

1       **Mineralisation of 2,4-dichlorophenoxyacetic acid by acoustic**  
2       **or hydrodynamic cavitation in conjunction with the**  
3       **Advanced Fenton Process**

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18  
19       **Abstract**

20  
21       The mineralisation of 2,4-dichlorophenoxyacetic acid (2,4-D) in  
22       the presence of zero-valent iron and hydrogen peroxide (the  
23       Advanced Fenton process – AFP) whilst being subjected to acoustic  
24       or hydrodynamic cavitation is reported. If the reaction is merely  
25       stirred then there is 57% removal of TOC whilst on irradiation the  
26       figure is 64% although the latter reaction is more rapid. Use of  
27       ultrasound alone results in only 11% TOC removal in 60 min of  
28       treatment time. Addition of iron powder marginally enhances the  
29       extent of degradation but an appreciable increase is observed in the  
30       presence of hydrogen peroxide which acts as a source for hydroxyl  
31       radicals by Fenton chemistry as well as by dissociation in the  
32       presence of ultrasound. The use of hydrodynamic cavitation in  
33       conjunction with the advanced Fenton process has also been found  
34       to be a useful tool for continuous remediation of water  
35       contaminated with 2,4-D. After 20 minutes of treatment the  
36       residual TOC is reduced to 30% and this probably represents the  
37       remaining highly recalcitrant small organic molecules.

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39       *Keywords:* zero valent iron; hydrogen peroxide; total organic  
40       carbon, advanced Fenton process, cavitation.

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## 43 1. Introduction

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45 2,4-Dichlorophenoxyacetic acid (2,4-D) is the most commonly used  
46 herbicide worldwide and owing to its potent auxin-like activity, it is  
47 also employed as a plant growth regulator. 2,4-D breaks down slowly  
48 in water, with a half-life of about 20 days, depending on environmental  
49 conditions and its degradation products are known to accumulate in  
50 the biosphere [1]. Different data have been reported for its toxicity;  
51 the LD<sub>50</sub> for rats is in the range of 100 to 500 mg/kg [2]. Although  
52 the toxic effects of 2,4-D are not completely known as yet, the World  
53 Health Organization has established a maximum tolerable value of 30  
54 µg/L for drinking water. 2,4-D is a pollutant raising great  
55 environmental concern because of its relatively high solubility in water  
56 and its hydrolytic breakdown generates an even more toxic compound,  
57 2,4-dichlorophenol (2,4-DCP). Most microorganisms lack enzyme  
58 systems for degrading these pollutants, which thus tend to accumulate  
59 in water and soil and as a result they are often termed recalcitrant or  
60 refractory compounds. Therefore a very important goal in  
61 environmental research is to develop an effective process for complete  
62 or partial degradation of 2,4-D or 2,4-DCP. Several studies have  
63 recommended advanced oxidation processes (AOPs) such as  
64 photocatalysis, radiolysis or sonolysis to break down and, possibly,  
65 eventually mineralise 2,4-D into non-toxic substances [3-5].

66 Fenton, photo-Fenton and Fenton-related processes have been in  
67 the forefront of the AOPs for the treatment of persistent organic  
68 pollutants in water. All of these processes depend on the generation  
69 of the hydroxyl radical, which is a powerful oxidant. Thus, complete  
70 mineralisation of 2,4-dichlorophenoxyacetic acid (2,4-D) has been  
71 reported using H<sub>2</sub>O<sub>2</sub> and ferrous ion (Fenton's reagent) [6-8] and the  
72 combination of H<sub>2</sub>O<sub>2</sub>/Fe<sup>3+</sup>/UV (photo-Fenton) has also been  
73 investigated extensively [9-12]. More recently the mineralisation of  
74 2,4-D using electrochemical techniques has also been studied [13-15].

75 The use of zero valent iron (ZVI) in a Fenton-type process for  
76 the mineralisation of pollutants has become of considerable interest  
77 over the last few years. Many reports exist of the use of ZVI in  
78 reducing conditions, but it is the presence of oxidants, and hydrogen  
79 peroxide in particular, which is pertinent to the current discussion.  
80 Doong and Chang [16] showed that Fe<sup>2+</sup> and Fe<sup>0</sup> both had a positive  
81 effect on the photo-assisted degradation of organophosphorous  
82 pesticides in the presence of hydrogen peroxide and Bergendahl and  
83 Thies [17] found that ZVI/H<sub>2</sub>O<sub>2</sub> was particularly effective for the  
84 oxidation of MTBE. We have described our results on the use of the  
85 advanced Fenton process (AFP) on the decomposition of the model  
86 pollutants benzoic acid and phenol in a batch process [18] and  
87 followed this up with an HPLC study of the degradation of phenol with  
88 hydroxyl radicals generated from ZVI and H<sub>2</sub>O<sub>2</sub> [19]. Waite et al. [20]  
89 have recently demonstrated that nanoscale zero-valent iron (nZVI)

90 oxidises the herbicide molonite in the presence of oxygen and have  
91 extended their work to batch and column experiments [21].

92 The enhancement of chemical reactions by the application of  
93 ultrasound is now a well-established technology, particularly in the  
94 area of wastewater remediation [22]. Recent reports on the  
95 application of ultrasound in the presence of ZVI to degrade  
96 pentachlorophenol [23] and the use of a novel catalyst in conjunction  
97 with ultrasound for the degradation of phenol [24] has prompted us  
98 now to report our results on the mineralisation of 2,4-D using  
99 ZVI/H<sub>2</sub>O<sub>2</sub>/US.

100 Hydrodynamic cavitation also generates similar conditions to the  
101 use of ultrasound in terms of generation of hydroxyl radicals as well as  
102 local hot spots and has been used for wastewater treatment  
103 applications [25-27]. A combination of hydrodynamic cavitation and  
104 the advanced Fenton process is more effective compared to the use of  
105 hydrodynamic cavitation alone [28] and hence this approach has also  
106 been applied for the degradation of 2,4-D.

107

## 108 **2. Experimental**

### 109 *2.1 Acoustic Cavitation*

110 A 20 kHz commercial ultrasonic processor (Cole Parmer)  
111 equipped with a titanium probe (1 cm diameter) operating in a pulse  
112 mode of 4 s on and 2 s off, was used for the experiments involving  
113 ultrasound. The intensity of the irradiation was adjusted to 50% of  
114 ultrasonic power amplitude, which corresponds to a calorimetric  
115 measurement of about 45 W. In a typical run, the probe was  
116 immersed in a 300 mL cylindrical glass vessel containing an aqueous  
117 solution of 2,4-dichlorophenoxyacetic acid (200 mL; 0.235 g/L), the  
118 pH was adjusted to 3.0 with dilute H<sub>2</sub>SO<sub>4</sub> (0.1 M) and the temperature  
119 was kept constant at 22 ± 2 °C during all reactions by an external  
120 cooling bath. The vessel was fitted with a magnetic stirrer and the  
121 temperature was kept constant at 22 ± 2 °C during all reactions by an  
122 external cooling bath. Samples were taken every 10 min during 60  
123 min of total irradiation time and filtered through 0.45 µm nylon  
124 membranes before being analysed for total organic carbon (TOC) using  
125 wet oxidation analysis (Model 700 TOC Analyser; OI-Analytical) using  
126 sodium persulphate as oxidizing agent and phosphoric acid for  
127 acidification.

128 The same experimental set-up equipped with a magnetic stirrer  
129 instead of the ultrasound probe was used for the silent experiments.  
130 In this case, the temperature was adjusted to 22 ± 2 °C during the  
131 reaction with a cooling bath similar to that employed in the ultrasound  
132 experiments and all results are the average of at least two runs.

133 The appropriate amounts of hydrogen peroxide (30%; 1.7 mL)  
134 and powdered iron (0.12 g) were added to the reactor just before  
135 switching the probe on (reaction time zero) for the experiments  
136 involving the combination treatment scheme.

## 137 2.2 Hydrodynamic cavitation

138 Hydrodynamic cavitation was generated using a specially  
139 constructed unit, termed a Hydrocavitator. The system consists of a  
140 reservoir with a 25 L capacity, a triplex plunger pump (Speck NP25)  
141 with a maximum discharge pressure of 4,500 psi, an orifice unit  
142 (orifice area about  $7. \times 10^{-7} \text{ m}^2$ ) and a catalyst bed. The heat  
143 exchanger ensures that the temperature does not rise above 30 °C. A  
144 schematic representation of the Hydrocavitator is shown in figure 1.  
145 An aqueous solution (8 L) of 2,4-D ( $0.235 \text{ gL}^{-1}$ ) was prepared and  
146 placed in the reservoir and the pH adjusted to 2.5 with 0.1 M  $\text{H}_2\text{SO}_4$ .  
147 The catalyst bed was filled with iron pieces (150 g) made from bending  
148 sheet iron (2 cm by 1 cm) in the middle. Hydrogen peroxide (30%, 46  
149 mL;  $1.9 \text{ gL}^{-1}$ ) was added to the reservoir and the pump was switched  
150 on. The temperature was kept at  $18 \pm 2 \text{ }^\circ\text{C}$  by the heat exchanger;  
151 the working pressure of 1500 psi was selected as being optimum for  
152 cavitation based on our earlier experimental investigations [29] and  
153 the flow rate was  $5.2 \text{ Lmin}^{-1}$ . Samples were removed for TOC analysis  
154 every 10 min with a total reaction time of 90 min.

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## 156 3.0 Results and discussion

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158 Both acoustic and hydrodynamic processes have been utilised to  
159 create cavitational bubbles, which can implode, producing high  
160 temperature and pressure resulting in the formation of hydroxyl  
161 radicals by the decomposition of water. Generally, insufficient radicals  
162 are produced from water alone so the process is often supplemented  
163 with the addition of other oxidants such as hydrogen peroxide and can  
164 be further enhanced with the use of zero valent iron in a pseudo-  
165 Fenton process. One such hybrid technology that has been developed  
166 and patented utilises HC in conjunction with hydrogen peroxide and  
167 zero valent iron to enhance the treatment process [30].

168 Initially, the aqueous solution of 2,4-D was magnetically stirred  
169 and irradiated with ultrasound for 60 min in the absence of all  
170 additives (Figure 2). There was some removal of TOC content but only  
171 after a lag period of about 30 min when the rate increased to give a  
172 final value of 11%. When the above experiment was repeated but  
173 with the addition of iron powder (0.12g) a further slight enhancement  
174 in degradation (18%) over a similar time of treatment was observed.  
175 The presence of iron particles leads to an increase in the cavitational  
176 intensity as the solid particles act as nuclei for surface cavitation  
177 thereby increasing the number of cavitational events occurring in the

178 reactor. Also the presence of iron particles in combination with  
179 hydrogen peroxide generated from the cavitation phenomena results  
180 in Fenton-like chemistry leading to enhanced degradation. Liang et al.  
181 [31] have reported similar observations with sonochemical degradation  
182 of 2 chlorophenol in the presence of iron powder. It is expected that  
183 the contribution of Fenton chemistry to overall wastewater treatment  
184 in this system is low as the amount of hydrogen peroxide formed is  
185 minimal. Thus, in order to enhance the Advanced Fenton degradation  
186 of 2,4-D, extra hydrogen peroxide was added into the reactor.  
187 Experiments were done in the absence and presence of ultrasound and  
188 the results are also shown in Figure 2.

189 When an aqueous solution of 2,4-D is rapidly stirred (magnetic  
190 stirrer) with zero-valent iron powder in the presence of hydrogen  
191 peroxide there is an initial fast drop in residual TOC content over 30  
192 min and then the removal rate falls and begins to level out (Figure 2).  
193 If the identical reaction is repeated but this time ultrasound is applied  
194 to the reaction then an even more rapid degradation of the pollutant is  
195 observed but this also levels off after about 20 min. Cravatto et al.  
196 [32] have reported a similar intensification with the use of ultrasound  
197 for degradation of aromatic halides, halogenated phenols and  
198 polychlorinated biphenyls in polluted waters, whereas Neppolian et al.  
199 [33] have reported comparable results for degradation of methyl tert-  
200 butyl ether. It has also been observed that, although the rate of  
201 removal of TOC is greater for the ultrasonic case, the final results after  
202 one hour of treatment are not vastly dissimilar (57% versus 64%  
203 respectively). The levelling off of the degradation is probably due to  
204 two factors: (a) the  $H_2O_2$  has been consumed after about 40 min in  
205 the case of stirring alone and around 20 min for the US case and (b)  
206 the residual organics are relatively recalcitrant compounds so further  
207 degradation is limited. Previous work [28] has shown that addition of  
208 hydrogen peroxide sequentially or higher amounts of oxidant have  
209 little effect on the overall result as the remaining organics are  
210 recalcitrant under the conditions used. Zhang et al. [34] have also  
211 reported an optimum extent of degradation of CI reactive black 8  
212 which did not increase even with addition of higher dosages of the  
213 oxidant.

214 The results obtained with the use of hydrodynamic cavitation in  
215 conjunction with the advanced Fenton process are shown in Figure 3. It can be  
216 seen that there is a rapid decrease in organic content within 20 min and  
217 thereafter the value remains the same at about 30% residual TOC content. The  
218 addition of more hydrogen peroxide at this stage did not lead to further  
219 reduction in TOC content, similar to the case of ultrasound induced cavitation as  
220 discussed earlier. The effectiveness of the degradation augmented by  
221 hydrodynamic cavitation is probably due to the combined effect of the advanced  
222 Fenton process in producing more hydroxyl radicals and super-efficient mixing  
223 provided by the Hydrocavitator. Our earlier work [28] has also demonstrated

224 intensified degradation of phenolic species by a combination of hydrodynamic  
225 cavitation and advanced Fenton process.

226 It is interesting to compare the efficacies of acoustic and hydrodynamic  
227 cavitation in enhancing the degradation process. It is observed that in 20 min of  
228 treatment time (beyond this time, the increase in the TOC removal is only  
229 marginal), the combination of acoustic cavitation and the advanced Fenton  
230 process gives around 60% TOC removal whereas 70% TOC removal is observed  
231 with hydrodynamic cavitation combined with advanced Fenton process. The  
232 extent of energy supplied for generation of cavitation in the reactor system is  
233 approximately similar in both the cases (450 W/L) though the volume treated  
234 using hydrodynamic cavitation reactors is much higher as compared to acoustic  
235 cavitation reactor (8 L as compared to only 200 mL). Thus, it appears that  
236 hydrodynamic cavitation is more suitable for treating effluent at a much larger  
237 scale of operation as compared to acoustic cavitation generated using a horn  
238 type system. Sivakumar and Pandit [25], Kalumuck and Chahine [27] and  
239 Gogate et al. [35] have reported that the hydrodynamic cavitation reactors are  
240 indeed more energy efficient compared to acoustic cavitation units for a variety  
241 of wastewater treatment applications.

242

#### 243 **4. Conclusions**

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245 The use of zero-valent iron and hydrogen peroxide in  
246 conjunction with acoustic or hydrodynamic cavitation is a very  
247 effective means of destroying high concentrations of 2,4-D. A  
248 combination of advanced Fenton process and cavitation has been  
249 observed to intensify the degradation process by way of turbulence  
250 and generation of additional free radicals. The results achieved using  
251 the Hydrocavitator are particularly good in that this unit operates in a  
252 continuous mode and hence large volumes of contaminated water  
253 might be treated very cost-effectively particularly with low levels of  
254 polluted water, at equivalent energy dissipation levels.

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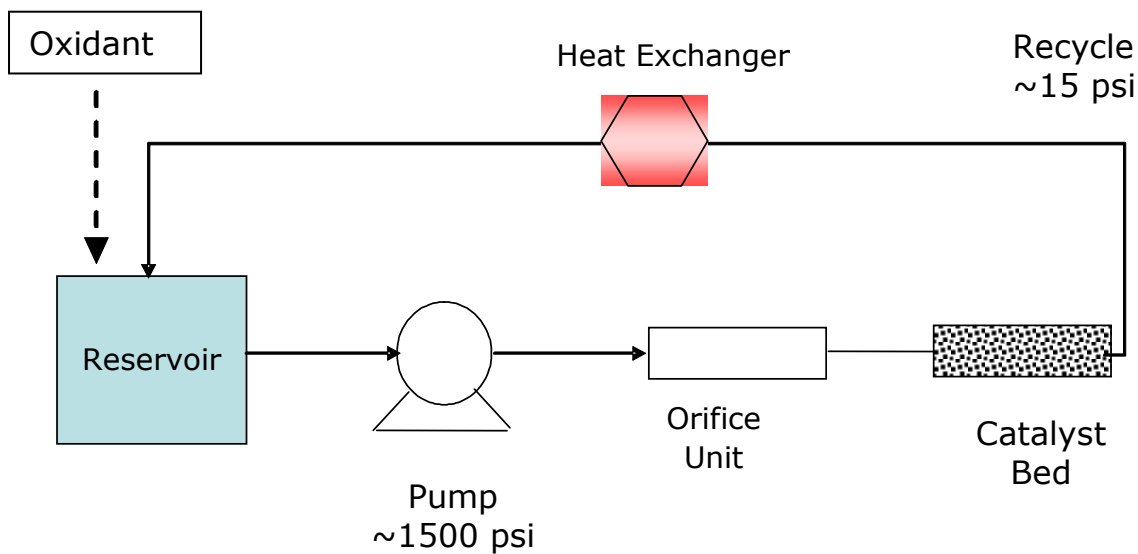
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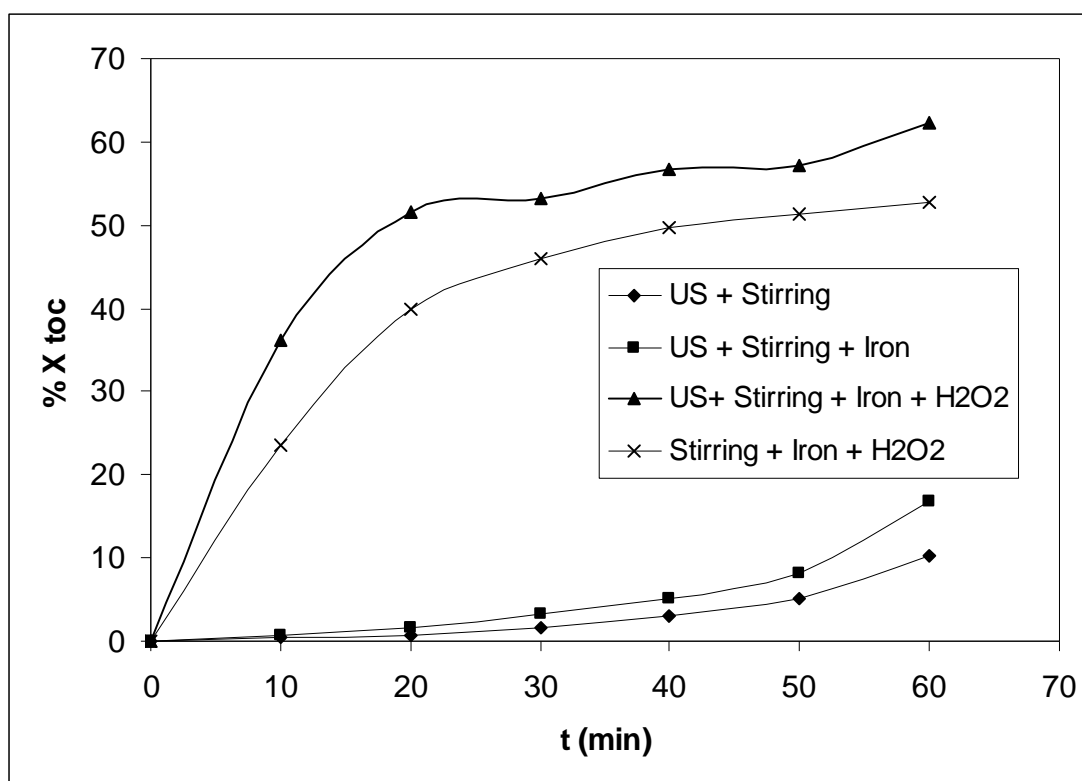
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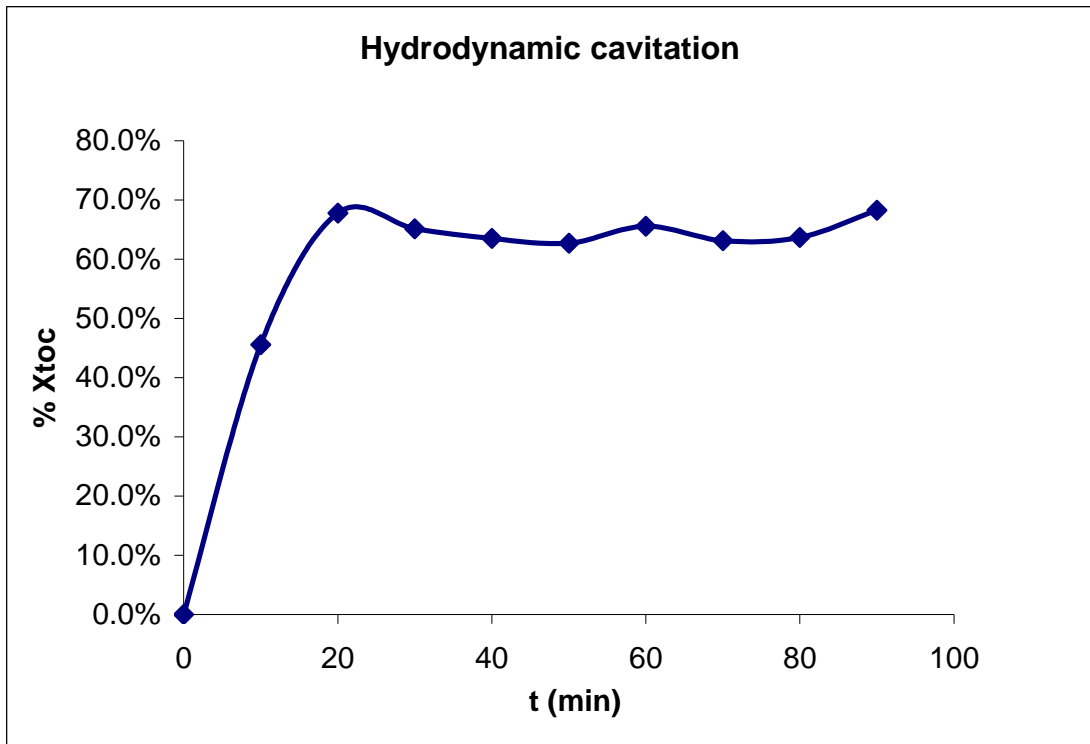
**Figure 1: Schematic representation of the Hydrocavitator**



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**Figure 2: Degradation profile for various treatment schemes involving acoustic cavitation**

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**Figure 3: Degradation profile for the combination of hydrodynamic cavitation and advanced Fenton process**