitation does not get enhanced appreciably by increasing the extent of dilution of the pesticide industry effluent.
- The rate and extent of COD reduction of 1.38 × 10^{-3} \text{ min}^{-1} and 14.77 \% obtained by using individual hydrodynamic cavitation have enhanced significantly (approximately by 80\%) to 2.47 × 10^{-3} \text{ min}^{-1} and 25.69 \% by using HC in combination with 0.75 g/h of ozone. Similarly, the rate and extent of TOC reduction of 0.56 × 10^{-3} \text{ min}^{-1} and 6.58 \% obtained in case of HC has also enhanced to 1.5 × 10^{-3} \text{ min}^{-1} and 16.63 \% by using HC+ Ozone process. The treatment of the pesticide industry effluent using HC + Ozone (3 g/h) process for the duration of 120 min enhanced the biodegradability index of the effluent from 0.121 to 0.324 making it suitable for the microbial degradation.
- The rate of TOC and COD reduction of 0.56 × 10^{-3} \text{ min}^{-1} and obtained in case of individual hydrodynamic cavitation has also enhanced roughly by 10 and 5 times by using HC in combination with 10 g/L of H₂O₂ respectively.
- The combined process of HC and H₂O₂ has proved to be the most energy efficient and cost effective since electrical cost of 10250.99 Rs. /m³ incurred during HC has appreciably reduced to 1951.63 Rs. /m³ (i.e. almost by 4 times) when HC was combined with 10 g/L of H₂O₂. Although the cost incurred during HC has successfully reduced by combining it with process intensifying agents, the reduced treatment costs are still prohibitive. However, this work has clearly indicated the direction in which more efforts are needed.
Appendix 6A

Sample calculation for determination of cavitational yield and cost of electricity for the combined process of hydrodynamic cavitation and ozone

Moles of the effluent degraded after 120 min (based on COD) = 0.0272 moles/L

Electrical power supplied = 1.7 kW

Treatment volume = 6 L, Ozone supplied = 3.0 g/h

Energy input to the system in 120 min

\[ = \text{Energy input to (HC + ozonator + oxygen concentrator)} \times \text{Time in sec} \]
\[ = (1100 + 180 + 420) \times 120 \times 60 = 1.224 \times 10^7 \text{ J} \]

Cavitational yield in moles of effluent degraded per unit energy supplied

\[ = \frac{\text{Moles of the effluent degraded}}{\text{Energy input to the system in 120 min.}} \]
\[ = 2.224 \times 10^{-9} \text{ moles degraded/J} \]

First order reaction rate constant, \( k = 3.45 \times 10^{-3} \text{ min}^{-1} \)

Treatment time required for obtaining 60 % COD reduction (t)

\[ = \frac{\ln(40/100)}{k} = 4.427 \text{ h} \]

Power consumption

\[ = \frac{\text{Electrical power supplied} \times \text{Treatment time}}{\text{Treatment volume}} \]
\[ = 1.7 \times 4.427 / 6 \times 10^{-3} = 1254.18 \text{ kWh/ m}^3 \]

Cost of electrical energy required (considering 1 kWh = Rs. 5.06/-)

\[ = 1254.18 \times 5.06 = 6346.16 \text{ Rs./ m}^3 \]

References


