Effect of intensifying additives on the degradation of thiamethoxam using ultrasound cavitation

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A B S T R A C T

The present study has investigated the degradation of thiamethoxam using ultrasound cavitation (US) operated at a frequency of 20 kHz and its combination with intensifying additives viz. hydrogen peroxide, Fenton and photo-Fenton reagent. At the outset, the performance of US (20 kHz) has been maximised by the optimization of process parameters. Highest rate of degradation of thiamethoxam was observed at the optimum ultrasonic power density of 0.22 W/mL, thiamethoxam concentration of 10 ppm and the pH of 2. The established optimum values of operating parameters were used further in case of combined treatment approaches. The effect of concentration of H_2O_2 on the rate of degradation of thiamethoxam in the case of US + H_2O_2 process has confirmed the existence of optimum concentration of H_2O_2 with the ratio of thiamethoxam: H_2O_2 as 1:10. US + Fenton process indicated the optimal molar ratio of $FeSO_4 \cdot 7H_2O : H_2O_2$ as 1:15. The combined processes of US + H_2O_2, US + Fenton and US + photo-Fenton have resulted in the extent of degradation of 20.47 ± 0.61%, 34.41 ± 1.03% and 85.17 ± 2.56% respectively after 45 min. of operation. These combined processes lead to the synergistic index of 2.04 ± 0.06, 2.26 ± 0.07 and 2.42 ± 0.07 in case of US + H_2O_2, US + Fenton and US + photo-Fenton processes respectively over only US/stirring treatment with the additive. Additionally, the extent of mineralization and the energy efficiency of individual and combined processes have been compared. US + photo-Fenton process has been found to be the best strategy for effective degradation of thiamethoxam with a significant intensification benefit. The by-products formed during the ultrasonic degradation of thiamethoxam have been identified by using LC-MS/MS analysis.

1. Introduction

Discharge of effluent from pesticide manufacturing industries and extensive use of pesticides in the agricultural fields frequently leads to the contamination of both surface and ground water streams. Development of an effective method for the degradation of these pesticides is highly essential since most of the pesticides are toxic and hazardous in nature. Thiamethoxam, the target organic pollutant used in this research work, belongs to the neonicotinoid class of insecticides [1]. It has been extensively applied for the protection of crops from a variety of chewing and sucking pests and also for seed and household treatment [2]. Since thiamethoxam is highly soluble in water (4.1 g/L) it can easily enter into both surface and ground water streams.

Advanced oxidation processes (AOPs) have gained popularity among various wastewater treatment processes, since they are capable of degrading most of the complex pesticide compounds [3–6]. In case of AOPs, the degradation of organic pollutant occurs due to the generation of strong oxidising OH⁺ radicals and their attack on the target pollutants [3,5,7–11]. Various AOPs have been applied so far for the degradation of pesticides viz. Fenton and photo-Fenton processes [12–14], photolytic processes [15,16], photo-catalytic processes [2,17,18], and cavitation based techniques [19–23]. Cavitation is an emerging AOP which deals with a continuous formation of large number of small cavities in the aqueous solution of the target pollutant, followed by rapid growth of these cavities to the unstable size. Further violent collapse of these cavities releases large magnitude of energy and generates strong oxidising OH⁺ radicals [11,21,24–28]. In US, the cavitation is produced by using low frequency ultrasound wave consisting of alternate compressions and rarefaction cycles of adequate amplitude [6,22]. In the case of US, the degradation of organic pollutant occurs due to thermal dissociation or cleavage of H_2O and dissolved O_2 molecules into strong oxidising OH⁺ radicals, oxygen atoms (O⁺), hydrogen atoms (H⁺) and hydroperoxyl radicals ($HO_2^•$) [6,25]. These generated radicals then diffuse into the bulk solution and further oxidize the target pollutants.

However, US often leads to lower rates of degradation of the target pollutants when used individually. The rate of degradation of target pollutants obtained by the application of US can be further intensified by combining US with various other AOPs such as H_2O_2 [6,21,23,25], Fenton [4,6,19,22,29] and photo-Fenton processes [6] etc.

AOPs such as photocatalysis (UV + TiO_2) [1,2,23] and ozonation (UV + O_3) [30] have been utilised by many researchers for the degradation of thiamethoxam. However, previous studies have not yet reported the application of US and US based combined processes for the degradation of thiamethoxam. Present research work demonstrates the study of degradation of thiamethoxam using US based AOPs due to their various beneficial effects. It mainly includes better utilization of OH$^\cdot$ radicals and lower mass transfer resistances due to the increased turbulence created by US. Operating parameters viz. ultrasonic power density, initial concentration of thiamethoxam and operating pH of the solution have been optimised for maximising the efficacy of US. Further enhancement in the rate of degradation of thiamethoxam has also been obtained by combining US with H_2O_2, Fenton and photo-Fenton processes.

2. Materials and methods

2.1. Materials

Technical grade thiamethoxam ($C_8H_{10}ClN_5O_3S$) of purity 97.27% was procured from Crop Life Science Ltd., Gujarat, India. Analytical grade Ferrous sulfate ($FeSO_4 \cdot 7H_2O$), hydrogen peroxide (H_2O_2 = 30% w/v), sulphuric acid (H_2SO_4) and sodium sulfite (Na_2SO_3) were procured from Merck, India. Distilled water was used for the preparation of thiamethoxam solution of desired concentration.

2.2. Experimental set-up

Fig. 1 indicates the schematic representation of an experimental set-up used in the present study. The experimental set-up essentially comprises of a low frequency ultrasonic processor (Frequency = 20 kHz, Power = 500 W, make = Johnson Plastosonic Pvt. Ltd., India), a quartz reactor having a facility of a cooling jacket (Capacity = 250 mL), a temperature indicator, two UV tubes (8 W each) and a wooden shield. The amplitude of the ultrasonic processor can be altered from 25% to 100% which ultimately varies the actual power dissipation into the system. The ultrasonic probe (tip diameter = 13 mm) was dipped in the aqueous solution of thiamethoxam (depth = 2 cm) during all the experiments based on US based processes. The reaction temperature inside the reactor was maintained at 30 ± 2 °C by passing cold water through a cooling jacket. Experiments involving photolytic and photo-Fenton based processes were carried out in the presence of ultraviolet light source. Wooden cabinet has been used to ensure the blockage of harmful ultraviolet irradiations.

2.3. Experimental methodology

During all the experiments the temperature and the volume of solution were kept constant at 30 ± 2 °C and 250 mL respectively. An operating pH of the solution was adjusted to the desired value by adding 1.0 M H_2SO_4. Sonication was carried out for 120 min of treatment time using ultrasonic horn set at the time scale of 6 s on and 4 s off. The pulsed (on/off) mode of ultrasonic horn was used for better temperature control since adequate time will be available for heat dissipation [9].

Initially, the optimization of amplitude of ultrasonic processor was carried out varying the amplitude viz. 25%, 50%, 75% and 100%. The initial concentration of thiamethoxam was 20 ppm and the pH of the solution was adjusted to 2.0. Further, the initial concentration of thiamethoxam was optimized by varying the concentration of thiamethoxam in the range of 10–35 ppm using the interval of 5 ppm. These experiments were carried out at the optimised amplitude of 100% and the operating pH of 2.0. In addition to this, an operating pH of the solution was also optimised by varying the pH from 2 to 7.9 (2, 3, 4, 6 and 7.9). These experiments were carried out at the optimised amplitude as 100% and the optimised initial concentration of thiamethoxam as 10 ppm.

All further experiments of US based combined approaches were conducted at the optimised operating parameters. It includes the amplitude of 100%, the initial thiamethoxam concentration of 10 ppm and the pH of 2.0. Enhancement in the rate of degradation of thiamethoxam
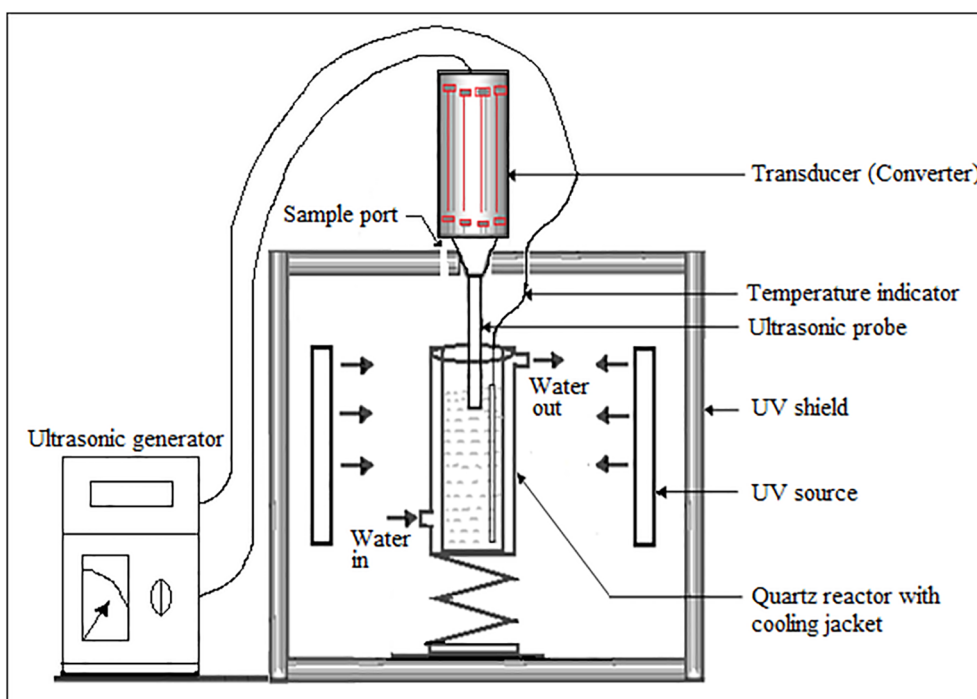

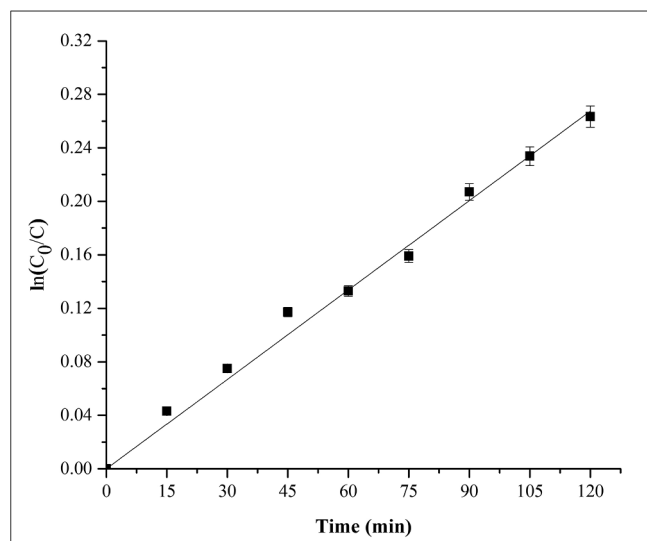**Fig. 1.** Schematic diagram of an experimental set-up.

Fig. 2. First order degradation of thiamethoxam (Operating conditions: volume = 250 mL, pH = 2.0, temperature = 30 ± 2 °C, amplitude = 100%, initial concentration of thiamethoxam = 10 ppm).

was obtained by combining US with H_2O_2, Fenton and photo-Fenton processes. Enhancement in the rate of degradation of thiamethoxam was obtained by combining US with H_2O_2, Fenton and photo-Fenton processes. The experiments were performed by combining US with hydrogen peroxide by varying the molar ratio of thiamethoxam:H_2O_2 viz. 1:2, 1:5, 1:10, 1:15, 1:20 and 1:30. These experiments were performed in order to obtain the optimum molar ratio of thiamethoxam:H_2O_2.

The combination of US and Fenton's process was also employed for the degradation of thiamethoxam by varying the molar ratio of $FeSO_4 \cdot 7H_2O$: H_2O_2 such as 1:50, 1:40, 1:30, 1:25, 1:20, 1:15 and 1:10 at a fixed optimum loading of H_2O_2. Furthermore, the combination of US and photo-Fenton process was also employed at the optimal molar ratio of $FeSO_4 \cdot 7H_2O$: H_2O_2. In order to obtain the synergistic effect of a combination of US with process intensifying additives, the experiments were also carried out using conventional stirring at the optimized loading of intensifying additives. The mineralization study of thiamethoxam was also carried out on the basis of reduction in total organic carbon (TOC) by the application of various conventional and US based combined processes. Energy efficiency of individual and combined processes was also compared by calculating their cavitational yield. Further, LC-MS/MS analysis was carried out for identifying the byproducts formed during the ultrasonic degradation of thiamethoxam using US + photo-Fenton process.

2.4. Analysis

UV–VIS Spectrophotometer (LABINDIA: UV 3000+) set at a maximum wavelength of 252 nm was used to determine the change in the concentration of thiamethoxam at given interval of time. In order to ensure the determination of accurate concentration of thiamethoxam, 0.25 M Na_2SO_3 (quenching agent) was added to the sample withdrawn during all experiments involving a combination of US with process intensifying additives. The percentage reduction in TOC obtained during various processes at optimum conditions has been analyzed using TOC analyzer of Shimadzu Corporation, Japan.

LC-MS/MS analysis of degradation by-products of thiamethoxam has been carried out using Agilent Technologies 1260 infinity series HPLC and Agilent Technologies 6460 triple-quad LC-MS/MS. It consists of eclipse plus C18 column with dimensions 4.60 × 100 mm having particle size of 5 μm. Mobile phase consists of (A) 5 mM ammonium formate in water + 0.1% formic acid and (B) 5 mM ammonium formate

in methanol + 0.1% formic acid. The flow rate of mobile phase was maintained at 1 mL/min (0–7 min. 20% B, 7–12 min. 50% B, 12–15 min. 80% B, 15–18 min. 100% B and 18–20 min. 20% B). Samples were ionized using an electrospray ion source for LC-MS/MS measurement in positive ionization mode and full scan acquisition from m/z 50 to 500. The collision energy varied as 1, 5, 10 and 20 V according to requirement of the different measurement and the other parameters were set as follows: capillary voltage of 3500 V, nitrogen as the drying gas (temperature = 250 °C, flow rate = 8 L/min.), nebulizer gas (pressure = 55 psi), fragmentor voltage = 135 V, nozzle voltage = 500 V, sample size = 5 μL. All the experiments were repeated at least twice and the reported values are average of the different experimental runs. The experimental errors were within ± 3% of the reported value of the extent of degradation or reaction rate constant. Error bars have also been shown to depict the variation which was within 3% of the reported average value.

3. Result and discussion

3.1. Degradation kinetics for thiamethoxam

In order to investigate the kinetics of ultrasonic degradation of thiamethoxam, initially the experiment was conducted using an initial concentration of thiamethoxam as 10 ppm. The operating volume, temperature, amplitude and pH of solution were kept constant at 250 mL, 30 ± 2 °C, 100% and 2.0 respectively. The reaction rate constant, k for the degradation of thiamethoxam was calculated using equation Eq. (1) by assuming first order kinetics

$$\ln\left(\frac{C_0}{C}\right) = k \times t \tag{1}$$

where, C_0 is the concentration of thiamethoxam at time t = 0 in mg/L, C is the concentration of thiamethoxam at any time t in mg/L, k is the rate constant (min^{-1}) and t is the time in minutes. Fig. 2 clearly indicates that the plot of $\ln(C_0/C)$ v/s time (t) is a straight line passing through origin (k = (2.24 ± 0.07) × 10^{-3} min^{-1}, R^2 = 0.99 ± 0.01), which confirms that the rate of degradation of thiamethoxam follows the first order reaction kinetics.

3.2. Effect of ultrasonic power density

The optimization of ultrasonic power density i.e. actual power dissipation into the solution (W/mL) is very essential to maximize the performance of ultrasonic reactors since it directly affects the intensity of cavitation phenomena and the treatment costs. The power density of ultrasonic processor was optimised by changing the power of ultrasonic processor such as 25%, 50%, 75% and 100%. The ultrasonic power density determined in our previous research work [6] was utilised here since the same ultrasonic processor was applied. The ultrasonic power density calculated by calorimetric study was 0.12 W/mL, 0.16 W/mL, 0.19 W/mL and 0.22 W/mL for 25%, 50%, 75% and 100% amplitudes respectively. The initial concentration of thiamethoxam, operating temperature and operating volume of thiamethoxam solution was set at 20 ppm, 30 ± 2 °C and 250 mL respectively. The results obtained showing the effect of ultrasonic power density on the extent of degradation of thiamethoxam have been illustrated in Fig. 3. Enhancement in the extent of degradation of thiamethoxam has been observed by increasing the power density of ultrasonic processor. It has clearly observed that by increasing the power density of ultrasonic processor from 0.12 to 0.22 W/mL, the percentage degradation of thiamethoxam increases from 0.52 ± 0.02% to 9.95 ± 0.30% for 120 min of sonication.

Enhancement in the percentage degradation of thiamethoxam with an increase in the ultrasonic power density might be due to the generation of higher number of cavities resulting into more intense cavitation phenomena [6,29]. The increased cavitational activity further
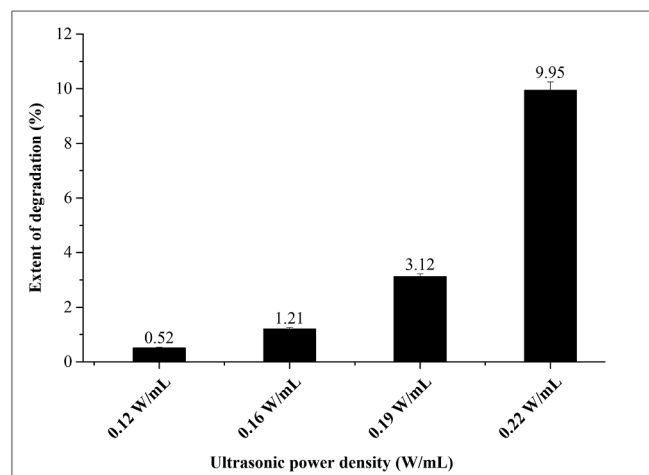
Fig. 3. Effect of ultrasonic power density on the percentage degradation of thiamethoxam (Operating conditions: volume = 250 mL, pH = 2.0, temperature = 30 ± 2 °C, initial concentration of thiamethoxam = 20 ppm).

produces a higher number of OH• radicals and thus increases the percentage degradation of thiamethoxam [6].

Sun et al. [29] have studied the degradation of azo dye acid black 1 using US and have also indicated that the degradation efficiency of azo dye acid black 1 increases with an increase in the ultrasonic power density from 0 to 50 W L^{-1} within 30 min of operation.

3.3. Effect of dilution of thiamethoxam

In order to investigate the effect of dilution of thiamethoxam on its rate of degradation, experiments were conducted by varying the initial concentration of thiamethoxam from 35 ppm to 10 ppm. The operating temperature and pH of the solution were kept constant at 30 ± 2 °C and 2.0 respectively.

The results obtained for the effect of dilution of thiamethoxam have been presented in Fig. 4. Similarly, percentage degradation of thiamethoxam, first order degradation rate constants, k and total moles of thiamethoxam degraded have been summarised in Table 1. The maximum extent of degradation of 23.15 ± 0.69% was obtained at an initial concentration of thiamethoxam at 10 ppm using only US. Results have clearly indicated that the rate constant, k increases from
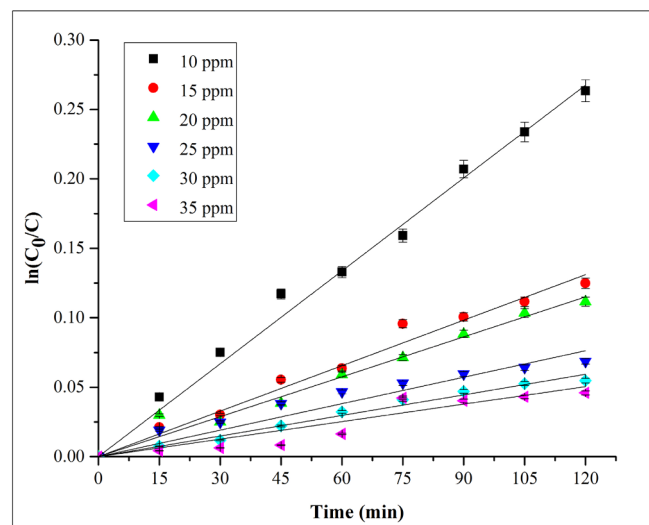

Fig. 4. Kinetics of ultrasonic degradation of thiamethoxam at different initial concentrations of thiamethoxam (Operating conditions: volume = 250 mL, pH = 2.0, temperature = 30 ± 2 °C and amplitude = 100%).

$(0.40 \pm 0.01) \times 10^{-3}$ min^{-1} to $(2.24 \pm 0.07) \times 10^{-3}$ min^{-1} with an increase in the dilution of thiamethoxam and changing the concentration from 35 ppm to 10 ppm. However, the total moles of thiamethoxam degraded after 120 min of operation increases only marginally from $(1.35 \pm 0.04) \times 10^{-6}$ mol to $(1.99 \pm 0.06) \times 10^{-6}$ mol i.e. only 47% increases with an increase in the dilution of thiamethoxam by 350% and the concentration reducing from 35 ppm to 10 ppm. Hence, dilution of thiamethoxam to a greater extent may not be beneficial since it will not significantly increases the total moles of thiamethoxam degraded but will need to process significantly larger volumes of the effluents due to such dilution.

The obtained results of increased rate of degradation of thiamethoxam at lower initial concentration may be due to the fact that at lower initial concentration of thiamethoxam the number density of OH• radicals available would be sufficient for the effective degradation of thiamethoxam. However, at higher concentration of thiamethoxam, the number density of OH• radicals available is not increasing since cavitation conditions remain the same. This may lead to less possibility of attack of OH• radicals on the molecules of thiamethoxam which in turn may lower the overall rate of degradation of thiamethoxam. These results have been well supported by a similar trend observed in the previous studies. Mishra and Gogate [24] have studied the effect of initial concentration of Rhodamine B (10, 25, 50 and 100 ppm) on its decolorization efficiency using only US. It was reported that the percentage degradation of Rhodamine B increases by decreasing the initial concentration of Rhodamine B. Sivakumar et al. [25] have also observed the similar results for the ultrasonic degradation of p-nitrophenol by varying the initial concentration of p-nitrophenol over the range of 10 ppm to 500 ppm.

3.4. Effect of the initial pH of the solution

Determination of an optimum pH of the target organic pollutant solution plays a very vital role in the enhancement of its rate of degradation using US based processes [31–33]. In this study, the initial pH of thiamethoxam solution was set at 2, 3, 4, 6 and 7.9 by adding H$_2$SO$_4$ as per the requirement. All the experiments have been conducted at the optimal initial concentration of thiamethoxam as 10 ppm, temperature of 30 ± 2 °C and for sonication time of 120 min. The results obtained indicating the effects of pH on the rates of degradation of thiamethoxam have been depicted in Fig. 5. The results quoted in Table 2 have clearly indicated that the first order reaction rate constant, k increases from $(0.47 \pm 0.01) \times 10^{-3}$ min^{-1} to $(2.24 \pm 0.07) \times 10^{-3}$ min^{-1} by lowering the pH of the thiamethoxam solution from natural pH of 7.9 to acidic pH of 2. Accordingly, maximum extent of degradation of thiamethoxam of 23.15 ± 0.69% was observed at pH of 2.0. The obtained results have been credited to the fact that the acidic environment lowers the recombination rate of OH• radicals resulting into superior oxidation potential [6]. Due to this, the rate of degradation of thiamethoxam enhances at lower pH since large number of hydroxyl radicals are available under acidic conditions.

The previous reports of some researchers have also indicated similar results of higher rate of degradation of organic pollutants at lower pH. Bagal and Gogate [21] have demonstrated the ultrasonic degradation of alachlor and have observed that acidic condition favours the rate of degradation of alachlor. Significant increase in the rate of degradation of alachlor was observed by lowering the initial pH of the solution from 11.0 to 3.0. Similar results indicating the beneficial effects of acidic condition have also been observed by Patil and Gogate [8] and Sun et al. [29] for the degradation of methyl parathion and acid black 1 respectively using cavitation based processes.

3.5. Ultrasound cavitation in the presence of hydrogen peroxide (H$_2$O$_2$)

Hydrogen peroxide is a key oxidant, which plays a very significant role in the ultrasonic degradation of organic pollutants. It dissociates

Table 1
Effect of dilution of thiamethoxam on the performance of US.

Initial Concentration (ppm)	Extent of degradation (%) after 120 min of operation	Total moles of thiamethoxam degraded after 120 min of operation, $n \times 10^6$	First order rate constant, $k \times 10^3$ (min^{-1})
35	4.49 ± 0.03	1.35 ± 0.04	0.40 ± 0.01
30	5.32 ± 0.16	1.37 ± 0.04	0.50 ± 0.02
25	6.62 ± 0.20	1.42 ± 0.04	0.65 ± 0.02
20	9.95 ± 0.30	1.46 ± 0.04	0.96 ± 0.03
15	11.74 ± 0.35	1.51 ± 0.05	1.10 ± 0.03
10	23.15 ± 0.69	1.99 ± 0.06	2.24 ± 0.07
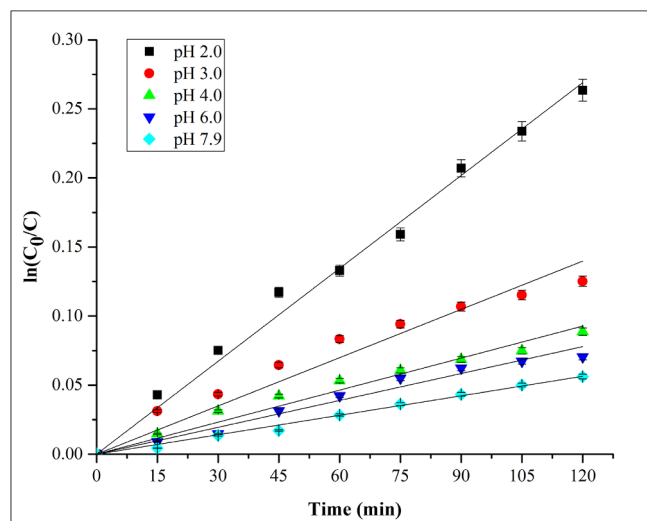
Fig. 5. Kinetics of ultrasonic degradation of thiamethoxam at different operating pH (Operating conditions: volume = 250 mL, initial concentration of thiamethoxam = 10 ppm, temperature = 30 ± 2 °C and amplitude = 100%).
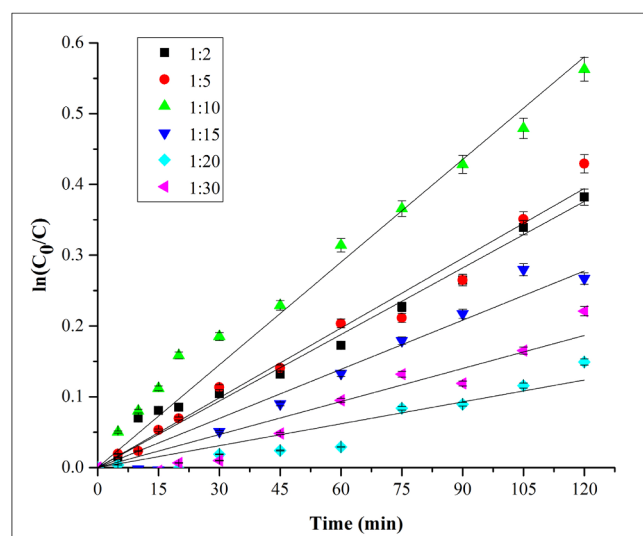
Table 2
Effect of operating pH of thiamethoxam solution on the performance of US.

Operating pH	Extent of degradation (%) after 120 min of operation	First order rate constant, $k \times 10^3$ (min^{-1})
2	23.15 ± 0.69	2.24 ± 0.07
3	11.76 ± 0.35	1.17 ± 0.04
4	8.26 ± 0.25	0.77 ± 0.02
6	6.79 ± 0.20	0.65 ± 0.02
7.9	5.46 ± 0.16	0.47 ± 0.01

easily due to the cavitational activity leading to the formation of highly oxidative OH• radicals, since the bond energy of O-O bond (146 kJ/mole) is insignificant as compared bond energy of O–H bond (467 kJ/mole) [11]. In the present research work, the combined process of US and hydrogen peroxide has been studied to intensify the rate of degradation of thiamethoxam.

Effect of concentration of H_2O_2 on the performance of US + H_2O_2 process has been studied by changing the molar ratio of thiamethoxam: H_2O_2 such as 1:2, 1:5, 1:10, 1:15, 1:20 and 1:30. The kinetics of degradation of thiamethoxam in presence of US and H_2O_2 has been illustrated in the Fig. 6. The extent of degradation of thiamethoxam and the rate constant, k have been presented in Table 3. It has been observed that the rate of degradation of thiamethoxam enhances substantially by increasing the concentration of H_2O_2 till the optimum molar ratio of thiamethoxam to H_2O_2 as 1:10. However, increasing the loading of H_2O_2 beyond this optimum value has caused a reduction in the rate of degradation of thiamethoxam.

The obtained results have been credited to the fact that the dissociation reaction of H_2O_2 due to the cavitation phenomena is favoured till the optimal concentration of H_2O_2. However, at very high

Fig. 6. Kinetics of ultrasonic degradation of thiamethoxam at different molar ratio of thiamethoxam: H_2O_2 (Operating conditions: volume = 250 mL, initial concentration of thiamethoxam = 10 ppm, pH = 2.0, temperature = 30 ± 2 °C and amplitude = 100%).

Table 3
Effect of loading of H_2O_2 on the performance of US + H_2O_2 process for the degradation of thiamethoxam.

Molar ratio of Thiamethoxam:H_2O_2	Extent of degradation (%) after 120 min of operation	First order rate constant, $k \times 10^3$ (min^{-1})
1:2	31.75 ± 0.95	3.13 ± 0.09
1:5	34.89 ± 1.05	3.29 ± 0.10
1:10	43.03 ± 1.29	4.83 ± 0.14
1:15	15.12 ± 0.45	2.31 ± 0.07
1:20	13.85 ± 0.42	1.03 ± 0.03
1:30	19.82 ± 0.59	1.56 ± 0.05

concentration of H_2O_2, instead of dissociation reaction the undesired recombination and scavenging reactions of OH• radical are the predominating one. During such reactions OH• radicals combines with each other leading to the generation of H_2O_2 and other free radicals such as $HO_2^•$ and O• with less oxidation potential [6,22,26]. Jawale et al. [7], Golash and Gogate [11], Shriwas and Gogate [20] have also reported the existence of an optimal concentration of H_2O_2 and observed that the higher concentration of hydrogen peroxide beyond an optimum loading rather lowers the rate of degradation of organic pollutants.

The combined process of US and H_2O_2 applied for the degradation of thiamethoxam has shown synergistic effect, since the first order degradation rate constant, k obtained by the application of US + H_2O_2 process under the optimized conditions has found to be higher $((4.83 \pm 0.14) \times 10^{-3} \ min^{-1})$ as compared to the addition of the rate constants, k obtained in the case of US $((2.24 \pm 0.07) \times 10^{-3} \ min^{-1})$ and H_2O_2 $((0.13 \pm 0.00) \times 10^{-3} \ min^{-1})$ individual processes . The

synergistic coefficient (f) for the US + H_2O_2 process (Eq.(2)) can be obtained as follows:

$$f = \frac{k_{(US+H_2O_2)}}{k_{(US)} + k_{(H_2O_2)}} = 2.04 \pm 0.06 \qquad (2)$$

The synergistic effect obtained has clearly indicated that the combined process of US + H_2O_2 enhances the rate of generation of $OH^\bullet$ radicals due to the increased rate of dissociation of H_2O_2 and their effective utilization in the presence of US. These beneficial effects further increase the rate of degradation of thiamethoxam. Many researchers have also confirmed that US + H_2O_2 leads to a higher number of $OH^\bullet$ radicals as compared to that obtained in the case of US and hydrogen peroxide individual processes. Patil et al. [22] have reported the synergistic effect by combining US with hydrogen peroxide for the degradation of imidacloprid. The synergistic coefficient of 2.47 was obtained using ultrasonic horn and 2.85 using ultrasonic bath. Raut-Jadhav et al. [6] have also reported that the degradation of methomyl shows the synergistic effect by combining US with hydrogen peroxide. The synergistic coefficient was observed to be 25.74 at an optimal molar ratio of methomyl: H_2O_2 as 1:30.

3.6. Ultrasound cavitation in the presence of Fenton's reagents

Fenton's process is based on the reaction between H_2O_2 and homogeneous catalyst, ferrous ions (Fe^{2+}) i.e. Fenton's reagent under the acidic conditions for the formation of highly oxidative $OH^\bullet$ radicals [28]. This process also utilizes the oxidative capacity of the generated $OH^\bullet$ radicals for the treatment of organic pollutants [5]. Although, the degradation rate of organic pollutant enhances with an increase in the concentration of Fenton's reagent, it is always recommended to obtain the optimum concentration of Fe^{2+} ions and H_2O_2. This is because, very high concentration of Fe^{2+} ions may further increase the total dissolved solids (TDS) content of the effluent stream and also increase the amount of iron sludge produced [28]. In addition to this, the large quantity of H_2O_2 acts as a scavenger of generated $OH^\bullet$ radicals and may contribute further to the higher chemical oxygen demand (COD) of the effluent. The performance of US and Fenton's individual processes can be maximised by combining these processes.

The effect of US + Fenton process on the rate of degradation of thiamethoxam has been studied by changing the molar ratio of ferrous sulphate to H_2O_2 as 1:50, 1:40, 1:30, 1:25, 1:20, 1:15 and 1:10. All the experiments for US + Fenton process were performed at the optimal molar ratio of thiamethoxam to H_2O_2 as 1:10. The results obtained showing the kinetics of degradation of thiamethoxam have been presented in Fig. 7. The extent of degradation of thiamethoxam and its initial reaction rate constant have been summarized in Table 4. It has been clearly observed that both the extent of degradation of thiamethoxam and the first rate constants, k increases with an increase in the loading of Fe^{2+} ions till the optimal molar ratio of $FeSO_4 \cdot 7H_2O$ to H_2O_2 as 1:15. However, beyond the optimum loading of Fe^{2+} ions, reduction in the degradation rate of thiamethoxam has been observed. The obtained results have been attributed to the fact that with an increase in the loading of Fe^{2+} ions, more number of H_2O_2 molecules will decompose to produce the highly reactive hydroxyl radicals. However, beyond an optimal value of Fe^{2+} ions, very high concentration of hydroxyl radicals will favour the scavenging reactions leading to the recombination of hydroxyl radicals producing hydrogen peroxide with less oxidative capacity.

Sun et al. [29] have studied the ultrasonic degradation of acid black 1 and have also reported that the degradation efficiency of acid black 1 increases from 57.87% to 97% with an increase in the loading of Fe^{2+} ions from 0.01 to 0.05 mM. Findings of other researchers have also established similar trend for the degradation of organic pollutants such as methyl parathion [20], alachlor [21] and rhodamine B [24]. US + Fenton process has also shown synergy, since under the
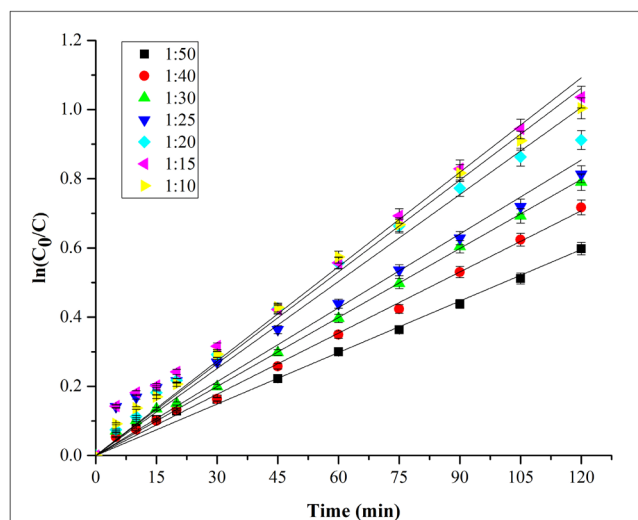

Fig. 7. Kinetics of ultrasonic degradation of thiamethoxam at different molar ratios of ferrous sulphate to H_2O_2 (Operating conditions: volume = 250 mL, solution pH = 2.0, initial concentration of thiamethoxam = 10 ppm, temperature = 30 ± 2 °C, molar ratio of thiamethoxam: H_2O_2 = 1:10 and amplitude = 100%).

Table 4
Effect of molar ratio of ferrous sulphate to H_2O_2 on the performance of US + Fenton process.

Molar ratio of $FeSO_4 \cdot 7H_2O$: H_2O_2	Extent of degradation (%) after 120 min of operation	First order rate constant, $k \times 10^3$ (min^{-1})
1:50	45.01 ± 1.35	4.96 ± 0.15
1:40	51.18 ± 1.54	5.90 ± 0.18
1:30	54.61 ± 1.64	6.65 ± 0.20
1:25	55.66 ± 1.67	7.12 ± 0.21
1:20	59.82 ± 1.79	8.38 ± 0.25
1:15	64.50 ± 1.94	9.10 ± 0.27
1:10	63.35 ± 1.90	8.84 ± 0.27

optimized conditions the first order degradation rate constant, k obtained for US + Fenton process ((9.10 ± 0.27) $\times 10^{-3}$ min^{-1}) was very high as compared to the addition of the rate constants, k obtained for US ((2.24 ± 0.07) $\times 10^{-3}$ min^{-1}) and Fenton ((1.77 ± 0.05) $\times 10^{-3}$ min^{-1}) individual processes. The synergistic coefficient (f) for the combination of US + Fenton process (Eq.(3)) can be obtained as follows:

$$f = \frac{k_{(US+Fenton)}}{k_{(US)} + k_{(Fenton)}} = 2.26 \pm 0.07 \qquad (3)$$

Synergistic effect obtained in case of US + Fenton process has been attributed to the fact that the Fenton's process in presence of US enhances the rate of formation of $OH^\bullet$ radicals due to the regeneration of the Fenton's reagent (i.e. conversion of Fe^{3+} to Fe^{2+} ions) and better utilization of hydroxyl radicals in presence of US. Similar trend has been observed by some researchers when US + Fenton process was applied for the degradation of organic pollutants such as triazophos [3], imidacloprid [5], methomyl [6,10] etc.

3.7. Ultrasound cavitation in the presence of photo-Fenton process

The US + photo-Fenton process has also been applied for further improving the rate of degradation of thiamethoxam [6]. To meet this objective, the experiments have been carried out for obtaining the extent of degradation of thiamethoxam by using photo-Fenton process and US + photo-Fenton process at the optimised molar ratio of ferrous

sulphate to H_2O_2 as 1:15. Two UV tubes (diameter = 1.6 cm and length = 28.5 cm) of 8 W each were used as a source of irradiation and were kept at a distance of 2 cm from the quartz reactor. After a treatment time of 45 min, the extent of degradation of thiamethoxam was obtained to be 11.06 ± 0.33% and 24.09 ± 0.72% by applying US and photo-Fenton processes individually. It has been noticed that the percentage degradation of thiamethoxam has significantly increased to 85.17 ± 2.56% by using combined process of US and photo-Fenton over the same period of time. Hence, US + photo-Fenton process has shown appreciable synergy effect and the synergistic coefficient (η) can be computed by using (Eq.(4)) as

$$\eta = \frac{\text{Extent of degradation}_{(US+photo-Fenton)}}{\text{Extent of degradation}_{(US)} + \text{Extent of degradation}_{(photo-Fenton)}}$$
$$= 2.42 \pm 0.07 \qquad (4)$$

Synergy obtained may be due to the higher rate of formation and improved utilization of OH· radicals, regeneration of the homogeneous catalyst (ferrous sulphate ions) and higher exposure of the targeted organic pollutant to the ultraviolet light due to turbulence caused by the US. Similar synergistic effect was also observed in case of the degradation of imidacloprid [5] and methomyl [6] by the application of combined process of cavitation and photo-Fenton process.

3.8. Comparison of degradation and energy efficiency of individual and combined processes

The performance of individual and combined processes employed for the degradation of thiamethoxam can be analysed by comparing the extent of degradation of thiamethoxam and the total energy consumption. Fig. 8 depicts the extent of degradation of thiamethoxam obtained in case of various individual and combined processes. It has been observed that the extent of degradation of thiamethoxam obtained in case of individual US process has been considerably enhanced by combining it with H_2O_2, Fenton and photo-Fenton processes. After 45 min of treatment, the extent of degradation of thiamethoxam obtained using US was merely 11.06 ± 0.33% which has significantly increased to 20.47 ± 0.61%, 34.41 ± 1.03% and 85.17 ± 2.56% by using US + H_2O_2, US + Fenton and US + photo-Fenton processes respectively. Highest extent of degradation of thiamethoxam was observed by applying US + photo-Fenton process. The results obtained
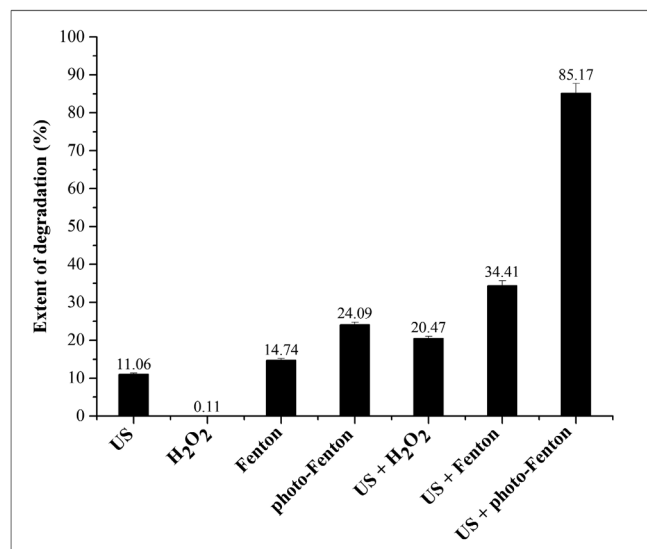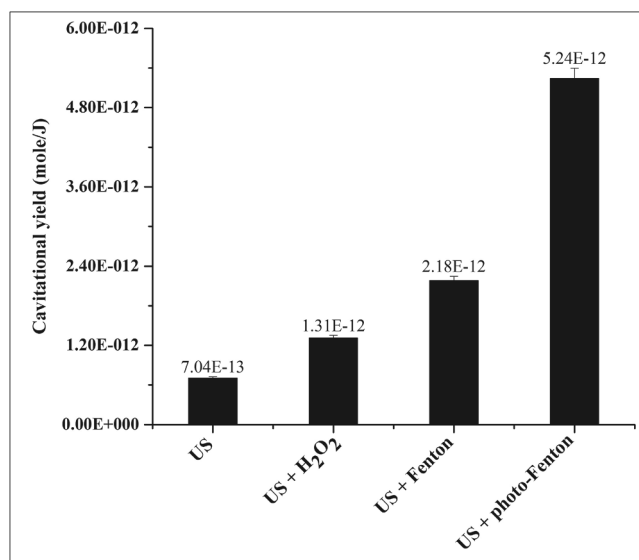

Fig. 9. Energy efficiency of US and US based combined processes based on cavitational yield (Operating conditions: treatment time = 45 min, molar ratio of thiamethoxam: H_2O_2 = 1:10, molar ratio of $FeSO_4 \cdot 7H_2O$: H_2O_2 = 1:15).

have been ascribed to the fact that US + photo-Fenton process leads to the higher extent of degradation of thiamethoxam due to the regeneration of the catalyst, better utilization of OH· radicals and higher exposure of the thiamethoxam to ultraviolet light due to turbulence created by US.

Although, a comparison of the extent of degradation of organic pollutant plays a significant role in the selection of the effective process, it is also essential to compare the energy efficiency of these US and US based combined processes. Energy efficiency of US, US + H_2O_2, US + Fenton and US + photo-Fenton has been calculated and compared based on the cavitational yield calculated at the optimised conditions. The cavitational yield can be calculated as (Eq.(5)) [10].
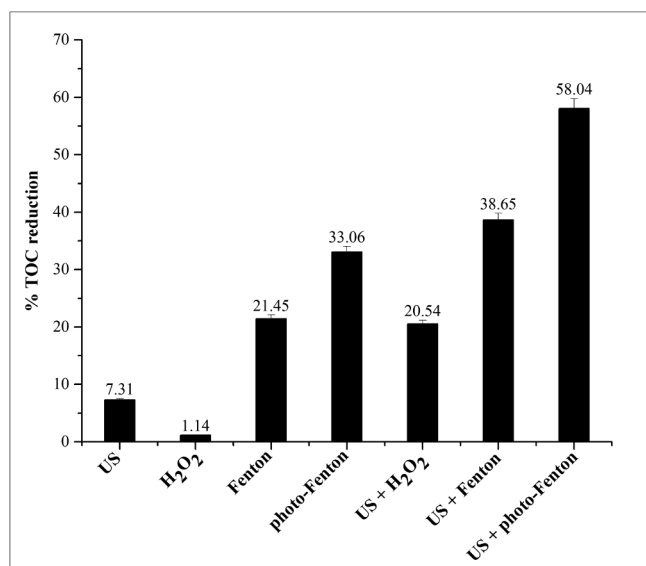
$$\text{Cavitational yield} = \frac{\text{Moles of thiamethoxam degraded}}{\text{Energy supplied to the system}} \text{ (mole/J)} \qquad (5)$$

The cavitational yield obtained after 45 min of treatment time for US and various US based combined processes has been illustrated in Fig. 9. The energy efficiency of US was significantly enhanced by coupling it with hydrogen peroxide, Fenton and photo-Fenton processes. The cavitational yield of $(7.04 \pm 0.23) \times 10^{-13}$ mol/J obtained by applying US has significantly increased to $(1.31 \pm 0.04) \times 10^{-12}$ mol/J, $(2.18 \pm 0.07) \times 10^{-12}$ mol/J and $(5.24 \pm 0.16) \times 10^{-12}$ mol/J by applying US + H_2O_2 and US + Fenton and US + photo-Fenton process respectively. Hybrid technique of US + photo-Fenton is around 7.44 times more energy efficient than US for the degradation of thiamethoxam. The stepwise calculation for obtaining the cavitational yield for the US + photo-Fenton process has been illustrated in Appendix A.

The comparison of the extent of degradation and energy efficiency of various US based processes has clearly indicated that US + photo-Fenton process is the most effective and energy efficient process as of now for the degradation of thiamethoxam.

3.9. Mineralization study

The extent of mineralization of thiamethoxam has been studied on the basis of percentage reduction in total organic carbon (TOC) after the application of various individual processes viz. US, H_2O_2, Fenton and photo-Fenton and various hybrid processes viz. US + H_2O_2, US + Fenton, photo-Fenton and US + photo-Fenton. The results depicting the extent of mineralization of thiamethoxam have been

Fig. 8. Comparison of percentage degradation of thiamethoxam obtained by applying individual and combined processes (Operating conditions: treatment time = 45 min, molar ratio of thiamethoxam: H_2O_2 = 1:10, molar ratio of $FeSO_4 \cdot 7H_2O$: H_2O_2 = 1:15).

Fig. 10. Extent of mineralization of thiamethoxam obtained during various processes (Operating conditions: treatment time = 120 min, molar ratio of thiamethoxam: H_2O_2 = 1:10, molar ratio of $FeSO_4\cdot7H_2O$: H_2O_2 = 1:15).

summarised in the Fig. 10. It has been observed that % TOC reduction obtained by applying US has further enhanced by combining the US with H_2O_2, Fenton and photo-Fenton processes. % TOC reduction of 7.31 ± 0.22%, 33.06 ± 0.99%, 20.54 ± 0.62% and 38.65 ± 1.16% has been achieved after 120 min of treatment time by applying US, photo-Fenton, US + H_2O_2 and US + Fenton process respectively. Highest extent of mineralization of 58.04 ± 1.74% was observed using US + photo-Fenton process (optimal molar ratio of thiamethoxam: H_2O_2 = 1:10 and $FeSO_4\cdot7H_2O$: H_2O_2 = 1:15). Although, the extent of degradation of thiamethoxam was very high in the case of US + photo-Fenton process, moderate extent of mineralization has been observed. This may be due to the fact that energy provided by US + photo-Fenton process was not sufficient to completely convert the long chain complex molecules of thiamethoxam into very short chain molecules, CO_2 and H_2O. Hence, such processes shall be followed by conventional biological processes for ensuring the complete mineralization of thiamethoxam as the short chain molecules may be amenable to the biological treatment.

3.10. Identification of the degradation by-products of thiamethoxam

The degradation by-products of thiamethoxam generated by the application of a combined process of US and photo-Fenton were analyzed by using LC-MS/MS. Degradation by-products of thiamethoxam verified by LC-MS/MS analysis have been summarised in Appendix B. Total nine degradation by-products of thiamethoxam have been identified viz. P1 (thiamethoxam urea, m/z 247), P2 (m/z 115), P3 (m/z 194), P4 (m/z 156), P5 (m/z 398), P6 (m/z 172), P7 (m/z 323), P8 (m/z 307), P9 (m/z 99). The results obtained have been well supported by the literature reported. Sojic et al. [30] have identified four similar intermediate by-products viz. P2, P3, P4 and P5 during the degradation of thiamethoxam using UV, O_3 and UV/O_3 hybrid processes. Furthermore, Yang et al. [23] have also identified P1 (thiamethoxam urea), P2, P6, P7 and P8 as the intermediate by-products during photocatalytic degradation of thiamethoxam using TiO_2. Urzedo et al. [34] have identified P2 and P9 as the similar intermediate by-products during photolytic degradation of thiamethoxam. Zabar et al. [2] have identified the clothianidin (molecular weight, Mw = 249) thiamethoxam urea (Mw = 247) and a compound with Mw 205 as the degradation by-products during photocatalytic degradation of thiamethoxam using immobilised TiO_2.

The scheme of probable degradation pathway and chemical structures of by-products generated during the degradation of thiamethoxam by applying US + photo-Fenton process have been illustrated in Fig. 11. Degradation pathway has been proposed based on four identified degradation by-products P1 (thiamethoxam urea), P2, P6 and P9. Based on reported literature, three unidentified degradation by-products C1 ($C_8H_{11}ClN_4OS$, m/z 246) [30,34], C2 ($C_8H_{12}N_4O_2S$, m/z 228) [34] and C3 ($C_4H_7N_3O$, m/z 113) [34] are also incorporated in the probable degradation mechanism for the sake of completeness. The initial step may involve the elimination of NO_2 from thiamethoxam leading to the creation of compound C1. Further hydrolysis of compound C1 has resulted in the formation of compound P1 (thiamethoxam urea, $C_8H_{10}ClN_3O_2S$, m/z 247). The conversion of compound P1 or C1 to compound C2 may be due to fast nucleophilic substitution of the Cl atom by the OH group connected at the thiazolic ring of compound C1 [1,34]. Further cleavage of methoxy bridge of compound C2 leads to the formation of thiazolic ring containing compound P2 and oxadiazine ring containing compound C3. Identified degradation by-product P9 might have formed due to removal of NH group from compound C3. The decomposition of compound C2 might have resulted in the opening of oxadiazine ring and the formation of compound P6. Urzedo et al. [34] have reported that further breakdown of by-product P2 may form volatile compounds carbonyl sulfide and isocyanic acid. All the degradation by-products of thiamethoxam can be further mineralized into inorganic substances such as CO_2 and H_2O [23].

4. Conclusions

Based on the studies carried out and the obtained results for the degradation of thiamethoxam using US based processes, the following conclusions can be drawn.

- Rate of degradation of thiamethoxam can be amplified by increasing the ultrasonic power density, since it intensifies the cavitation phenomena. Maximum extent of degradation of 9.95 ± 0.30% has been obtained at the ultrasonic power density of 0.22 W/mL due to the limitation of the equipment used.
- Acidic environment is more favourable for the degradation of thiamethoxam using US. The extent of degradation of thiamethoxam by applying US was highest at pH of 2 (23.15 ± 0.69%).
- The effect of concentration of H_2O_2 on the performance of US + H_2O_2 process has confirmed the existence of optimum concentration of H_2O_2 with optimum molar ratio of thiamethoxam to H_2O_2 as 1:10, beyond which adverse effects have been observed.
- Combination of US with H_2O_2 has significantly augmented the rate of degradation of thiamethoxam resulting into the synergistic effect with the coefficient of 2.04 ± 0.06.
- The effect of concentration of Fenton's reagent on the performance of US + Fenton process has established the optimal molar ratio of ferrous sulphate to H_2O_2 as 1:15. This process also leads to the synergistic effect with the coefficient of 2.26 ± 0.07
- The comparison of degradation and energy efficiency of individual and combined processes has clearly indicated coupling of US with photo-Fenton process to be the most effective one leading to the highest percentage of degradation and mineralization of thiamethoxam with the maximum synergistic coefficient of 2.42 ± 0.07
- LC-MS/MS analysis has confirmed the formation of by-products P1 to P9 during the degradation of thiamethoxam using US + photo-Fenton process. Degradation by-products P1 (thiamethoxam urea, $C_8H_{10}ClN_3O_2S$, m/z 247), P2 (C_4H_5NOS, m/z 115), P6 ($C_5H_8N_4OS$, m/z 172) and P9 ($C_4H_7N_2O$, m/z 99) have been successfully used further to propose the probable degradation pathway of thiamethoxam.

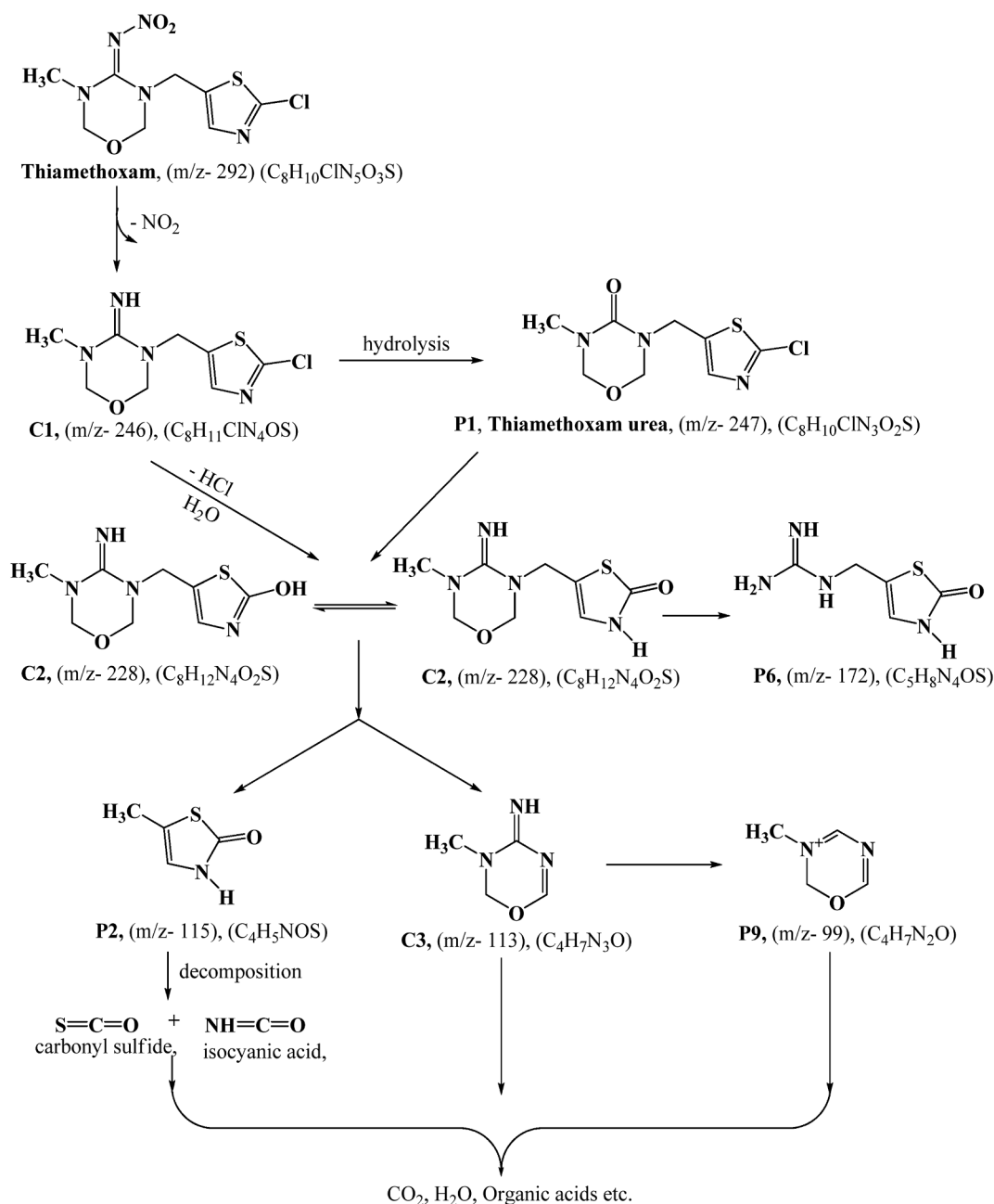Overall, it has been concluded that the combination of US with

Fig. 11. Probable degradation pathway based on by-products of thiamethoxam generated during US + photo-Fenton process.

other AOPs results into enhanced degradation of thiamethoxam leading to a synergistic effect. The US + photo-Fenton process has been observed to be the best treatment strategy for the degradation of thiamethoxam based on the studies carried out and reported in this work.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix. A

Example calculations for computing the cavitational yield for US + photo-Fenton process:
Molar ratio of $FeSO_4 \cdot 7H_2O$: H_2O_2 = 1:15
Energy supplied by US in 45 min = Power × Time
= 500 × (45 × 60) = 13,50,000 J
Energy supplied by UV source in 45 min
= Power × Time
= 16 × (45 × 60) = 43,200 J
Total Energy supplied by US + photo-Fenton process in 45 min

$= 13,50,000 + 43,200 = 13,93,200$ J

Initial concentration of thiamethoxam (C_{A0})

$= 10$ mg/L $= \frac{10 \times 10^{-3}}{291.71} \times 0.250$

$= 8.57 \times 10^{-6}$ mol

Concentration of thiamethoxam at t $= 45$ min (C_A)

$= 1.48$ mg/L $= \frac{1.48 \times 10^{-3}}{291.71} \times 0.250$

$= 1.27 \times 10^{-6}$ mol

Moles of Thiamethoxam degraded $= C_{A0} - C_A = 7.30 \times 10^{-6}$ mol

Cavitational yield $= \frac{7.30 \times 10^{-6}}{13,93,200}$

$= 5.24 \times 10^{-12}$ mol/J

Appendix B

LC-MS/MS fragmentation data for degradation intermediates of thiamethoxam.

Peak label	Precursor ion (m/z)	Retention time (min)	Collision energy (V)	Product ions m/z (Relative abundance)
Thiamethoxam	292	4.45	1	292(32), 246(13), 211(100), 132(18)
			5	292(7), 246(8), 211(100), 181(9), 132(29)
			10	211(100), 181(31), 132(70)
			20	211(27), 181(63), 175(7), 152(8), 132(100), 122(13), 69(11)
P1(Thiamethoxam urea)	247	4.50	1	247(100), 212(54), 182(22), 179(15), 115(16)
			5	247(59), 217(18), 212(59), 182(100), 179(36), 158(11), 115(11)
			10	212(74), 182(100), 181(56), 179(33)
			20	215(12), 182(100), 179(16), 158(19), 149(17), 71(11), 57(9)
P2	115	1.50	1	115(100), 83(10), 71(11)
			5	115(100), 83(23), 71(13)
			10	115(100), 84(49), 83(36), 71(55), 70(34), 55(33)
			20	115(15), 84(63),83(11), 70(100), 56(39), 55(87)
P3	194	1.30	1	194(100)
			5	194(100), 158(41)
			10	194(100), 135(69)
			20	194(18), 135(72), 107(28), 58(100)
P4	156	1.40	1	156(100), 126(42), 110(6)
			5	156(68), 126(100), 98(8), 69(8)
			10	156(35), 126(100), 98(9), 69(8)
			20	126(36), 98(29), 71(49), 69(100), 55(28)
P5	398	10.80	1	73(100)
			5	87(61), 73(100)
			10	219(53), 87(62), 73(100)
			20	87(27), 73(100)
P6	172	1.35	1	172(100), 142(30), 114(6)
			5	172(43), 142(100), 113(14)
			10	172(100), 142(74), 114(37), 113(55), 112(22), 57(30)
			20	172(13), 57(100), 55(14)
P7	323	17.00	1	323(100)
			5	323(100)
			10	323(100), 123(21), 71(13)
			20	323(53), 277(67), 187(74), 95(100), 71(91), 67(74)
P8	307	1.16	1	310(16), 307(100), 289(32), 279(35), 218(24), 163(25)
			5	307(100), 227(24), 149(29), 88(15)
			10	307(32), 230(34), 165(100), 132(32), 96(37)
			20	165(100), 148(14), 62(17)
P9	99	13.40	1	99(100)
			5	99(100), 81(16), 55(6)
			10	99(100), 81(92), 55(12)
			20	99(4), 81(100), 63(17), 55(6)

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