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Intensification of degradation of methomyl (carbamate group pesticide) by using the combination of ultrasonic cavitation and process intensifying additives

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ABSTRACT

In the present work, the degradation of methomyl has been carried out by using the ultrasound cavitation (US) and its combination with H_2O_2, Fenton and photo-Fenton process. The study of effect of operating pH and ultrasound power density has indicated that maximum extent of degradation of 28.57% could be obtained at the optimal pH of 2.5 and power density of 0.155 W/mL. Application of US in combination with H_2O_2, Fenton and photo-Fenton process has further accelerated the rate of degradation of methomyl with complete degradation of methomyl in 27 min, 18 min and 9 min respectively. Mineralization study has proved that a combination of US and photo-Fenton process is the most effective process with maximum extent of mineralization of 78.8%. Comparison of energy efficiency and cost effectiveness of various processes has indicated that the electrical cost of 79892.34 Rs./m^3 for ultrasonic degradation of methomyl has drastically reduced to 2277.00 Rs./m^3, 1518.00 Rs./m^3 and 807.58 Rs./m^3 by using US in combination with H_2O_2, Fenton and photo-Fenton process respectively. The cost analysis has also indicated that the combination of US and photo-Fenton process is the most energy efficient and cost effective process.

1. Introduction

Methomyl is a broad spectrum insecticide which belongs to the family of oxime carbamate pesticides [1]. It has been widely used all over the world because of its powerful control against many insects and pests. It can easily cause contamination of both ground and surface water resources, due to its high solubility (57.9 g/L, 20 °C) in water and a low-sorption affinity to soils [2]. Presence of methomyl in water bodies can cause potential impact on the human health and environment because of its toxic and hazardous nature [3].

Various studies have been reported in the literature for the degradation of methomyl, which mainly includes the application of advanced oxidation processes such as photocatalytic [2–5] and Fenton, photo-Fenton processes [1,5,6]. Tamimi et al. [1] have investigated the degradation of methomyl in aqueous solutions by using Fenton (H_2O_2/Fe^{2+}) and photo-Fenton (H_2O_2/Fe^{2+}/UV) process. Complete degradation of methomyl was achieved after 60 min of operation with 23% and 48% of TOC reduction in case of Fenton and photo-Fenton processes respectively. In other study, Tamimi et al. [2] have reported that photocatalytic degradation of methomyl using Degussa-P25 TiO_2 could lead to 80% TOC removal in less than 4 h. Tomasevic et al. [3] have studied the photocatalytic degradation of methomyl in water using Fe-ZSM-5 zeolite and AlFe-pillared montmorillonite catalysts under halogen lamp light and obtained 100% TOC removal within 4 h using 5 g/L Fe-ZSM-5 zeolite. Malato et al. [5] have also carried out photocatalytic degradation of water-soluble pesticides (diuron, imidacloprid, formetanate and methomyl) by the application of photo-Fenton and solar light driven photocatalytic process using TiO_2. Photo-Fenton process was found to be more efficient than the photocatalysis process on the basis of both, the extent of degradation as well as extent of mineralization of methomyl. Mico et al. [6] have reported enhancement in the performance of photo-Fenton reaction at high salinity conditions when applied for the oxidation of methomyl. However, the degradation of methomyl by the application of ultrasound cavitation is not yet reported in the literature, to the best of

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our knowledge. Ultrasound cavitation is an emerging advanced oxidation process which can be used for the effective degradation of organic pollutants [7]. It consists of mainly three steps occurring repetitively: nucleation, rapid growth of cavities during the compression/rarefaction cycles and the implosion of the cavities once they reach a critical size [8]. Implosion of the cavities subsequently induces thermal dissociation of water and dissolved oxygen molecules to convert them into reactive species such as hydroxyl radicals ($OH^{\cdot}$), hydrogen atoms ($H^{\cdot}$), oxygen atoms ($O^{\cdot}$) and hydroperoxyl radicals ($HO_2^{\cdot}$) (Eqs. (1)–(3)) [8,9]. In addition to this, ultrasound cavitation also generates hot spots, strong acoustic streaming and intense fluid turbulence at very short time scale [10].

$$H_2O+))) \rightarrow OH^{\cdot} + H^{\cdot} \tag{1}$$

$$O_2+))) \rightarrow 2O^{\cdot} \tag{2}$$

$$OH^{\cdot} + O^{\cdot} \rightarrow HO_2^{\cdot} \tag{3}$$

where “)))” signifies ultrasound waves.

The radicals generated may reach the water-cavity interface or diffuse into the bulk solution where they can oxidize the target pollutant. However, the degradation efficiency of ultrasonic reactors is not very promising and economically attractive if applied individually. For this reason, ultrasound cavitation is generally combined with H_2O_2, Fenton, photo-Fenton, ozone, photocatalytic process, etc. for the intensification of degradation of organic pollutants [7,8].

Present work deals with the application ultrasound cavitation in combination with H_2O_2, Fenton and photo-Fenton process for accelerating the rate of degradation of methomyl that can be otherwise obtained using individual ultrasound cavitation. It also includes the optimization of operating parameters such as initial pH of the solution and ultrasound power density for maximizing the performance of ultrasound cavitation. In addition to this, extent of mineralization, energy efficiency and cost effectiveness of individual US and hybrid processes have also been studied in order to obtain the most effective and economical process for the degradation of methomyl.

2. Materials and methods

2.1. Materials

Commercial grade methomyl (Dupont) was used as a model organic pollutant without further purification. The structure of the methomyl is as shown in Fig. 1. Hydrogen peroxide (30% w/v), ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$), sodium sulfite (Na_2SO_3) and sulfuric acid (H_2SO_4) all of AR grade were obtained from Thomas Baker, 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.

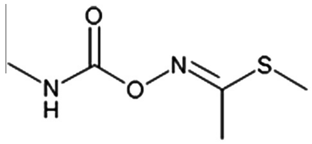

Fig. 1. Molecular structure of methomyl.

2.2. Experimental set up

Schematic representation of experimental set up has been given in Fig. 2. It essentially consists of ultrasonic processor, quartz reactor, temperature indicator, UV source and wooden UV shield. Ultrasonic cavitation was induced by using a low frequency (20 kHz) ultrasonic processor (make-Johnson Plastosonic Pvt. Ltd., India) having a tip diameter of 13 mm and maximum power dissipation of 500 W with a facility of varying amplitude viz. 25%, 50%, 75% and 100%. The tip was immersed in the aqueous solution of methomyl to the depth of 1 cm. All the experiments were carried out in a 250 mL quartz reactor with a cooling jacket to control the temperature increase due to cavitational effects and UV irradiation. The reaction temperature was maintained at 28 ± 3 °C (ambient conditions) by continuously circulating cold water through the cooling jacket. UV source was used in case of photo-Fenton process and its combination with ultrasonic cavitation. Wooden UV shield has been provided to eliminate the possibility of exposure to harmful UV irradiation.

2.3. Experimental methodology

All the experiments were performed with 250 mL aqueous solution of methomyl having initial concentration of 25 ppm. Initially, the effect of power density (i.e. energy input per milliliter of solution) on the rate of sonochemical degradation of methomyl was studied by varying the ultrasonic irradiation amplitude viz. 25%, 50%, 75% and 100%. Calorimetric study was performed to obtain the calorimetric efficiency of the horn at varying operating amplitudes. Further, the effect of initial pH on sonochemical degradation of methomyl was also investigated by varying the pH in the range of 2.5–7.5 (2.5, 3, 5 and 7.5). Initial pH was adjusted by adding H_2SO_4 as per the requirement.

In order to increase the degradation efficiency of methomyl, the experiments were also carried out by combining the ultrasonic cavitation with process intensifying additives such as H_2O_2 and Fenton reagent. The effect of loading of H_2O_2 on sonochemical degradation of methomyl was investigated by varying the molar ratio of methomyl to H_2O_2 viz. 1:10, 1:20, 1:30, 1:40 and 1:50 for fixed initial concentration of methomyl (25 ppm) to determine an optimal concentration of H_2O_2.

The combined process of ultrasonic cavitation and Fenton chemistry was also employed for the degradation of methomyl. The effect of loading of ferrous ions on sonochemical degradation of methomyl has been evaluated by varying molar ratio of Fe^{2+}: H_2O_2 viz. 1:50, 1:40 and 1:30 at fixed optimal concentration of H_2O_2. Furthermore, the combined process of ultrasonic cavitation and photo-Fenton process was also utilized to further enhance the rate of degradation of methomyl. Two UV lamps of 8 W each were used as a source of ultraviolet light. In order to obtain the synergistic effect, the efficacy of hybrid processes (combinations of AOP’s) was compared with the efficacy of individual processes based on the rate and the extent of degradation of methomyl accomplished. For this reason experiments were also carried out at optimized loadings of additives in the absence of ultrasound i.e. conventional approach of only stirring.

The mineralization study of methomyl was also carried out by analyzing total organic carbon content of the samples obtained at optimized conditions.

2.4. Analysis

High pressure liquid chromatography (HPLC) equipped with C18 column of dimensions 4.6 × 250 mm (make-JASCO, Japan Spectroscopic Corporation, Japan) was used to determine the concentration of methomyl at a set interval of time. The mobile phase consists of a mixture of 30% acetonitrile and 70% water with flow rate maintained at 1 mL/min and UV detector set at wavelength of 234 nm. Quenching agent (0.5 N sodium sulfite) has been added

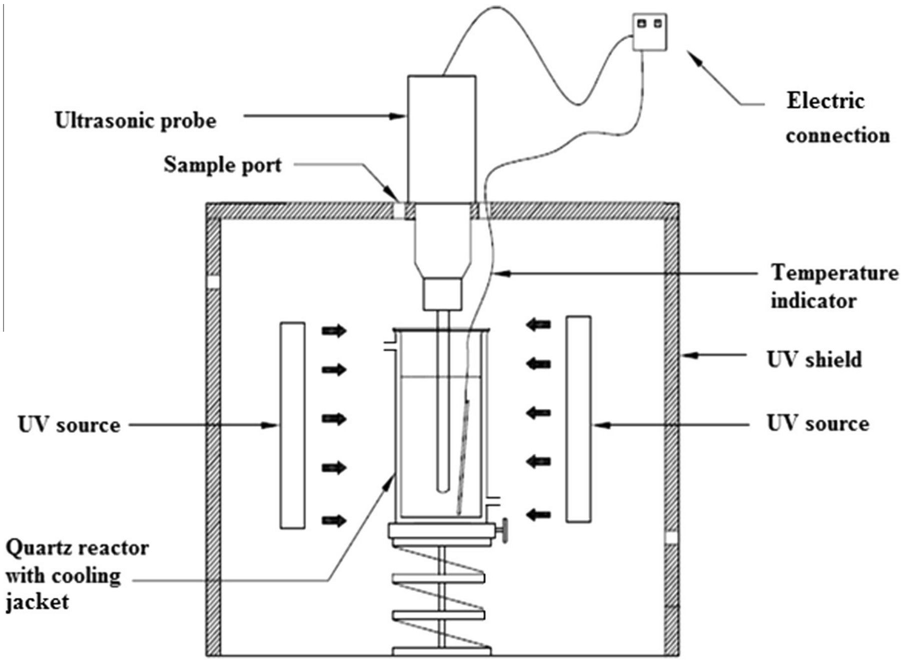

Fig. 2. Schematic representation of experimental set-up.

immediately to the samples withdrawn, so as to obtain the accurate concentration of methomyl at any instance of time. The extent of mineralization of methomyl at various optimum conditions was analyzed by using total organic carbon analyzer (make-Shimadzu corporation, Japan).

3. Results and discussion

3.1. Effect of the power density

Ultrasonic power density is an important parameter in deciding the effectiveness of the sonochemical reactors since it greatly affects the number of cavitational effects, collapse intensity and economy of the sonochemical processes [11]. For this reason the optimization of ultrasonic power density becomes very essential. The effect of ultrasonic power on the rate of degradation of methomyl has been investigated by varying the amplitude viz. 25%, 50%, 75% and 100% yielding 125 W, 250 W, 375 W and 500 W of theoretical energy input. All the experiments have been carried out by keeping the volume of the aqueous solution of methomyl constant (250 mL) with an initial concentration of 25 ppm. Calorimetric study has been performed to determine the actual power dissipated into the solution [12]. The calorimetric efficiency has been evaluated by using Eq. (4).

$$\text{Calorimetric efficiency} = \frac{m \times C_p \times \Delta T}{\text{Electrical energy supplied} \times \text{time of operation}} \tag{4}$$

where m is the mass of water in kg, C_p is specific heat of water in J/kg °C and ΔT is the rise in temperature in °C. Calorimetric efficiency has been utilized further to determine the power density i.e. energy dissipated per mL of the solution as shown in Eq. (5)

$$\text{Power density} = \frac{\text{Electrical energy input in W} \times \text{Calorimetric efficiency}}{\text{Volume of solution}} \tag{5}$$

The results obtained for the effect of power density are illustrated in Fig. 3. Calorimetric efficiency and power density calculated at various amplitudes have been depicted in the Table 1 along with the effect of power density on the reaction rate constant and the extent of degradation of methomyl. It has been observed that the rate of degradation of methomyl increases with an increase in the power density till the optimal value of 0.155 W/mL and then with further increase in the power density, the rate of degradation of methomyl was reduced. Augmentation of the ultrasonic power density from 0.118 W/mL to 0.155 W/mL has significantly increased the reaction rate constant from 1.651 × 10^{-3} min^{-1} to 3.806 × 10^{-3} min^{-1} respectively. However, further enhancement of the ultrasonic power density to 0.185 W/mL and 0.218 W/mL has witnessed reduction in the reaction rate constant to 3.268 × 10^{-3} min^{-1} and 2.875 × 10^{-3} min^{-1} respectively.

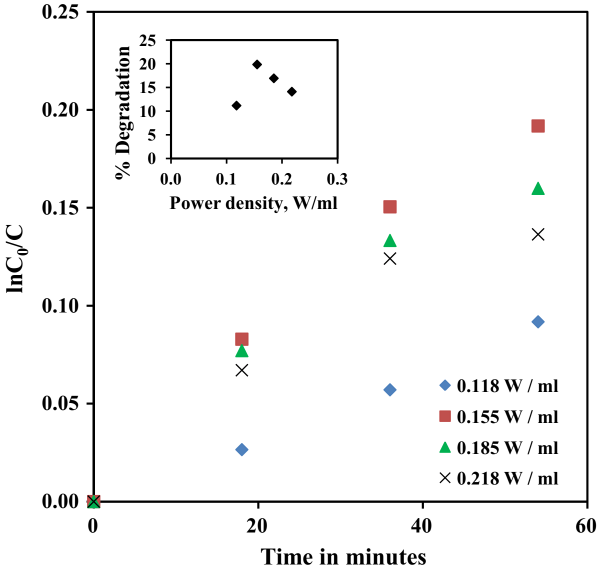

Fig. 3. Effect of power density on rate of degradation of methomyl using US (subjected to: volume of sample – 250 mL, pH – 3.0, concentration of methomyl – 25 ppm).

Table 1
Effect of power density on reaction rate constant and extent of degradation of methomyl.

Amplitude (%)	Input energy *W*	Calorimetric efficiency %	US Power density *W*/mL	$k \times 10^3$ min^{-1}	Extent of degradation after 72 min
25	125	23.639	0.118	1.651	11.15
50	250	15.528	0.155	3.806	19.83
75	375	12.360	0.185	3.268	16.91
100	500	10.893	0.218	2.875	14.09

The results obtained are credited to the fact that with an increase in the power density, the number of cavities generated would be higher, resulting into more profound cavitation phenomena [9]. Net production of hydroxyl radicals will also be higher due to increased cavitational activity leading to a higher rate of degradation of organic pollutant [13,14]. However, when ultrasonic power density increases beyond an optimal value, the number density of the cavities generated would be so high that sound wave may get scattered and the collapse pressure effect may get dampened. In addition to this the size of the cavity would also be very large at higher power density, resulting into insufficient or less intense cavity collapse [15]. As a consequence, less number of hydroxyl radicals would be generated resulting into the lower rate of degradation of methomyl at very high ultrasonic power density. Credence to this discussion can be obtained by similar findings reported in the literature. Guo et al. [15] have also observed that the rate of degradation of levofloxacin increases with an increase in the ultrasound power till the optimal ultrasound power density of 0.346 W/mL and then the rate of degradation started decreasing rapidly with further increase in the ultrasound power. Furthermore, similar results of maximum degradation rate at an optimum ultrasound power have also been obtained in case of sonochemical degradation of chlorinated compounds [16] and acetic acid [17].

3.2. Effect of the initial pH of solution

Methomyl, being a non volatile compound, its sonochemical degradation mainly occurs by the generation and subsequent attack of hydroxyl radicals. It has been observed by many researchers that the rate of production of hydroxyl radicals during cavitation strongly depends on the initial pH of the solution [11–19]. Considering this, the effect of pH has been investigated over the pH range of 2.5–7.5. The obtained results of effect of pH have been illustrated in Fig. 4. It has been observed that reducing initial pH of the solution to acidic side significantly enhances the rate of degradation of methomyl. By reducing the initial pH of the solution from 7.5 to 2.5, the rate of degradation of methomyl significantly augmented from 0.564×10^{-3} min^{-1} to 4.861×10^{-3} min^{-1}. For this reason, all the further experiments were performed with an optimal pH of 2.5 since it leads to a maximum extent of degradation of methomyl (28.57%).

The results obtained are attributed to the fact that acidic conditions inside the cavitation reactors leads to a lower recombination rate of hydroxyl radicals with higher oxidation potential [18,19]. Hence, the rate of degradation of methomyl would ultimately enhance at lower pH due to the availability of higher number of hydroxyl radicals. The obtained results of higher rate of degradations at an acidic pH are in accordance with the findings of other researchers. Sonochemical degradation of other pesticides such as alachlor [18] and methyl parathion [19] have also indicated that the rates of degradation are higher under acidic pH.

3.3. Combination of ultrasonic cavitation and H_2O_2

Hydrogen peroxide can be utilized as an intensifying agent for enhancing the sonochemical degradation organic pollutants, since it readily dissociates in the presence of cavitation and generates highly reactive hydroxyl radicals (Eq. (6)) [20–24]. This is because, dissociation energy required for breaking the O–O bond in H_2O_2 is only 213 kJ/mol as compared to dissociation energy of 418 kJ/mol required for breaking the O–H bond in H_2O_2 [8]. Hence, the addition of H_2O_2 to ultrasonic cavitation reactor could further accelerate the rate of degradation of methomyl. However, an optimal concentration of H_2O_2 exists and exceeding the concentration of H_2O_2 beyond an optimal value may leads to undesirable reactions of scavenging of the already generated free radicals (Eqs. (7)–(9))

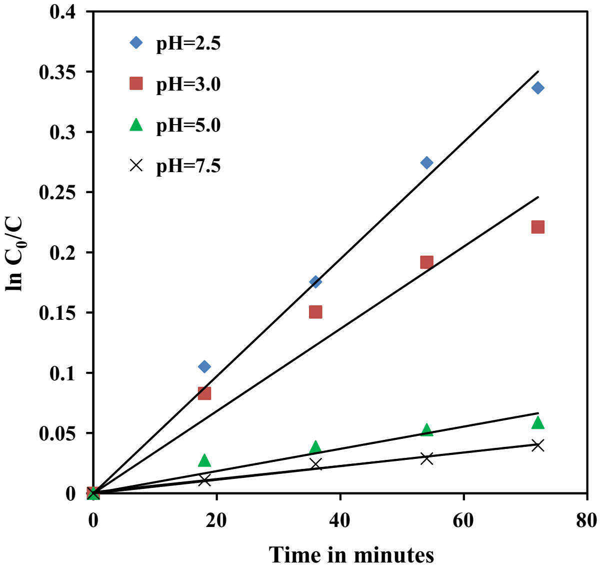

Fig. 4. Effect of pH on rate of degradation of methomyl using US (subjected to: volume of sample – 250 mL, amplitude – 50%, concentration of methomyl – 25 ppm).

$$H_2O_2 +)))US \rightarrow 2OH^{\cdot} \quad (6)$$

$$2OH^{\cdot} \rightarrow H_2O_2 \quad (7)$$

$$H_2O_2 + OH^{\cdot} \rightarrow HO_2^{\cdot} + H_2O \quad (8)$$

$$2HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \quad (9)$$

In view of this, the effect of loading of H_2O_2 on the sonochemical degradation of methomyl have been investigated by varying the molar ratio of methomyl to H_2O_2 viz. 1:10, 1:20, 1:30, 1:40 and 1:50. The obtained results of the effect of H_2O_2 loading was fitted to first order rate of degradation as illustrated in Fig. 5. It can be seen that the rate of degradation of methomyl increases with an increase in the molar ratio of methomyl:H_2O_2 till the optimal molar ratio of 1:30, beyond which the rate of degradation of methomyl starts reducing. The results obtained are obviously due to higher rate of generation of hydroxyl radicals at higher loading of H_2O_2 leading to an elevated rate of degradation of methomyl. However, at very high concentration of H_2O_2 beyond an optimal value, the scavenging and recombination reactions of hydroxyl radicals are dominating instead of desired dissociation reaction of H_2O_2

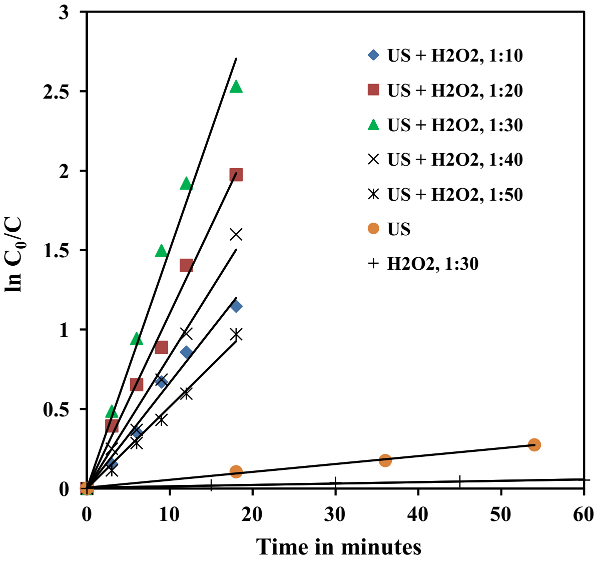

Fig. 5. Effect of H_2O_2 on the rate of degradation of methomyl using US + H_2O_2 process (subjected to: volume of sample – 250 mL, amplitude – 50%, concentration of methomyl – 25 ppm).

and subsequent attack of OH· radicals. Goel et al. [20], Nam et al. [21] and Ku et al. [22] have also reported that an optimal concentration of H_2O_2 exists and an excessive amount of H_2O_2 beyond an optimal value reduces the degradation rates. However, the optimal concentration of H_2O_2 would not be the same for different organic pollutants as its location is decided by its *HLB* (Hydrophile–Lipophile Balance) value.

Synergistic effect has been observed by combining the ultrasonic cavitation and H_2O_2, since the rate of degradation of methomyl obtained in case of combined process has found to be extremely high as compared to the rate of degradation of methomyl obtained in the case of individual ultrasonic cavitation and H_2O_2. Synergistic coefficient (*f*) based on the rate of degradation of methomyl can be obtained as (Eq. (10))

$$f = \frac{k_{(HC+H_2O_2)}}{k_{HC} + k_{H_2O_2}} = 25.74 \tag{10}$$

Combination of ultrasonic cavitation and H_2O_2 resulting in a significant synergistic effect may be due to the higher rate of dissociation of H_2O_2 into hydroxyl radicals in the presence of cavitation along with their effective utilization due to high fluid turbulence created during cavitation, resulting into higher rate of degradation of methomyl [23,24].

3.4. Combination of ultrasonic cavitation and Fenton process

Fenton process has found wide applications in the treatment of waste water containing organic pollutants, due to its ability to produce highly reactive hydroxyl radicals through the iron catalyzed dissociation of H_2O_2 in acidic conditions (Eq. (11)) [1]. Hydroxyl radicals generated can further degrade the targeted organic pollutant and may lead to its complete mineralization.

Intensification of the rate of degradation of organic pollutant can be achieved by a combination of ultrasonic cavitation with Fenton reagent, since it leads to a higher generation of hydroxyl radicals via regeneration of catalyst (i.e. Fe^{2+}) as per Eqs. (12) and (13) [18,19]. In addition to this, as per Eq. (6) some part of H_2O_2 directly dissociates in the presence of cavitation generating additional hydroxyl radicals.

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^{\cdot} \tag{11}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe\text{-}(HO_2)^{2+} + H^+ \tag{12}$$

$$Fe\text{-}(HO_2)^{2+}+)))US \rightarrow Fe^{2+} + HO_2^{\cdot} \tag{13}$$

With this background, the combination of ultrasonic cavitation and Fenton process has been investigated by carrying out the experiments at the constant optimal molar ratio of methomyl to H_2O_2 of 1:30 and varying the molar ratio of Fe^{2+}:H_2O_2 viz. 1:50, 1:40 and 1:30. The obtained results have been illustrated in the Fig. 6. It has been observed that the rate of the degradation of methomyl increases with an increase in the amount of ferrous ions due to higher generation of hydroxyl radicals.

The combination of ultrasonic cavitation with Fenton process leads to a synergistic effect since the rate of degradation of methomyl of $4.861 \times 10^{-3}\ \text{min}^{-1}$ and $7.754 \times 10^{-3}\ \text{min}^{-1}$ obtained in case of individual processes of ultrasonic cavitation and Fenton process has substantially increased to $172.855 \times 10^{-3}\ \text{min}^{-1}$ by applying a combination of ultrasonic cavitation and Fenton process. The synergistic coefficient (*f*) based on the reaction rate constant can be calculated as (Eq. (14)),

$$f = \frac{k_{(HC+Fenton)}}{k_{HC} + k_{Fenton}} = 13.70 \tag{14}$$

The synergistic effect of the combination of ultrasonic cavitation and Fenton process has confirmed the fact that combined process leads to a higher generation of hydroxyl radicals, since the Fe^{2+} ions get regenerated in the presence of cavitation resulting into higher rate of dissociation of H_2O_2 [25]. Additionally, high fluid turbulence created by cavitation also leads to an improved utilization of hydroxyl radicals. Findings reported in the literature have also confirmed that as compared to individual ultrasonic cavitation, its combination with Fenton chemistry leads to a higher rate of degradation of organic pollutants such as bisphenol A [25], ibuprofen [26], paracetamol [27], 1,4-dioxane [28], etc.

3.5. Combination of ultrasonic cavitation and photo-Fenton process

In a conventional photo-Fenton process, in addition to the hydroxyl radicals generated due to the dissociation of hydrogen peroxide in the presence iron catalyst (Eq. (11)), the formation of hydroxyl radicals also occurs by the following reaction (Eq. (15)) [1]:

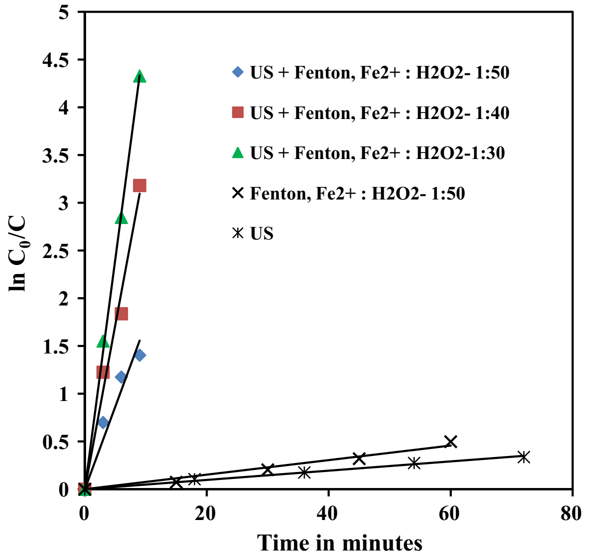

Fig. 6. Effect of molar ratio of Fe^{2+}: H_2O_2 on the rate of degradation of methomyl using US + Fenton process (subjected to: volume of sample – 250 mL, amplitude – 50%, concentration of methomyl – 25 ppm, molar ratio of methomyl: H_2O_2 = 1:30).

$$Fe^{3+} + H_2O + h\nu \rightarrow OH^{\cdot} + Fe^{2+} + H^+ \quad (15)$$

Hence, UV energy not only generates the additional hydroxyl radicals but also leads to regeneration of catalyst through restoring of Fe^{2+} ions. Combination of ultrasonic cavitation with the photo-Fenton process can further augment the rate of generation of hydroxyl radicals and hence can be used for the intensification of the degradation of methomyl.

In view of this, experiments have been conducted with an aim of comparing the rates of degradation of methomyl obtained in the case of individual ultrasonic cavitation (US), conventional photo-Fenton process and a combination of US with photo-Fenton process. The obtained findings have been illustrated in Fig. 7. Significant synergistic effect has been observed since, the first order reaction rate constant of $4.861 \times 10^{-3}\,\text{min}^{-1}$ and $15.455 \times 10^{-3}\,\text{min}^{-1}$ obtained in case of individual US and photo-Fenton process has drastically amplified to $574.412 \times 10^{-3}\,\text{min}^{-1}$ by combining US and photo-Fenton process with complete degradation of methomyl in just 9 min. The synergistic effect can be quantified by determining the synergistic coefficient (*f*) based on reaction rate constant as (Eq. (16)),

$$f = \frac{k_{(\text{HC+photo-Fenton})}}{k_{\text{HC}} + k_{\text{photo-Fenton}}} = 28.27 \quad (16)$$

The obtained synergistic effects can be attributed to the beneficial effects of the combination of ultrasonic cavitation and photo-Fenton process. It includes enhanced generation and effective utilization of hydroxyl radicals, restoring of iron catalyst and an increase in the probability of exposure of target pollutant to the UV light due to effective mixing by cavitation. Torres et al. [29], Segura et al. [30] and Raut-Jadhav et al. [31] have also demonstrated that the combined process of cavitation and photo-Fenton process is more effective as compared to the individual processes.

3.6. Mineralization study

Generally, CO_2, H_2O and some stable intermediates are the final oxidation products obtained during the degradation of organic pollutants using advanced oxidation processes. These stable intermediate which could not be degraded further, contribute to the total organic carbon content of the sample [32]. Hence, mineralization study has been carried out by evaluating the extent of TOC reduction obtained using various individual and combined processes. The results obtained have been given in Fig. 8. It can be seen that TOC reduced merely by 9.57% when the degradation of methomyl was carried out by using only ultrasonic cavitation process. However, combining ultrasonic cavitation with the intensifying additives has shown considerable enhancement in the extent of TOC reduction. After treatment of 72 min, extent of mineralization of 26.9% and 55.32% has been obtained by combining ultrasonic cavitation with H_2O_2 and Fenton process respectively. Combined process of ultrasonic cavitation and photo-Fenton process has proved to be the most effective process with a maximum extent of mineralization of 78.8%. Overall, all the combined processes lead to higher rate of mineralization of methomyl as compared to individual ultrasonic cavitation due to increased generation of $OH^{\cdot}$ radicals in case of combined processes.

3.7. Power consumption and cost effectiveness

Electrical power consumption plays an important role in estimating the cost effectiveness of the ultrasonic cavitation based processes, since electric energy consumption represents a significant fraction of the operating cost of such processes [30]. A simple economical comparison of the individual ultrasonic cavitation and different hybrid processes has been given in Table 2. Costing of the process has been evaluated on the basis of energy dissipated in the system, considering the approximate cost of electricity in India as Rs. 5.06/kWh.

Power consumption (kWh/m^3) during individual US and US based hybrid processes has been evaluated based on the treatment time needed for the complete degradation of methomyl. A need of extremely high power consumption in the case of individual ultrasonic cavitation makes the stand alone process too expensive, mainly due to the low rate of degradation of methomyl leading to very high treatment time. However, the combination of US with H_2O_2 or Fenton or photo-Fenton process makes the process economically attractive, primarily due to drastic reduction in the treatment time required for obtaining a complete degradation of methomyl. The affirmation of the hybrid processes to be more economical is credited to the fact that hybrid processes lead to an increased generation of hydroxyl radicals, which subsequently increases the rate of degradation of methomyl [33]. Although,

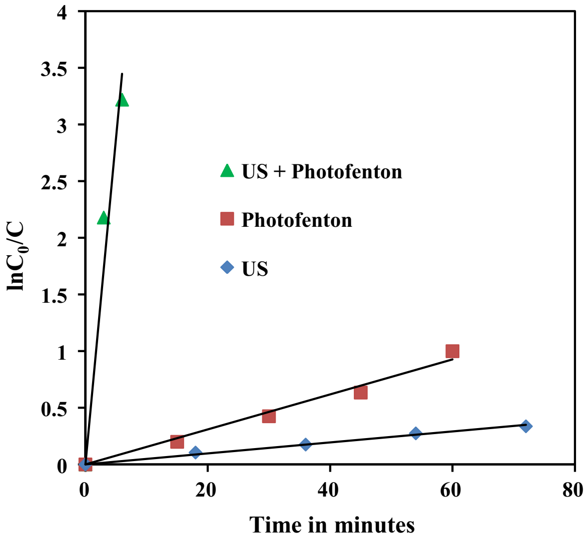

Fig. 7. Comparison of rate of degradation of methomyl obtained in case of individual photo-Fenton, US and hybrid process US + Photo-Fenton.

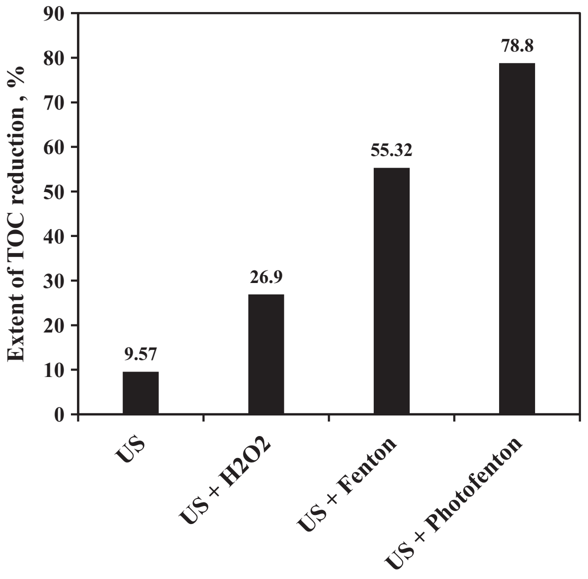

Fig. 8. Comparison of extent of TOC reduction obtained in case of various hybrid processes.

Table 2
Comparison of power consumption and cost effectiveness of various processes.

Process	Power supplied in W/l	% Degradation	Treatment time in min	Power consumption kWh/m^3	Cost of electricity in Rs./m^3
US	1000	28.7	72	15789.00	79892.34
US + H_2O_2	1000	100	27	450.00	2277.00
US + Fenton	1000	100	18	300.00	1518.00
US + photo-Fenton	1064	100	9	159.60	807.58

additional energy was required, a combination of US and photo-Fenton process has proved to be the most cost effective one, since the rate of degradation of methomyl was very high leading to a complete degradation of methomyl in just 9 min. Thus, the cost of methomyl degradation of 79892.34 Rs./m^3 incurred during US has reduced almost by 98 times i.e. to 807.58 Rs./m^3 when US was combined with photo-Fenton process. The detailed sample calculations have been demonstrated in the Appendix A.

The results obtained are analogous to the findings reported in the literature. Mahamuni and Adewuyi [34] have reported that the cost of phenol degradation of $15536.59/1000 gallon required in case of ultrasonic cavitation got reduced by more than 100 times when ultrasonic cavitation is combined with Fenton process ($137.626/1000 gallon). Jyoti and Pandit [35] have also demonstrated that the cost of ultrasonic treatment of 9.75 Rs./l of water for the destruction of total coliforms reduced to 7.62 Rs./l when US was combined with 5 mg/l of H_2O_2 and further significantly reduced to 0.36 Rs./l when US was combined with 2 mg/l of O_3.

4. Conclusions

The detailed investigation of the effect of the operating parameters and process intensifying additives on the rate of degradation of methomyl has established the following important conclusions:

- Rate of degradation of methomyl increases with an increase in the ultrasound power density till it reaches an optimal value at 0.155 W/mL of power dissipation, beyond which the reduction in the rate of degradation of methomyl was observed.
- Acidic conditions are found to be favorable with a maximum extent of degradation of 28.57% at an optimal pH of 2.5.
- Ultrasonic cavitation in combination with H_2O_2 has appreciably enhanced the rate of degradation of methomyl leading to a synergistic coefficient of 25.74. However, an optimal concentration of H_2O_2 exists (optimal molar ratio of methomyl:H_2O_2 is 1:30), beyond which the rate of degradation of methomyl rather reduces due to the scavenging of hydroxyl radicals.
- Ultrasonic cavitation in combination with Fenton or photo-Fenton process has also resulted in the intensification of the rate of degradation of methomyl with synergistic coefficient of 13.70 and 28.27 respectively.
- Ultrasonic cavitation in combination photo-Fenton was found to the most effective process yielding a complete degradation of methomyl in just 9 min with a maximum extent of mineralization of 78.8%.
- Electricity cost of 79892.34 Rs./m^3 required for ultrasonic degradation of methomyl has drastically reduced to 2277.00 Rs./m^3, 1518.00 Rs./m^3 and 807.58 Rs./m^3 by using US in combination with H_2O_2, Fenton and photo-Fenton process respectively.

Appendix A

Sample calculation of power consumption and cost of treatment for the complete degradation of methomyl

A. Ultrasound cavitation (with 50% amplitude):
   Electrical power supplied = 250 W and treatment volume = 250 mL = 0.25 l.
   Energy required = 250/0.25 W/l = 1000 kW/m^3.
   First order reaction rate constant, $k = 4.861 \times 10^{-3}$ min^{-1}.
   Treatment time required for obtaining 99% degradation of methomyl $(t) = \ln(1/100)/k = 947.37$ min = 15.789 h.
   Power consumption = energy required × treatment time = 1000 × 15.789 = 15789.00 kWh/m^3.
   Cost of electrical energy (considering 1 kWh = Rs. 5.06/–) = 15789.00 × 5.06 = 79892.34 Rs./m^3

B. Combination of ultrasonic cavitation with photo-Fenton process:
   Electrical power supplied = 250 + 16 = 266 W.
   Energy required = 266/0.25 = 1064 W/l = 1064 kW/m^3 (considering two UV lamps of 8 W each and treatment volume of 250 mL).
   Treatment time for complete degradation of methomyl = 9 min = 0.15 h.
   Power consumption = 1064 × 0.15 = 159.60 kWh/m^3.
   Cost of electrical energy = (159.60 × 5.06) = 807.58 Rs./m^3.

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