Chapter 7
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The energy associated with hydrodynamic cavitation (HC) and ultrasonic cavitation (US) based processes has been utilized successfully for the effective degradation of organic pollutants such as imidacloprid and methomyl. Apart from this, the toxicity of actual pesticide industry effluent has also reduced significantly by using HC based processes, making the effluent more amenable to biological operations. The efficacy of cavitation phenomena has enhanced significantly by the application of cavitation based hybrid processes, i.e. the combination of US or HC with various other AOPs such as H$_2$O$_2$, Fenton, photo-Fenton, ozone and photocatalytic process, provided an optimal concentration of additives are used.

The cavitation number ($C_v$) is the important dimensionless parameter which clearly depicts the intensity of cavitation phenomena, since the number density of cavities generated increases with a decrease in the cavitation number and hence, can eventually increase the total collapse pressure generated as a result of cavity collapse. Using a circular venturi as the cavitator, the cavitation number ($C_v$) in the range of 0.15 to 0.17 was found to be the most effective one for the degradation of imidacloprid (Optimum $C_v$-0.163) and methomyl (Optimum $C_v$-0.15). However, a cavitation number below the optimal range leads to the lower intensity of cavity collapse due to the condition of choked cavitation. In addition to the cavitation number, the inlet pressure to the cavitating device can also be used to obtain the flow conditions inside the cavitator. The optimum inlet pressure to the cavitating device required for maximizing the efficacy of hydrodynamic cavitation was 15 bar (throat dia. – 2.5 mm) for imidacloprid and 5 bar (throat dia. -2 mm) for methomyl. In case of ultrasound cavitation, the optimization of power density of the ultrasound processor greatly affects the efficacy of cavitation phenomena. The rate of degradation of methomyl was highest at the optimum power density of 0.155 W/mL. The optimization of initial pH of the solution in case of both HC and US has indicated that an acidic condition favors the rate of degradation of imidacloprid as well as methomyl.

The degradation of imidacloprid using HC based hybrid processes has demonstrated that the combined process of HC and Fenton at the molar ratio of imidacloprid: H$_2$O$_2$ as 1:40 and the molar ratio of Fe$^{2+}$: H$_2$O$_2$ as 1:40 is the most
energy efficient and effective technique resulting in the complete degradation of imidaclorpid with highest cavitational yield of $1.41 \times 10^{-9}$ moles/J and the extent of mineralization of 48.25%. The rate of degradation of $2.565 \times 10^{-3}$ min$^{-1}$ obtained in case of HC alone has dramatically increased to $250.749 \times 10^{-3}$ min$^{-1}$ by using HC in combination with Fenton process leading to the synergistic index of 3.636. The beneficial effects of combining the HC and fenton process are mainly due to the enhanced generation of hydroxyl radicals, regeneration of ferrous ion catalyst in the presence of cavitation and reduced mass transfer resistances due to improved turbulence created by cavitation. However, optimum loading of ferrous ions must be used while combining the HC with Fenton process, since the unutilized ferrous ions may contribute towards the increase in the total dissolved solid (TDS) content of the effluent stream and the formation of iron sludge.

Furthermore, the degradation of methomyl using HC based hybrid processes has conclusively established that the combined process of HC and 0.75 g/h of ozone is the most energy efficient and effective process yielding the complete degradation of methomyl in just 6 min with the extent of mineralization of 71% and the highest cavitation yield of $1.245 \times 10^{-9}$ moles/J. The rate of degradation of methomyl of $2.146 \times 10^{-3}$ min$^{-1}$ obtained in case of HC alone has significantly increased to $915.94 \times 10^{-3}$ min$^{-1}$ by using HC in combination with ozone process leading to the synergistic index 47.6. The combination of HC with ozone has substantially enhanced the rate of degradation of methomyl, since ozone dissociates in the presence of cavitation resulting into the higher generation of hydroxyl radicals. The mass transfer resistances, which is a major limiting factor for the application of ozone alone, has also eliminated due to the improved turbulence generated by the cavitation.

In addition to this, the degradation of methomyl using US based hybrid processes has also established that the hybrid processes are more energy efficient and effective as compared to individual US process. The rate of degradation of methomyl of $4.861 \times 10^{-3}$ min$^{-1}$ obtained in case of US alone has substantially increased to $150.217 \times 10^{-3}$ min$^{-1}$, $172.855 \times 10^{-3}$ min$^{-1}$ and $574.412 \times 10^{-3}$ min$^{-1}$ leading to the synergistic index of 25.74, 13.70 and 28.27 by using US in combination with H$_2$O$_2$, fenton and photo-fenton processes respectively. The comparison of photocatalytic degradation of methomyl using anatase TiO$_2$ and rGO-TiO$_2$ nano-composite has proved that the photocatalytic activity of anatase TiO$_2$ can be enhanced significantly by anchoring the anatase TiO$_2$ on graphene sheets. The nano-composite rGO-TiO$_2$
demonstrated the highest photocatalytic activity as compared to the rGO-TiO$_2$ with the weight ratio of graphene to TiO$_2$ as 1:5, 1:10 and 1:40. The sono-photocatalytic degradation of methomyl using anatase TiO$_2$ and rGO-TiO$_2$(1:20) lead to the synergistic index of 1.97 and 1.324 respectively. The cost of the ultrasonic degradation of methomyl of 79892.34 Rs./m$^3$ has drastically reduced to 2282.00 Rs/m$^3$, 1523.17 Rs./m$^3$, 812.74 Rs./m$^3$, 1794.61 Rs./m$^3$ and 1345.96 Rs./m$^3$ by using US in combination with H$_2$O$_2$, Fenton, photo-Fenton, photocatalytic process using anatase TiO$_2$ and photocatalytic process using rGO-TiO$_2$ (1:20) respectively.

The comparison of US and HC for the degradation of methomyl has shown that, the higher rate of degradation and mineralization of methomyl is obtained by the application of US as compared to HC, since the ultrasonic cavitation phenomenon provides substantially higher intensity of collapse of the individual cavities than the hydrodynamic cavitation. However, HC process is easy to scale up and requires less cost of treatment as compared to US. The comparison of energy efficiency of US and HC (on the basis of cavitational yield) for the degradation of methomyl has demonstrated that the HC process is more energy efficient as compared US process.

The treatment of actual pesticide industry effluent using HC based hybrid processes has also demonstrated that HC in combination with H$_2$O$_2$ and ozone are capable of reducing the toxicity and enhancing the biodegradability of the pesticide industry effluent so that it can be further treated by using conventional biological processes. The treatment of the effluent using HC+Ozone (3g/h) process has enhanced the biodegradability index of the effluent from 0.121 to 0.324. The rate of TOC reduction of $0.56 \times 10^{-3}$ min$^{-1}$ obtained in case of HC has enhanced approximately by 5 and 11 times by using HC in combination with 3g/h of ozone and 10 g/L of H$_2$O$_2$ respectively. Similarly, the rate of COD reduction of $1.382 \times 10^{-3}$ min$^{-1}$ obtained in case of HC has also enhanced roughly by 2.5 and 5 times by using HC in combination with 3g/h of ozone and 10 g/L of H$_2$O$_2$ respectively. The combined process of HC and H$_2$O$_2$ has proved to be the most energy efficient and cost effective since electrical cost of 10250.99 Rs. /m$^3$ incurred during HC has appreciably reduced to 1951.63 Rs/m$^3$ (i.e. almost by 4 times) when HC was combined with 10 g/L of H$_2$O$_2$.

Overall, it can be concluded that cavitation based hybrid processes are more effective and economically attractive as compared to individual cavitation processes (US or HC) due to higher rates of degradation or mineralization of pesticide compounds and higher energy efficiency.