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Effect of process intensifying parameters on the hydrodynamic cavitation based degradation of commercial pesticide (methomyl) in the aqueous solution

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ABSTRACT

Methomyl, a carbamate pesticide, is classified as a pesticide of category-1 toxicity and hence shows harmful effects on both human and aquatic life. In the present work, the degradation of methomyl has been studied by using hydrodynamic cavitation reactor (HC) and its combination with intensifying agents such as H_2O_2, fenton reagent and ozone (hybrid processes). Initially, the optimization of operating parameters such pH and inlet pressure to the cavitating device (circular venturi) has been carried out for maximizing the efficacy of hydrodynamic cavitation. Further degradation study of methomyl by the application of hybrid processes was carried out at an optimal pH of 2.5 and the optimal inlet pressure of 5 bar. Significant synergetic effect has been observed in case of all the hybrid processes studied. Synergetic coefficient of 5.8, 13.41 and 47.6 has been obtained by combining hydrodynamic cavitation with H_2O_2, fenton process and ozone respectively. Efficacy of individual and hybrid processes has also been obtained in terms of energy efficiency and extent of mineralization. HC + Ozone process has proved to be the most effective process having highest synergetic coefficient, energy efficiency and the extent of mineralization. The study has also encompassed the identification of intermediate by-products generated during the degradation and has proposed the probable degradation pathway. It has been conclusively established that hydrodynamic cavitation in the presence of intensifying agents can effectively be used for complete degradation of methomyl.

1. Introduction

Large amounts of pesticides have been used across the globe for the purpose of increased cultivation; however their residues have posed serious threats to the environment and mankind [1]. Methomyl, $C_5H_{10}O_2N_2S$, is a broad spectrum insecticide which belongs to the family of oxime carbamate pesticides. It has been classified as a very toxic and hazardous pesticide by many agencies such as World Health Organization (WHO), Environment Protection Agency (EPA), European Chemical Classification (ECC), etc. It can easily cause contamination of both ground and surface water resources, due to its high solubility in water (57.9 g/L, 20 °C) and a low-sorption affinity to soils [2].

Application of Advanced Oxidation Processes (AOPs) has found to be a promising technology for the degradation of various insecticides and pesticides. AOPs are based primarily on the formation and subsequent attack of the highly reactive hydroxyl radicals, leading to the destruction/oxidation of the target pesticide compound [3]. Cavitation is an emerging AOP and not many studies have been reported for its application in the degradation of pesticides. It is the phenomena of formation, growth and collapse of large number of cavities in the liquid medium [4]. Two most important ways of generating cavitating conditions are acoustic cavitation (US) and hydrodynamic cavitation (HC). If the cavitation occurs by a passage of high frequency sound wave it is called as an acoustic cavitation and if it occurs by pressure variation in the flowing liquid due to the presence of throttling devices such as venturi, orifice etc., it is called as hydrodynamic cavitation [5]. It

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is reported in the literature that hydrodynamic cavitation is more energy efficient and can easily be scaled up to industrial scale as compared to acoustic cavitation [6,7]. The principle of hydrodynamic cavitation can be described by using Bernoulli's theorem.

$$P_{\text{static}} + P_{\text{dynamic}} = \text{Constant} = P_{\text{static}} + \frac{1}{2}\rho v^2$$

where P_{static} and P_{dynamic} are static and dynamic pressures, ρ and v are the density and velocity of the liquid at the throat of the cavitating device. When the liquid passes through a cavitating device, the fluid velocity increases due to a decrease in the flow area and hence increases the dynamic pressure. Since, the sum of dynamic and static pressure is constant according to the Bernoulli's equation; increase in dynamic pressure subsequently reduces the static pressure. If the static pressure falls below the cavitation threshold of the solvent (i.e. the vapor pressure of the solvent) millions of cavities are generated. Recovery of static pressure in the downstream section of the cavitating device causes violent collapse of these cavities resulting into the formation of localized hot spots and highly reactive $OH^{\cdot}$ and $H^{\cdot}$ radicals [8]. The two key mechanisms responsible for the degradation of organic pollutants using hydrodynamic cavitation are, the thermal decomposition/pyrolysis of organic pollutant entrapped in the cavities due to the generation of transient temperature pressure conditions (localized hot spots) and secondly, the reaction of free radicals with the organic pollutant occurring at the cavity–water interface [9].

Some of the AOPs which have been applied in the past for the degradation of methomyl include fenton process [4], photofenton process [4,10] and photocatalytic oxidation process [11,12]. However, to the best of our knowledge, degradation study of methomyl by employing hydrodynamic cavitation reactors and their combination with other AOPs is not yet reported in the literature.

In the current work, the degradation of methomyl has been studied by using hydrodynamic cavitation reactors and the two important operating parameters, pH and inlet pressure to the cavitating device have been optimized in order to maximize the cavitational effect. An attempt has also been made to enhance the rate of degradation of methomyl by using hydrodynamic cavitation in combination with the intensifying agents such as H_2O_2, ozone and fenton reagent. The main focus of the work is to compare the rates of degradation, energy efficiency and the extent of mineralization of methomyl that can be obtained by using individual hydrodynamic cavitation reactor and its combination with intensifying agents (hybrid processes) to determine the synergetic effect of combined processes. In addition to this, current work also proposes a probable degradation pathway of methomyl by identifying the oxidation by-products and intermediates generated during the degradation process of methomyl. In short, the present work deals with the application of hydrodynamic cavitation (HC) and hydrodynamic cavitation based hybrid techniques such as HC + H_2O_2, HC + Fenton, HC + Ozone for the effective degradation carbamate pesticide, methomyl in aqueous solutions.

2. Materials and methods

2.1. Materials

Commercial grade methomyl (Dupont) was used as a model organic pollutant without further purification. Hydrogen peroxide (30% w/v), ferrous sulfate ($FeSO_4{\cdot}7H_2O$), sodium sulfite (Na_2SO_3) and sulfuric acid (H_2SO_4) all of AR grade were obtained from S D Fine Chemicals Ltd., Mumbai, India. Acetonitrile and water used for HPLC analysis were purchased from S D Fine Chemicals Ltd., Mumbai, India of HPLC grade. All chemicals were used as received from the supplier.

2.2. Experimental set-up

Hydrodynamic cavitation setup used in the present work is as shown in the Fig. 1. The setup primarily consists of a holding tank, a positive displacement pump (capacity 1.1 KW), pressure gauges (P_1, P_2 and P_3), valves (V_1, V_2 and V_3), flanges, main line and a bypass line. Holding tank was surrounded by a cooling jacket to control the temperature, as it likely to increases due to the heat liberated during cavitation. The suction line from the pump is connected to the bottom of the holding tank and discharge line from the pump is branched into two lines; main line and bypass line. The main line houses the flanges which are used to accommodate the cavitating device and a valve is provided in the bypass line to control the flow through the main line. Pressure gauges are provided at appropriate places to measure the inlet pressure to the

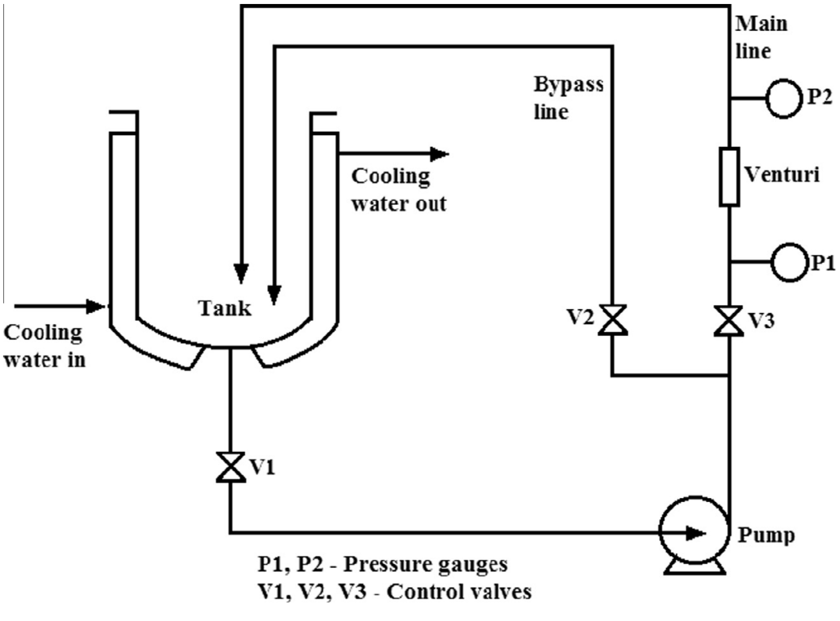

Fig. 1. Schematic representation of hydrodynamic cavitation set-up.

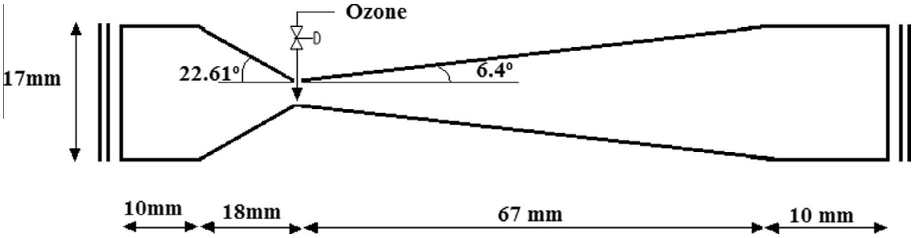

Fig. 2. Geometric specifications of a circular venturi (cavitating device).

cavitating device and fully recovered downstream pressure. Circular venturi has been used as a cavitating device in the present work. The geometric specifications of the circular venturi and the insertion point of ozone have been furnished in the Fig. 2. The dimensions of the cavitating device used in the present study are based on the optimized parameters found out by Bashir et al. [13] using CFD analysis. For the combined process of hydrodynamic cavitation and ozone, the design of the cavitator was modified for introducing the ozone at the throat of the venturi. A small circular opening of diameter 2 mm was fabricated at the throat region keeping all other dimensions of the cavitator identical.

The material of construction of the entire setup except the cavitating device is stainless steel (SS316), whereas cavitating device, circular venturi is made up of brass.

2.3. Experimental methodology

All the experiments were performed with 5 L of aqueous solution of methomyl having an initial concentration of 25 ppm. The holding tank was filled with aqueous solution of methomyl and after starting the reciprocating pump, the control valve in the bypass line was used to control the flow in the main line to regulate the required inlet pressure to the cavitating device. The solution of methomyl was circulated through the set-up for 120 min and sample was collected after regular interval of time to determine the concentration of methomyl remaining in the sample.

Initially the effect of variation of operating pH was studied, followed by the optimization of inlet pressure to the cavitating device. Experiments were performed to determine an optimal pH, by altering the operating pH in the range of 2–6 (2, 2.5, 3, 4 and 6). Further experiments were performed at an optimal pH of 2.5 and varying inlet pressure from 2 to 7 bar (2, 3, 4, 5, and 7 bar) by using hydrodynamic cavitation reactor without the addition of intensifying agent H_2O_2. In addition to this, effect of inlet pressure was also studied in presence of set amount of H_2O_2 to determine the essential inlet pressure required for effective dissociation of H_2O_2 in presence of hydrodynamic cavitation.

The experiments of combination of hydrodynamic cavitation and H_2O_2 were performed by using various molar ratios of methomyl: H_2O_2 such as 1:5, 1:10, 1:15, 1:20, 1:30, and 1:40 to determine the optimal concentration of hydrogen peroxide. Fenton chemistry was also employed along with hydrodynamic cavitation at the fixed optimal molar ratio of methomyl:H_2O_2 as 1:30 and varying molar ratio of ferrous sulfate:H_2O_2 as 1:20, 1:30, 1:40 and 1:50. Ferrous sulfate has been used as a homogeneous fenton catalyst.

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 2 g/h (0.5, 0.75, 1 and 2 g/h). Ozonator with a capacity of 180 W (make – Eltech Engineers, India) was used for generating ozone with a maximum capacity of 10 g/h of ozone. Oxygen (94% purity) was used as a feed to the ozonator which was produced through an oxygen generator (capacity – 420 W and oxygen output – 1–5 LPM). The generated ozone was then constantly injected at the throat of the venturi. The formation of large numbers of tiny ozone bubble is expected due to extreme temperature pressure conditions and high turbulence in the cavitation zone.

For quantifying the synergetic effect, the experiments were also carried out at optimized loadings of intensifying agents in the absence of hydrodynamic cavitation i.e. conventional approach of only stirring.

2.4. Analysis

Concentration of methomyl at a set interval of time was determined using high pressure liquid chromatography (HPLC) equipped with C18 column of dimensions 4.6 × 250 mm and UV detector (make – Agilent Technologies, USA). The mobile phase used in HPLC determination consists of acetonitrile: water mixture (30:70 v/v) with flow rate maintained at 1 mL/min and UV detector set at wavelength of 234 nm. In order to obtain the accurate concentration of methomyl at any instance, particularly in case of H_2O_2 and fenton process, 0.5 N sodium sulfite has been added immediately to the samples withdrawn, as a quenching agent. In addition to this, the extent of mineralization of methomyl into end products (such as CO_2 and H_2O) was also analyzed using total organic carbon analyzer (make-Shimadzu corporation, Japan) at various optimum conditions.

3. Results and discussion

3.1. Effect of operating pH

It is well reported in the literature that the initial pH of the solution plays an important role in the degradation of many organic pollutants using cavitational reactors [14,15]. With this background, the effect of pH has been studied by carrying out the experiments at different pH in the range of 2–6. The results obtained are depicted in the Fig. 3 and Table 1. It has been observed that the rate of degradation of methomyl increases significantly with a decrease in the solution pH and could be fitted with first order kinetics. The rate of degradation of methomyl of $0.72 \times 10^{-3}\ \text{min}^{-1}$ obtained at pH of 6 was substantially increased to $22.17 \times 10^{-3}\ \text{min}^{-1}$ by reducing the solution pH to 2.5. However, with further increase in the acidity of solution (at pH of 2.0) the rate of degradation of methomyl marginally decreases. Hence, all further experiments were performed with the optimal pH of 2.5.

Since methomyl is a non volatile compound (Henry law constant is 2×10^{-11} atm m^3/mole), it cannot get penetrated into the expanding cavities and hence pyrolysis/thermal decomposition is not the dominant degradation mechanism in the case of methomyl. Instead, the formation and subsequent attack of $OH^{\cdot}$ radicals is a prevailing mechanism in the degradation of methomyl and it depends to some extent on the solution pH. Substantial increase

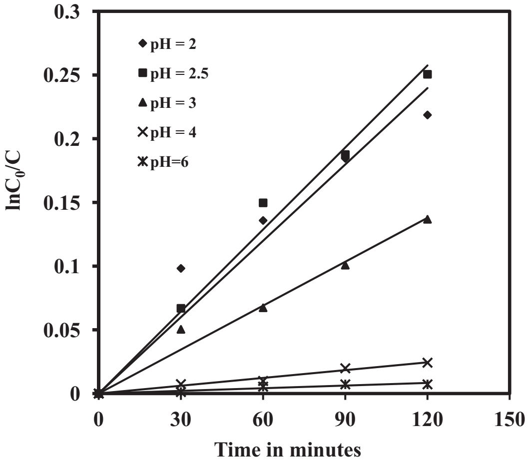

Fig. 3. First order degradation of methomyl at various pH (subjected to the initial concentration of methomyl – 25 ppm, capacity – 5 L, inlet pressure – 5 bar).

Table 1
Effect of operating pH on first order reaction rate constant, *k* and extent of degradation.

Operating pH	% Degradation	$k \times 10^3$ min^{-1}
2	19.64	1.998
2.5	22.17	2.146
3	12.78	1.149
4	2.39	0.204
6	0.72	0.069

in the rate of degradation of methomyl at acidic conditions has confirmed the profound role of pH on the rate of degradation of methomyl.

The results obtained may be attributed to the fact that an acidic condition favors the generation of hydroxyl radicals by suppressing the recombination reaction of OH$^{\cdot}$ radicals. Hence, more number of OH$^{\cdot}$ radicals will be available at the cavity-water interface for the oxidation of methomyl, resulting into increased degradation rates at acidic pH. In addition to this, the oxidation potential of hydroxyl radicals is also superior under acidic conditions [16,17]. Similar illustrations reported in the literature also indicate that acidic conditions are favorable for the degradation of organic pollutants using cavitational reactors. Patil et al. [16] have also observed that the rate of ultrasonic degradation of imidacloprid increases with a decrease in the pH of the solution and the highest rate of degradation of imidacloprid was obtained at pH of 3. Mishra and Gogate [17] have investigated the effect of pH on the degradation of Rhodamine-B using hydrodynamic cavitation reactors at different pH in the range of 2.5–11. They have also reported significant increase in the rate of decolorization of the dye with a decrease in the solution pH. Overall, it can be concluded that the study of effect of pH on the rate of degradation of organic pollutants is very essential for maximizing the performance of cavitational reactors, with an underlying fact that the value of optimal pH will be dependent on the type of the target pollutant.

3.2. Effect of inlet pressure and cavitation number

Initially, the degradation of methomyl in the aqueous solution has been investigated under different pump outlet pressures, in the range of 2–7 bar without the addition of any intensifying agent such as H_2O_2 or oxygen. The results obtained have been demonstrated in Fig. 4. It can be seen that the maximum rate of degradation of methomyl was obtained at the optimal pump discharge pressure of 3 bar. However, for the application of combination of hydrodynamic cavitation and intensifying agents, it becomes essential to determine an optimal inlet pressure sufficient for effective dissociation of the added intensifying agent in the presence of cavitation. Hence, an attempt was also made to study the effect of inlet pressure in the presence of set amount of H_2O_2. The results obtained have been illustrated in the Fig. 5. The results obtained have indicated that the optimum inlet pressure of 5 bar was necessary for an effective dissociation of H_2O_2 leading to a maximum rate of degradation of methomyl. Table 2 provides cavitation number and the details of first order reaction rate constant and the extent of degradation obtained with and without the addition of H_2O_2. Cavitation number (C_v) is the important dimensionless number which can clearly reflect the cavitating condition inside the cavitator [18]. Cavitation number can be defined as

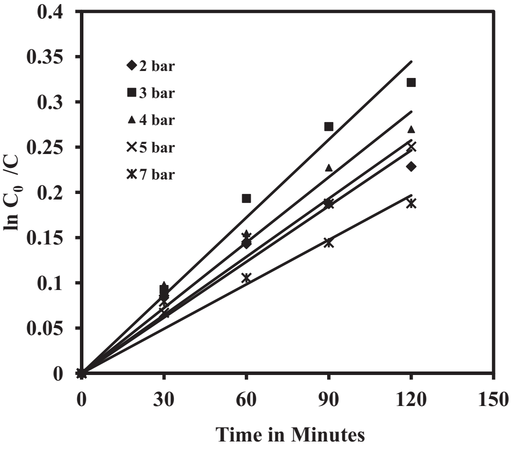

Fig. 4. First order degradation of methomyl at various inlet pressures (concentration of methomyl: 25 ppm, amount of methomyl: 5 lit, time of run: 2 h, pH: 2.5).

$$C_V = \left(\frac{P_2 - P_v}{\frac{1}{2} \rho v_o^2} \right)$$

where, P_2 is the fully recovered downstream pressure, P_v is the vapor pressure of the liquid and v_o is the velocity at the throat of the cavitating device.

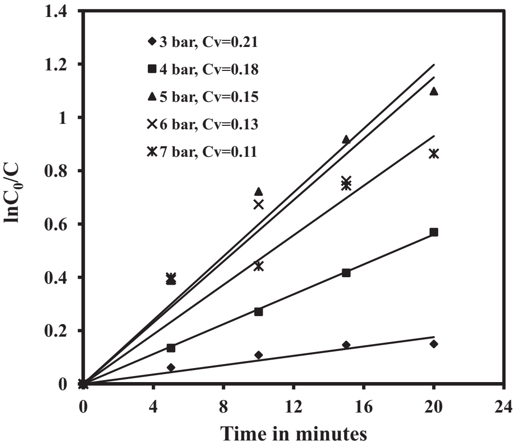

Fig. 5. First order degradation of methomyl at various inlet pressures in presence of H_2O_2 (concentration of methomyl: 25 ppm, amount of methomyl: 5 lit, pH: 2.5, molar ratio of methomyl to H_2O_2 = 1:5).

Table 2
Effect on inlet pressure on first order reaction rate constant, *k* and extent of degradation with and without addition of H_2O_2.

Without addition of H_2O_2			With addition of H_2O_2, molar ratio of methomyl to H_2O_2: 1:05				
Inlet pressure (bar)	% Degradation after 2 h	$k \times 10^3$ min^{-1}	Inlet pressure (bar)	Volumetric flow rate (LPH)	Cavitation number (C_v)	% Degradation after 1 h	$k \times 10^3$ min^{-1}
2	20.43	2.054	3	340	0.21	33.13	8.776
3	27.49	2.871	4	375	0.18	65.06	28.024
4	23.64	2.409	5	410	0.15	72.01	59.868
5	22.17	2.146	6	445	0.13	57.41	57.492
7	17.13	1.638	7	470	0.11	57.35	46.478

It has been observed that with an increase in the inlet pressure, the volumetric flow rate of fluid through the circular venturi increases which ultimately decreases the cavitation number. It can be seen that an increase in the inlet pressure to the cavitating device increases the rate of degradation of methomyl up to the inlet pressure of 5 bar (i.e. $C_v = 0.15$). The rate of degradation of methomyl of 8.776×10^{-3} min^{-1} obtained at an inlet pressure of 3 bar (i.e. $C_v = 0.21$) significantly increased to 59.868×10^{-3} min^{-1} when the inlet pressure was increased to 5 bar ($C_v = 0.15$). This could be due to the fact that, at lower cavitation number or at higher inlet pressure, the number density of the cavities increases resulting into more intense cavity collapse [7]. Large quantum of hydroxyl ions generated due to violent collapse of the cavities and their effective utilization due to an increased fluid turbulence leads to higher rate of degradation of methomyl. However, further increasing the inlet pressure beyond 5 bar (or decreasing Cv below 0.15) has not shown any beneficial effects, may be due to the onset of choked cavitation [15]. Because at very high inlet pressure (i.e. at very low cavitation number), the number of cavities generated are so high, that they no longer behave as individual cavities and forms a vaporous cavity cloud resulting into the less intense cavitation phenomena [14]. Saharan et al. [19] have observed that the optimal cavitation number is dependent on the geometry of the cavitating device and the reported range of optimal cavitation number for circular venturi of similar dimensions is 0.13–0.18. The established results are in good agreement with the reported literature since the highest extent of degradation of methomyl was obtained at the optimal cavitation number of 0.15.

3.3. Effect of loading of H_2O_2 on efficacy of combined process, HC + H_2O_2

Hydrogen peroxide is a well known oxidizing agent due to its high oxidation potential of 1.78 eV [7]. But the efficiency of hydrogen peroxide is not very promising, when applied individually owing to the poor rate of dissociation of H_2O_2 into OH· radicals under conventional condition of stirring. However, it is well reported in the literature that H_2O_2 dissociates easily in presence of cavitation, generating large quantum of highly reactive OH· radicals [19–22]. Hence, H_2O_2 can be used as an intensifying agent for enhancing the rate of degradation of methomyl that can be achieved by using hydrodynamic cavitation reactors.

Effect of the loading of H_2O_2 on the performance of hydrodynamic cavitation reactor has been evaluated by varying the molar ratio of methomyl to H_2O_2 such as 1:5, 1:10, 1:15, 1:20, 1:30, and 1:40. The obtained results have been illustrated in Figs. 6 and 7. The initial reaction rate constant and extent of degradation are summarized in Table 3. The net result is that the extent of degradation of methomyl increases with an increase in the molar ratio of methomyl to H_2O_2 till an optimal molar ratio of 1:30, beyond which a decrease in the extent of degradation of methomyl has been observed. However, to the contrary, initial degradation rate of methomyl found to be decreasing with increasing loading of H_2O_2. It is worthy to note here that higher initial degradation rate of methomyl at lower loading of H_2O_2 may not be beneficial since the amount of H_2O_2 available for the degradation is not sufficient to provide higher extent of degradation of methomyl. Hence, on the basis of the extent of degradation of methomyl, it has been concluded that the optimal molar ratio of methomyl to H_2O_2 is 1:30. The decrease in the extent of degradation of methomyl

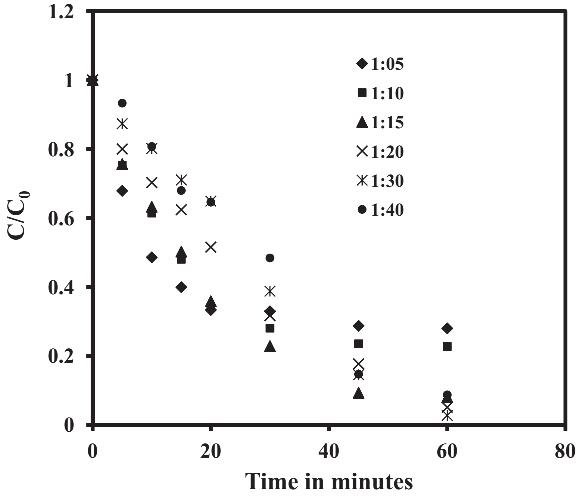

Fig. 6. Effect of various molar ratio of methomyl:H_2O_2 on removal of methomyl (concentration of methomyl: 25 ppm, amount of methomyl: 5 lit, pH: 2.5, inlet pressure: 5 bar).

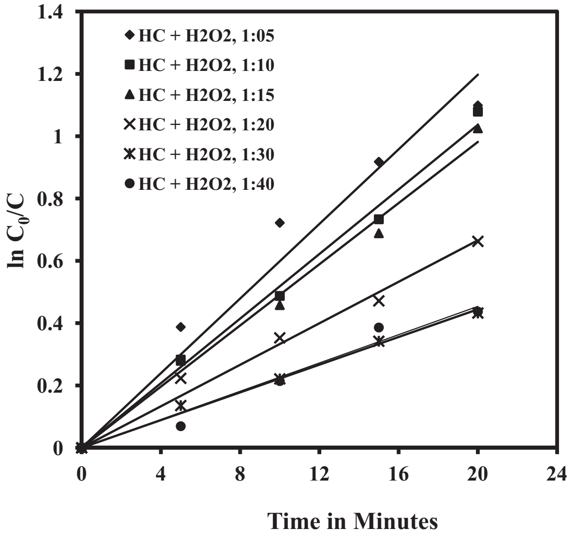

Fig. 7. First order degradation of methomyl at various molar ratio of methomyl: H_2O_2 (concentration of methomyl: 25 ppm, amount of methomyl: 5 lit, pH: 2.5, inlet pressure: 5 bar).

Table 3
Effect of loading of H_2O_2 on first order reaction rate constant, k and extent of degradation.

Process	Initial reaction rate constant $k \times 10^3$ min^{-1}	Extent of degradation after 60 min
HC	2.146	13.9
H_2O_2, 1:30	0.5	2.86
HC + H_2O_2, 1:05	59.86	72.013
HC + H_2O_2, 1:10	51.82	77.275
HC + H_2O_2, 1:15	49.08	91.918
HC + H_2O_2, 1:20	33.29	94.897
HC + H_2O_2, 1:30	22.23	97.246
HC + H_2O_2, 1:40	22.16	91.281

beyond the optimal molar ratio of 1:30 is due to the fact that the added hydrogen peroxide above the optimum loading ratio acts as a radical scavenger and hence the net extent of the degradation of methomyl reduces.

HC + H_2O_2 process applied for the degradation of methomyl showed synergetic effect, since the extent of degradation of methomyl obtained in the case of individual process of hydrogen peroxide (2.86%) and hydrodynamic cavitation (13.9%) increased dramatically to 97.5% by combining HC and H_2O_2 under the optimized conditions. Synergetic coefficient based on the extent of degradation of methomyl can be obtained as

$$\text{Synergetic coefficient} = \frac{\text{Extent of degradation}_{(HC+H_2O_2)}}{\text{Extent of degradation}_{HC} + \text{Extent of degradation}_{H_2O_2}} = 5.8$$

Observed synergetic effect may be due to the significant rate of dissociation of H_2O_2 in the presence of hydrodynamic cavitation leading to enhanced generation of hydroxyl radicals [22]. Similar trends, in terms of synergetic effect of the combination of hydrogen peroxide with cavitation processes have been reported in the literature for the degradation other organic pollutants. Gore et al. [7] have also witnessed the synergetic effect by combining hydrogen peroxide and hydrodynamic cavitation for the degradation of reactive orange 4 (RO_4). The synergetic coefficient of 3.87 was obtained at an optimized molar ratio RO_4:H_2O_2 of 1:30. Patil et al. [23] have also reported similar observations for the degradation of imidacloprid by application of combined process of HC and H_2O_2 and the synergetic coefficient obtained was 11.15. Hence, based on the established results and the reported literature it can be concluded that HC + H_2O_2 process is always more beneficial as compared to individual HC and H_2O_2 processes.

3.4. Effect of Fenton reagent loading on the efficacy of combined process, HC + Fenton

Fenton reagent can also be employed as an intensifying agent for enhancing the efficacy of hydrodynamic cavitation, since it can also lead to an improved generation and the utilization of hydroxyl radicals [21]. Conventional fenton process is nothing but the iron catalyzed dissociation of H_2O_2 into hydroxyl radicals under acidic conditions, during which ferrous ions are converted to ferric ions [24].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\cdot}$$

Combination of hydrodynamic cavitation with fenton reagent can further increase the production of hydroxyl radicals through regeneration of catalyst (i.e. Fe^{2+}) and dissociation of some part of H_2O_2 in presence of cavitation [25,26].

$$Fe^{3+} + H_2O_2 \rightarrow Fe\text{-}OOH^{2+} + H^+$$

$$Fe\text{-}OOH^{2+} +)))(HC) \rightarrow Fe^{2+} + HO_2^{\cdot}$$

$$H_2O_2 +)))(HC) \rightarrow OH^{\cdot} + OH^{\cdot}$$

Hence, fenton reagent can be utilized as an intensifying agent for accelerating the rate of generation of hydroxyl radicals.

Effect of loading of fenton reagent on the rate of degradation of methomyl has been investigated for various molar ratios of $FeSO_4$:H_2O_2 viz. 1:50, 1:40, 1:30 and 1:20 by application of HC + Fenton process. All the experiments have been carried out at the fixed optimal molar ratio of methomyl to H_2O_2 of 1:30 and using venturi as the cavitating device. The obtained results have been depicted in the Fig.8 and Table 4. It has been observed that the rate and extent of degradation of methomyl increases with an increase in the loading of ferrous ions resulting into complete degradation of methomyl in 30 min of operation using 1:20 M ratio of $FeSO_4$:H_2O_2. The rate of degradation of methomyl of 2.15×10^{-3} min^{-1} and 9.89×10^{-3} min^{-1} obtained in the case of individual processes of HC and conventional fenton process has substantially increased to 161.41×10^{-3} min^{-1} by applying the HC + Fenton hybrid process. The efficacy of the combination of HC and fenton process over individual processes can be determined in terms of synergetic coefficient based reaction rate constant.

$$\text{Synergetic coefficient} = \frac{k_{(HC+fenton)}}{k_{HC} + k_{fenton}} = 13.41$$

This synergetic effect can be attributed to the enhanced generation of hydroxyl radicals due to the regeneration of catalyst and improved utilization of hydroxyl radicals due to high fluid turbulence created by hydrodynamic cavitation.

The trend in the results obtained in the present work can be confirmed by looking at the similar findings reported in the

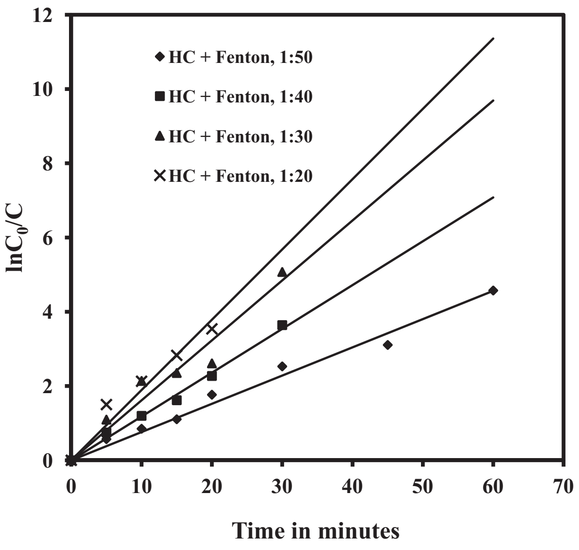

Fig. 8. First order degradation of methomyl at various molar ratio of Fe^{2+}:H_2O_2 (concentration of methomyl: 25 ppm, amount of methomyl: 5 lit, pH: 2.5, molar ratio of methomyl:H_2O_2 = 1:30, inlet pressure: 5 bar).

Table 4
Effect of various molar ratio of Fe^{2+}:H_2O_2 on first order reaction rate constant, k and extent of degradation.

Process	Rate constant, $k \times 10^3$ min^{-1}	% Degradation after 30 min
HC	2.146	6.46
Fenton, 1:30	9.89	29.26
HC + Fenton, 1:50	76.06	92.03
HC + Fenton, 1:40	117.98	97.38
HC + Fenton, 1:30	161.41	99.37
HC + Fenton, 1:20	189.31	100

literature. In our earlier work of the application of the combination of hydrodynamic cavitation and fenton process for the degradation of imidacloprid [27], it has been reported that the rate of degradation increases with an increase in the loading of $FeSO_4$ at a constant loading of H_2O_2. Synergetic effect has been observed by combining HC and fenton process with synergetic coefficient of 3.636. Guo et al. [28] have also observed higher extent of degradation of 2, 4-dinitrophenol in the coupled ultrasonic cavitation (US) and fenton process (98%) as compared to individual US (4%) and fenton processes (82%).

3.5. Effect of loading of ozone on efficacy of combined process, HC + Ozone

Ozonation process finds applications in the waste water treatment since ozone in aqueous solution can oxidize the organic pollutant due to its high oxidation potential 2.08 eV [7]. However, conventional ozonation process has serious limitation of slow mass transfer rate of ozone in aqueous solutions. Combining cavitation and ozonation process can overcome this limitation since high fluid turbulence created by cavitation phenomena can enhance the rate of mass transfer of ozone in aqueous solutions [29]. Beneficial effects of combined process are also due to the decomposition of ozone in the presence of cavitation to produce atomic oxygen (O), which after reacting with water generates highly reactive hydroxyl radicals [30–36]. In addition to this hydroxyl radicals are also generated by the dissociation of water due to cavitational effects.

$$O_3+)))(HC) \rightarrow O_2 + O$$

$$O + H_2O \rightarrow 2OH^{\cdot}$$

$$H_2O+)))(HC) \rightarrow OH^{\cdot} + H^{\cdot}$$

$$OH^{\cdot} + O_3 + \text{methomyl} \rightarrow \text{Oxidation products}$$

With this background, the effect of loading of ozone on the rate of degradation and rate of mineralization of methomyl have been evaluated by using various concentrations of ozone viz. 0.5, 0.75, 1.0 and 2.0 gm/h. The obtained results of rate of degradation and rate of mineralization of methomyl have been depicted in Figs. 9 and 10 respectively. It has been observed that the rate of degradation as well as the rate of mineralization of methomyl has increased remarkably with an increase in the loading of ozone. In order to investigate the synergistic effect of the combination of HC and ozonation process, efficacy of individual and combined processes have been compared based on the rate of degradation and rate of mineralization of methomyl. Table 5 summarizes the first order rate constant obtained for the processes of degradation and mineralization of methomyl.

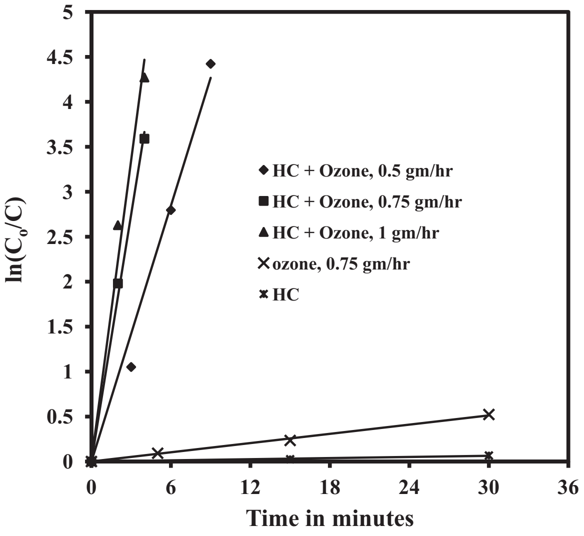

Fig. 9. First order degradation of methomyl at various loadings of ozone (concentration of methomyl: 25 ppm, amount of methomyl: 5 lit, pH: 2.5, inlet pressure: 5 bar).

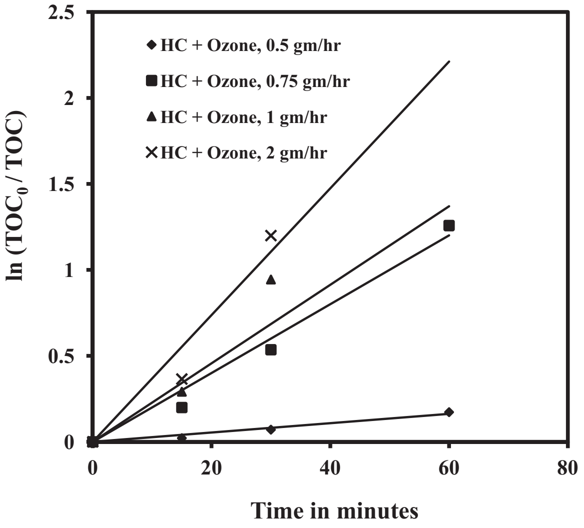

Fig. 10. Rate of mineralization of methomyl at various loadings of ozone (concentration of methomyl: 25 ppm, amount of methomyl: 5 lit, pH: 2.5, inlet pressure: 5 bar).

The rate of degradation of methomyl obtained in case of individual HC and conventional ozonation processes of 2.146×10^{-3} min^{-1} and 17.094×10^{-3} min^{-1} significantly increased to 915.94×10^{-3} min^{-1} in case of HC + Ozone process for 0.75 gm/h of ozone. Similarly, rate of mineralization of methomyl of 0.528×10^{-3} min^{-1} and 0.568×10^{-3} min^{-1} obtained in case of individual HC and conventional ozonation processes respectively appreciably increased to 20.00×10^{-3} min^{-1} in case of HC + Ozone process after utilizing 0.75 gm/h of ozone.

The synergistic effect observed can be quantified by determining the synergetic coefficient as

Synergetic coefficient based on rate of degradation

$$= \frac{k_{(\mathrm{HC+Ozone})}}{k_{\mathrm{HC}} + k_{\mathrm{Ozone}}} = 47.6$$

Synergetic coefficient based on rate of mineralization

$$= \frac{k'_{(\mathrm{HC+Ozone})}}{k'_{\mathrm{HC}} + k'_{\mathrm{Ozone}}} = 18.25$$

Table 5
Effect of loading of ozone on the rate of degradation and rate of mineralization of methomyl.

Process	Rate constant based on degradation $k \times 10^3$ min^{-1}	Rate constant based on mineralization $k' \times 10^3$ min^{-1}	% TOC reduction
HC	2.146	0.528	5.45 (after 120 min)
Conventional Ozone, 0.75 gm/h	17.094	0.568	5.96 (after 120 min)
HC + Ozone, 0.5 gm/h	474.071	2.709	6.83 (after 30 min)
HC + Ozone, 0.75 gm/h	915.94	20.001	41.47 (after 30 min)
HC + Ozone, 1 gm/h	1116.938	22.833	61.09 (after 30 min)
HC + Ozone, 2 gm/h	Instantaneous	36.858	69.87 (after 30 min)

Hence, the combination of hydrodynamic cavitation and ozonation has not only amplified the rate of degradation of methomyl, but also resulted in higher rate of mineralization of methomyl, as compared to individual HC and ozonation processes. The established results are attributed to the following facts

1. Additional oxidants such as atomic oxygen and hydroxyl radicals can be generated upon the dissociation of ozone in presence of hydrodynamic cavitation [30,31].
2. Combination of HC and ozonation process have shown synergism, since the reaction of methomyl with ozone in aqueous solution is very slow (17.094×10^{-3} min^{-1}) as compared to reaction of methomyl with hydroxyl radicals generated upon dissociation of ozone in presence of cavitation (915.94×10^{-3} min^{-1}).
3. Utilization rate of ozone and hydroxyl radicals is improved due to high fluid turbulence created by cavitation [29–36].
4. Mass transfer resistances offered for the dissolution of ozone in aqueous solution are also reduced by virtue of cavitation [29–36].

Similar investigations reported in literature have also confirmed that the combination of cavitation with ozonation gives higher rates of degradation than the conventional ozonation for the compounds such as nitrobenzene, 4-nitrophenol, and 4-chlorophenol [32], reactive blue 19 [33], azobenzene and methyl orange [34], pentachlorophenol [35], methyl tert-butyl ether (MTBE) [36] etc.

3.6. Comparison of energy efficiency of various hybrid processes

Energy efficiency of HC and HC based hybrid processes such as HC + H_2O_2, HC + Fenton and HC + Ozone can be compared by determining the cavitational yield of the processes. Cavitational yield can be defined as the ratio of moles of methomyl degraded per unit energy supplied to the system [7]. The only energy supplied to the system in case of individual HC and hybrid processes viz. HC + H_2O_2, HC + Fenton, is the electrical energy (1.1 kW) required to run the pump. However, in case of HC + Ozone process additional energy is needed to generate the ozone, which includes the electrical energy required to run the ozonator (180 W) and oxygen concentrator (420 W). Energy efficiency of various processes has been calculated in terms of cavitational yield and the comparison is given in Fig. 11.

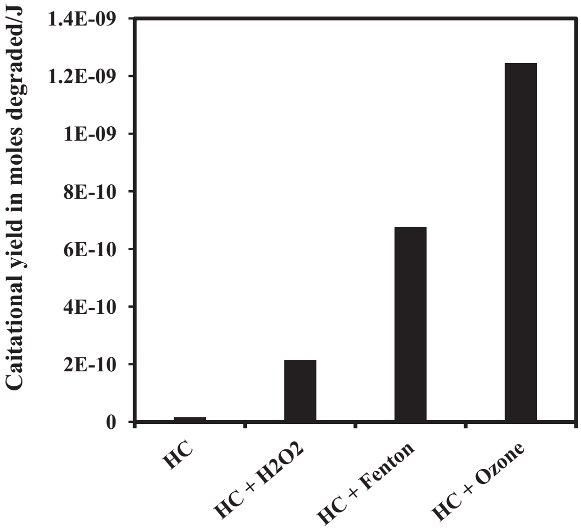

Fig. 11. Comparison of energy efficiency of various processes based on cavitational yield.

It has been observed that the energy efficiency of hydrodynamic cavitation is very low as compared to the energy efficiency of hybrid processes such as HC + H_2O_2, HC + Fenton and HC + Ozone process. The cavitational yield of 1.682×10^{-11}mole/J obtained in the case HC has been augmented roughly by 13 and 40 times as a result of combining the HC with H_2O_2 and Fenton process respectively. This is because, the rate of degradation of methomyl obtained in the case of HC + H_2O_2 and HC + Fenton process is very high as compared to individual HC process, although energy supplied to the combined processes and individual HC are identical. The results obtained are attributed to the fact that hydrodynamic cavitation facilitates the dissociation of H_2O_2 and the regeneration of catalyst (Fe^{2+}) [20–23] leading to increased generation of hydroxyl radicals resulting into higher rate of degradation of methomyl.

HC + Ozone process has been observed to be the most energy efficient process among the hybrid processes studied in the present work, even though additional energy was required for the generation of ozone. The sample calculation for determination of cavitational yield in case of HC + Ozone process has been given in Appendix A. The established results are due to higher oxidation potential of ozone as compared to H_2O_2 and easy dissociation of ozone into highly reactive hydroxyl radicals in the presence of cavitation [29–36].

3.7. Mineralization study

The complete degradation of organic pollutant does not guarantee the complete mineralization of the compound, since in addition to CO_2 and H_2O; some stable intermediates are also produced during the degradation of organic compound which accounts for the total organic carbon content (TOC) of the solution [15]. In view of this, mineralization study has been carried out by measuring the rate and the extent of TOC reduction obtained using various individual and hybrid AOP's. Rate of mineralization of various hybrid processes has been given in Fig. 12 and Table 6 summarizes the extent of mineralization and the first order rate constant for the different processes. It was found that TOC reduced merely by 5.45% with first order mineralization constant of 0.528×10^{-3} min^{-1} when the degradation was carried out with individual only hydrodynamic cavitation process. The extent of TOC reduction obtained in the case of HC has further enhanced by the addition

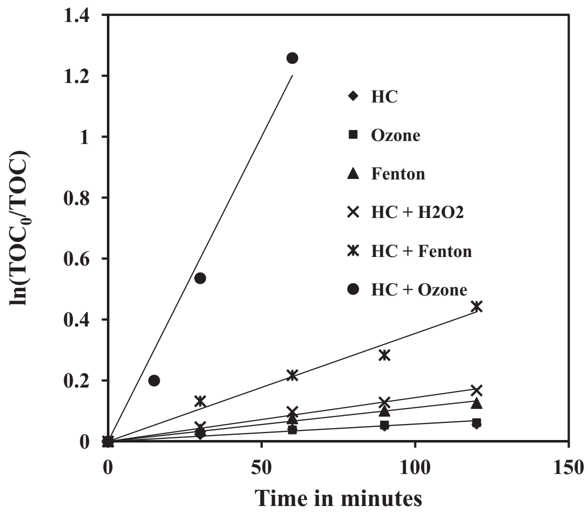

Fig. 12. Rate of mineralization obtained by applying various individual and hybrid processes.

Table 6
Mineralization study of methomyl using various individual and combined processes.

Process	Rate constant based on mineralization $k' \times 10^{-3}$ min^{-1}	% TOC removal after 120 min
H_2O_2	Negligible	Negligible
HC	0.528	5.45
Ozone	0.568	5.96
Fenton	1.108	9.57
HC + H_2O_2	1.439	15.4
HC + Fenton	3.534	35.79
HC + Ozone	20.001	70.79

of H_2O_2 or fenton reagent in combination with HC. Extent of mineralization of 15.4% and 35.79% has been obtained after 2 h in case of HC + H_2O_2 and HC + Fenton respectively. The extent of mineralization of methomyl obtained is not very promising, despite almost complete degradation of methomyl was obtained within 60 min using HC + H_2O_2 and within 30 min using HC + Fenton process.

Highest rate of mineralization was observed using HC + Ozone process as compared to other hybrid processes i.e. 70.79% of TOC reduction with first order mineralization constant of 20.001×10^{-3} min^{-1}. The results obtained are attributed to the fact that ozone has higher oxidation potential than H_2O_2 and ozone can readily dissociates into OH· radicals in the presence of HC [30,31], thereby intensifying the degradation of methomyl.

Overall, all the hybrid processes lead to higher rate of mineralization of methomyl as compared to individual HC due to increased generation of OH· radicals in the presence of hydrodynamic cavitation. However, rate of mineralization of methomyl has found to be much slower as compared to the rate of degradation of methomyl in case of all the processes studied in the present work due to the formation of some stable compounds which are difficult to degrade further.

3.8. Identification of intermediate by-products and possible degradation pathway

The intermediate by-products generated during the degradation of methomyl by applying HC + H_2O_2 process, have been analyzed with the help of liquid chromatographic mass spectroscopy (LC–MS) and are presented in Table 7. The identified intermediate by-products include methomyl oxime, methomyl sulfoxide oxime, methyl carbamic acid, compound with mass of 148, oxalic acid and glycolic acid. Tamimi et al. [37] have also identified intermediate by-products such as methomyl oxime, compound with molecular mass of 148, oxalic acid and glycolic acid generated during the photocatalytic degradation of methomyl. Furthermore, Tomasevic et al. [11] have also reported methomyl oxime as the main intermediate formed during photocatalytic degradation of methomyl. Majority of degradation by-products obtained in the present work are similar to the intermediates reported in the literature due to the identical principle of degradation i.e. generation and subsequent attack of OH· radicals. It should be noted here that, in addition to the peaks of successfully identified intermediates, several other peaks have also observed during LC–MS analysis, which could not be identified positively, but had molecular weights in the range of 88–144 Daltons.

Table 7
Identified degradation by-products of methomyl generated during HC + H_2O_2 process.

m/z by LCMS	Identified degradation by-products	Mw	Tentative assignment
163	Methomyl	162	[M + 1]
149	Compound as shown in Fig. 12	148	[M + 1]
105	Methomyl oxime	105	–
121	Methomyl sulfoxide oxime	121	–
74	Methyl carbamic acid	75	[M – 1]
89	Oxalic acid	90	[M – 1]
75	Glycolic acid	76	[M – 1]

On the basis of identified by-products and reported literature, a pathway of degradation of methomyl has been tentatively proposed in Fig. 13. Few unidentified byproducts are also included in the degradation pathway on the basis of reported literature for the sake of completeness.

It can be safely assumed that initially hydroxylation of methyl group attached to the nitrogen atom produces methomyl methylol, which in turn produces compound with molecular mass of 148 via decarboxylation of hydroxylated methyl group. Further degradation occurs mainly by the rupture of ester (or N–O) bond of methomyl or methomyl methylol or compound with molecular mass of 148, generating methomyl oxime, methomyl sulfoxide oxime, methyl carbamic acid and carbamic acid. It is reported in the literature that methomyl oxime may further get converted into acetonitrile by a Beckman rearrangement [37]. Subsequently, the series of hydroxylation reactions of acetamide generates various acids such as glycolic acid, oxalic acid and acetic acid, which after undergoing succession of decarboxylation reactions facilitates the complete mineralization of the entire molecule.

4. Conclusions

Degradation of methomyl has been studied in detail using hydrodynamic cavitation and further intensification of the degradation process was achieved via addition of intensifying agents such as H_2O_2, fenton reagent and ozone in combination with hydrodynamic cavitation. The main aim of using hybrid processes is to enhance the production of OH· radicals and thereby increasing the rate of degradation of methomyl. Depending upon the obtained results, following important conclusions can be established for degradation of methomyl.

- Optimization of process parameters such as inlet pressure to the cavitating device, cavitation number and initial pH of the solution plays an important role in maximizing the performance of hydrodynamic cavitation.
- Optimal inlet pressure of 5 bar with cavitation number of 0.1 and pH of 2.5 was required to exploit the maximum benefits of hydrodynamic cavitation.

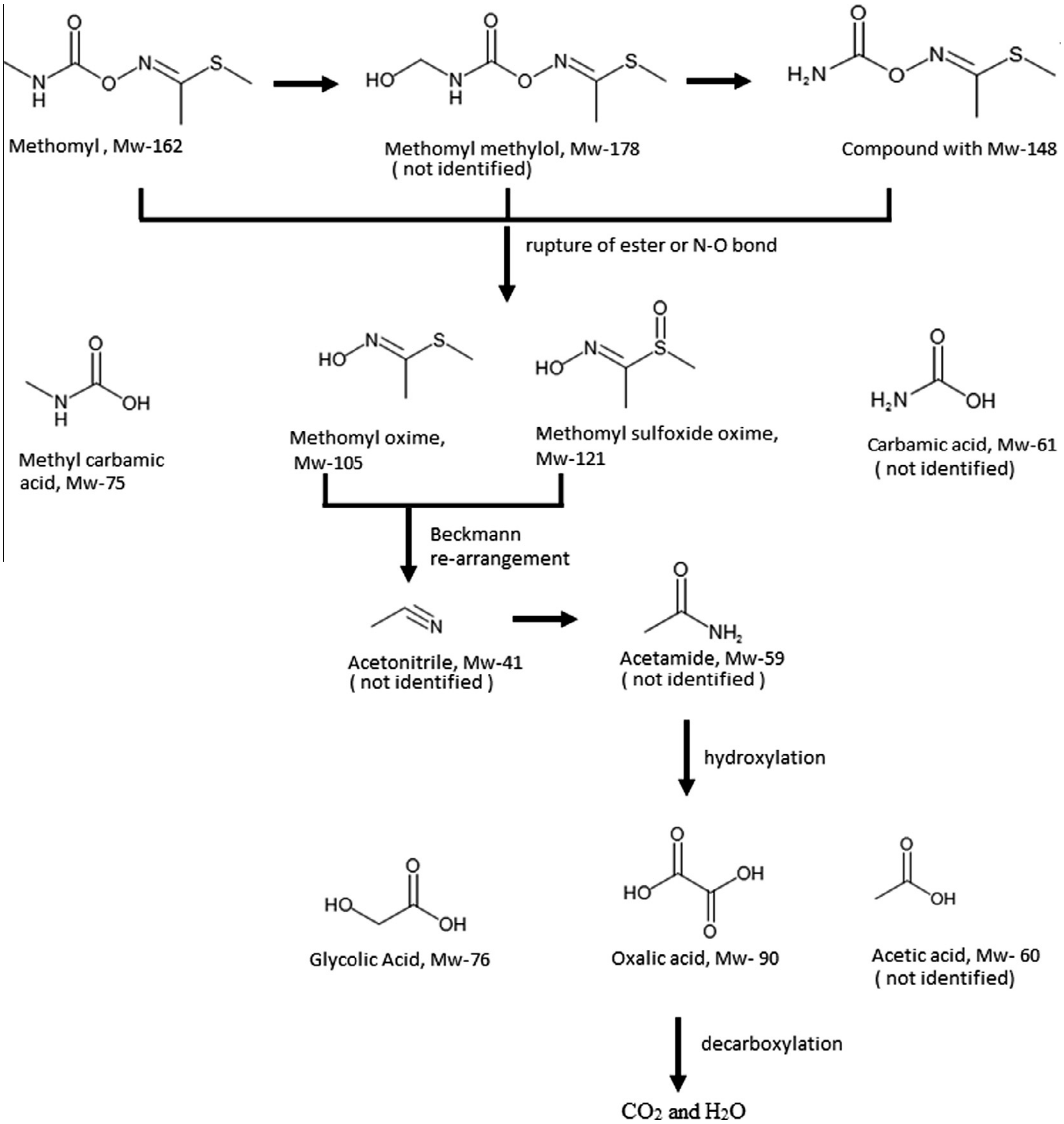

Fig. 13. Proposed reaction mechanism for the degradation of methomyl by applying hybrid process, HC + H_2O_2.

- Comparison of the rate of degradation of methomyl obtained in the case of hybrid and individual processes have confirmed that all the hybrid processes studied are more effective as compared to the individual processes.
- HC + H_2O_2 process lead to synergetic coefficient of 5.8 and HC + Fenton process lead to the synergetic coefficient of 13.41. HC + Ozone process has proved to be the most effective process with highest synergetic coefficient of 47.6.
- HC + Ozone process has also shown the highest extent of mineralization and energy efficiency among all the hybrid processes studied in the present work.

Hence, hydrodynamic cavitation based hybrid processes studied in the present work can be effectively used for the degradation of methomyl.

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Appendix A

Sample calculation for determination of cavitational yield in case of HC + Ozone process.

$$\text{Total moles of methomyl degraded in 6 min} = \text{Total moles of methomyl degraded in 6 min(moles/L)} * \text{Volume of solution (5L)} = 1.52 \times 10^{-4} \times 5 = 7.60 \times 10^{-4}\ \text{moles}$$

$$\text{Energy input to the system} = \text{Energy input to the(HC + ozonator + oxygen concentrator)in J/s} * \text{Time in s} = (1100 + 180 + 420) * 360 = 6.12 \times 10^{5}\ \text{J}$$

$$\text{Cavitational yield in moles/J} = \text{Total moles of methomyl degraded in 6 min} / \text{Energy input to the system in J} = 7.60 \times 10^{-4}/6.12 \times 10^{5} = 1.242 \times 10^{-9}\ \text{moles/J}$$

References

[1] V. Kitsiou, N. Filippidis, D. Mantzavinos, I. Poulios, Heterogeneous and homogeneous photocatalytic degradation of the insecticide imidacloprid in aqueous solutions, Appl. Catal. B Environ. 86 (2009) 27–35.

[2] M. Tamimi, S. Qourzal, N. Barka, A. Assabbane, Y. Ait-Ichou, Methomyl degradation in aqueous solutions by Fenton's reagent and the photo-Fenton system, Sep. Purif. Technol. 61 (2008) 103–108.

[3] S. Esplugas, J. Gimenez, S. Contreras, E. Pascual, M. Rodriguez, Comparison of different advanced oxidation processes for phenol degradation, Water Res. 36 (2002) 1034–1042.

[4] X. Wang, Y. Zhang, Degradation of alachlor in aqueous solution by using hydrodynamic cavitation, J. Hazard. Mater. 161 (2009) 202–207.

[5] D.V. Pinjari, A.B. Pandit, Cavitation milling of natural cellulose to nanofibrils, Ultrason. Sonochem. 17 (2010) 845–852.

[6] A.G. Chakinala, P.R. Gogate, A.E. Burgess, D.H. Bremner, Treatment of industrial wastewater effluents using hydrodynamic cavitation and the advanced Fenton process, Ultrason. Sonochem. 15 (2008) 49–54.

[7] M.M. Gore, V.K. Saharan, D.V. Pinjari, P.V. Chavan, A.B. Pandit, Degradation of reactive orange 4 dye using hydrodynamic cavitation based hybrid techniques, Ultrason. Sonochem. 21 (2014) 1075–1082.

[8] M. Franke, P. Braeutigam, Z. Wu, Y. Ren, B. Ondruschka, Enhancement of chloroform degradation by the combination of hydrodynamic and acoustic cavitation, Ultrason. Sonochem. 18 (2011) 888–894.

[9] T. Sivasankar, V.S. Moholkar, Mechanistic approach to intensification of sonochemical degradation of phenol, Chem. Eng. J. 149 (2009) 57–69.

[10] M.M. Mico, Jordi Bacardit, J. Malfeito, C. Sans, Enhancement of pesticide photo-Fenton oxidation at high salinities, Appl. Catal. B Environ. (2013) 162–169.

[11] A. Tomasevic, E. Kiss, S. Petrovic, D. Mijin, Study on the photocatalytic degradation of insecticide methomyl in water, Desalination 262 (2010) 228–234.

[12] S.R. Shirsath, D.V. Pinjari, P.R. Gogate, S.H. Sonawane, A.B. Pandit, Ultrasound assisted synthesis of doped TiO_2 nano-particles: characterization and comparison of effectiveness for photocatalytic oxidation of dyestuff effluent, Ultrason. Sonochem. 20 (2013) 277–286.

[13] T.A. Bashir, A.G. Soni, A.V. Mahulkar, A.B. Pandit, The CFD driven optimization of a modified venturi for cavitation activity, Can. J. Chem. Eng. 89 (2011) 1366–1375.

[14] S. Raut-Jadhav, V.K. Saharan, D. Pinjari, S. Sonawane, D. Saini, A. Pandit, Synergetic effect of combination of AOP's (hydrodynamic cavitation and H_2O_2) on the degradation of neonicotinoid class of insecticide, J. Hazard. Mater. 261 (2013) 139–147.

[15] V.K. Saharan, M.P. Badve, A.B. Pandit, Degradation of reactive red 120 dye using hydrodynamic cavitation, Chem. Eng. J. 178 (2011) 100–107.

[16] A.L. Patil, P.N. Patil, P.R. Gogate, Degradation of imidacloprid containing wastewaters using ultrasound based treatment strategies, Ultrason. Sonochem. 21 (2014) 1778–1786.

[17] K.P. Mishra, P.R. Gogate, Intensification of degradation of Rhodamine B using hydrodynamic cavitation in the presence of additives, Sep. Purif. Technol. 75 (2010) 385–391.

[18] M. Sivakumar, A.B. Pandit, Wastewater treatment: a novel energy efficient hydrodynamic cavitational technique, Ultrason. Sonochem. 9 (2002) 123–131.

[19] V.K. Saharan, M.A. Rizwani, A.A. Malani, A.B. Pandit, Effect of geometry of hydrodynamically cavitating device on degradation of Orange-G, Ultrason. Sonochem. 20 (2013) 345–353.

[20] P.R. Gogate, Treatment of wastewater streams containing phenolic compounds using hybrid techniques based on cavitation: a review of the current status and the way forward, Ultrason. Sonochem. 15 (2008) 1–15.

[21] M.V. Bagal, P.R. Gogate, Wastewater treatment using hybrid treatment schemes based on cavitation and Fenton chemistry: a review, Ultrason. Sonochem. 21 (2014) 1–14.

[22] J. Wang, X. Wang, P. Guo, J. Yu, Degradation of reactive brilliant red K-2BP in aqueous solution using swirling jet-induced cavitation combined with H_2O_2, Ultrason. Sonochem. 18 (2011) 494–500.

[23] P.N. Patil, S.D. Bote, P.R. Gogate, Degradation of imidacloprid using combined advanced oxidation processes based on hydrodynamic cavitation, Ultrason. Sonochem. 21 (2014) 1770–1777.

[24] C. Segura, C. Zaror, H.D. Mansilla, M.A. Mondaca, Imidacloprid oxidation by photo-fenton reaction, J. Hazard. Mater. 150 (2008) 679–686.

[25] A.A. Pradhan, P.R. Gogate, Degradation of p-nitrophenol using acoustic cavitation and Fenton chemistry, J. Hazard. Mater. 173 (2010) 517–522.

[26] C. Weng, Y. Lin, C. Chang, N. Liu, Decolourization of direct blue 15 by Fenton/ultrasonic process using a zero-valent iron aggregate catalyst, Ultrason. Sonochem. 20 (2013) 970–977.

[27] S. Raut-Jadhav, V.K. Saharan, D. Pinjari, S. Sonawane, D. Saini, A. Pandit, Intensification of degradation of imidacloprid in aqueous solutions by combination of hydrodynamic cavitation with various advanced oxidation processes (AOPs), J. Environ. Chem. Eng. 1 (2013) 850–857.

[28] Z. Guo, Z. Zheng, S. Zheng, W. Hu, R. Feng, Effect of various sono-oxidation parameters on the removal of aqueous 2,4-dinitrophenol, Ultrason. Sonochem. 12 (2005) 461–465.

[29] L.K. Weavers, M.R. Hoffmann, Sonolytic decomposition of ozone in aqueous solution: mass transfer effects, Environ. Sci. Technol. 32 (1998) 3941–3947.

[30] Z. Wu, M. Franke, B. Ondruschka, Y. Zhang, Y. Ren, P. Braeutigam, W. Wang, Enhanced effect of suction-cavitation on the ozonation of phenol, J. Hazard. Mater. 190 (2011) 375–380.

[31] Z. Wu, H. Shen, B. Ondruschka, Y. Zhang, W. Wang, D.H. Bremner, Removal of blue-green algae using the hybrid method of hydrodynamic cavitation and ozonation, J. Hazard. Mater. 235–236 (2012) 152–158.

[32] L.K. Weavers, F.H. Ling, M.R. Hoffmann, Aromatic compound degradation in water using a combination of sonolysis and ozonolysis, Environ. Sci. Technol. 32 (1998) 2727–2733.

[33] R. Lall, R. Mutharasan, Y.T. Shah, P. Dhurjati, Decolorization of the dye reactive blue 19, using ozonation, ultrasound, and ultrasound-enhanced ozonation, Water Environ. Res. 75 (2003) 171–179.

[34] H. Destaillats, A.J. Colussi, J.M. Joseph, M.R. Hoffmann, Synergistic effects of sonolysis combined with ozonolysis for the oxidation of azobenzene and methyl orange, J. Phys. Chem. A 104 (2000) 8930–8935.

[35] L.K. Weavers, N. Malmstadt, M.R. Hoffmann, Kinetics and mechanism of pentachlorophenol degradation by sonication, ozonation, and sonolytic ozonation, Environ. Sci. Technol. 34 (2000) 1280–1285.

[36] J.-W. Kang, M.R. Hoffmann, Kinetics and mechanism of the sonolytic destruction of methyl tert-butyl ether by ultrasonic irradiation in the presence of ozone, Environ. Sci. Technol. 32 (1998) 3194–3199.

[37] M. Tamimi, S. Qourzal, A. Assabbane, J.M. Chovelon, C. Ferronato, Y. Ait-Ichou, Photocatalytic degradation of pesticide methomyl: determination of the reaction pathway and identification of intermediate products, Photochem. Photobiol. Sci. 5 (2006) 477–482.