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Intensification of degradation of imidacloprid in aqueous solutions by combination of hydrodynamic cavitation with various advanced oxidation processes (AOPs)

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ABSTRACT

The degradation of imidacloprid (a systemic chloronicotinoid insecticide) has been carried out in the aqueous solutions using the combination of hydrodynamic cavitation (HC) with various other advanced oxidation processes such as fenton, photo-fenton, photolytic and photocatalytic processes. HC + fenton process significantly enhanced the rate of degradation of imidacloprid, which lead to a complete degradation of imidacloprid within 15 min of operation using the molar ratio of imidacloprid:H_2O_2 as 1:40 and the molar ratio of $FeSO_4{\cdot}7H_2O$:H_2O_2 as 1:40. Similar results of an increase in the rate of degradation of imidacloprid have also been obtained in case of HC + photo-fenton process. Synergetic index of 3.636 and 2.912 have been obtained using HC + fenton and HC + photo-fenton processes respectively. The combination of hydrodynamic cavitation with photolytic and photocatalytic processes have also resulted in the enhancement in the rate of degradation of imidacloprid, however synergetic effect has not been observed. Comparison of efficiency of all the processes applied has also been done by computing extent of mineralization achieved and energy requirement of the process.

Introduction

Contamination of surface and ground water streams due to pesticides is posing a direct threat to human health and environment, since they are usually toxic, recalcitrant to biological treatment, and tend to accumulate in the environment [1,2]. Imidacloprid, the target pollutant in the present study belongs to new class of insecticide called chloronicotinoids [3]. Because of its high efficiency against many pests, its use is increasing worldwide. Acute toxicity of imidacloprid on the bee population (oral $LD_{50} = 0.0037\ \mu g$/bee) [4,5] and aquatic environment [6,7] has already been reported.

Advanced oxidation processes (AOPs), are one of the most promising ways for the effective degradation of many organic pollutants such as pesticides [8]. The basic mechanism of AOPs includes the generation of highly reactive hydroxyl radicals having very high oxidative power ($E_0 = 2.8$ V) and further its subsequent attack on the pollutant to be treated [9]. AOPs for the degradation of pesticides include various processes such as fenton and photofenton process [9–11], photolytic process [12–14], photocatalytic process [15–18], cavitation techniques [19–21] etc.

Application of cavitation and energy associated with it has been pursued by many researchers for the degradation of various organic pollutants. Cavitation is the phenomena of formation, growth and subsequent collapse of the cavities/bubbles containing vapours of the medium and its constituents. In hydrodynamic cavitation, the cavitation is induced by the flow of the liquid through simple mechanical constrictions such as venturi or an orifice under controlled conditions [19]. As the liquid passes thorough the mechanical constriction such as venturi, orifice plate, etc., the pressure at the throat or vena-contracta of the constriction is reduced below the vapor pressure of the liquid at the operating temperature and produces millions of micro cavities. The cavities generated subsequently collapse, as the reduced pressure is recovered in the downstream section of the constriction. Cavitation is capable of degrading complex organic pollutants, since

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collapse of bubbles releases large magnitude of energy, generating localized 'hot spot' with extremely high temperature, pressure conditions at very short time scale (temperature of 10,000 K and pressures of about 1000 atm. for microseconds) which leads to the dissociation of water molecule into highly reactive species like hydroxyl, $H^\bullet$ radicals [20]. When applied individually cavitation often gives lower rates of the degradation, but the efficacy of cavitation can be significantly enhanced by combining it with other advanced oxidation processes such as fenton [19–22], photofenton [23,24], photolytic [25–27], photocatalytic process [28,29]. Combination of cavitation with other AOPs often leads to an intensification of the degradation of organic pollutants due to the enhanced generation of the hydroxyl radicals. In addition to this, the catalyst surface is kept clean, catalyst particles are kept well mixed in the suspension and the mass transfer resistances are reduced due to improved local turbulence by cavitation.

Various AOPs such as photofenton [2,11,16,18], photolytic [12–14] and photocatalytic degradation processes [3,15–18] have been reported in the literature for the degradation of imidacloprid. However the use of hydrodynamic cavitation based hybrid techniques for the degradation of imidacloprid has not yet been explored. The present work deals with the study of degradation of imidacloprid by application of hydrodynamic cavitation (HC) and hydrodynamic cavitation based hybrid techniques such as HC + fenton and HC + photo-fenton and HC + photolytic and HC + photocatalytic process. The main focus of this study is to harness the energy associated with hydrodynamic cavitation for intensification of the degradation process of imidacloprid.

Materials and methods

Materials

Commercial grade imidacloprid ($C_9H_{10}ClN_5O_2$, Mw – 255.7) which contains 70% pure imidacloprid was obtained from Bayer AG. The following chemicals were obtained from S D Fine Chemicals Ltd., Mumbai, India: hydrogen peroxide (30% w/v), ferrous sulphate ($FeSO_4 \cdot 7H_2O$), sodium sulfite (Na_2SO_3) and sulphuric acid (H_2SO_4). These chemicals were of AR grade and acetonitrile and water used for HPLC analysis were of HPLC grade. Niobium pentoxide (Nb_2O_5) of GR grade (average particle size: 2.5 μm) was obtained from Loba Chemie Pvt. Ltd., Mumbai, India. All chemicals were used as received from the supplier.

Experimental set-up

Experimental set-up used in the present study is schematically shown in Fig. 1. It essentially comprised of closed loop circuit containing a feed tank, positive displacement pump (P = 1.1 kW), pressure gauges and valves. Cooling jacket is provided to the feed tank for controlling the temperature increased due to heat liberated during cavitation. Suction side of the pump is connected to the bottom side of the feed tank and the discharge line from the pump is branched into two lines. The main line consists of circular venturi and second line is bypass line. In the present study circular venturi with 2 mm throat diameter is used as a cavitating device. The exact geometric specifications of circular venturi have also been provided in Fig. 2. A bypass line is provided to control the flow through the main lines. Control valves and pressure gauges are provided at appropriate places to control the flow rate through the lines and to measure the fluid pressures respectively. Alternatively, variable frequency drive (VFD) is also provided to control the motor rpm such that the flow through the main line can be controlled directly by changing the number of piston stroke of the positive displacement pump, while keeping bypass line closed.

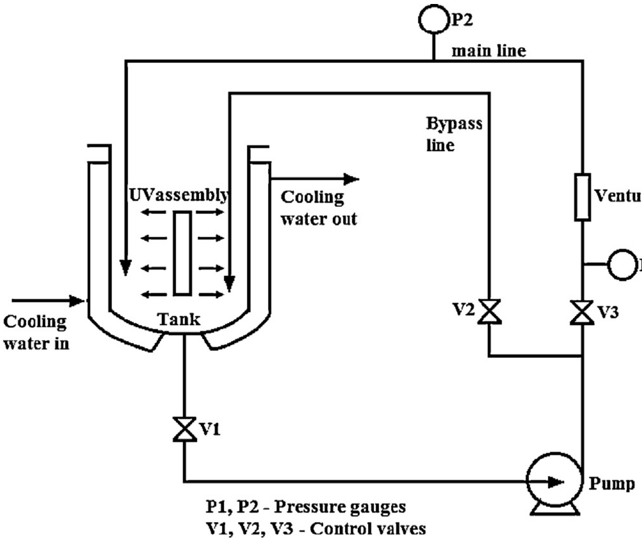

Fig. 1. Hydrodynamic cavitation set-up.

The material of construction of the entire system except cavitating device is stainless steel (SS316), whereas cavitating device, circular venturi is made up of brass. Portable UV assembly, made up of quartz, containing UV lamp (250 W, λ_{max} – 364 nm) with cooling jacket, is placed centrally in the feed tank for the UV irradiation. It was used while studying the techniques involving photofenton, photolytic and photocatalytic processes.

Hydrodynamic cavitation (HC)

All the experiments were performed with 5 L aqueous solution of imidacloprid with an initial concentration of 25 ppm. Initially, operating parameters such as inlet pressure and pH were optimized by varying inlet pressure from 5 to 20 bar (5, 10, 12.5, 15, 17.5 and 20 bar) at pH of 2.7 and by varying the pH from 2 to 7.5 (2, 2.7, 3, 4, 6, 7.5) at the inlet pressure of 15 bar, which includes 7.5 as natural pH of the aqueous solution of imidacloprid. The inlet pressures were controlled by adjusting piston stroke length and frequency of the pump and pH of the solution was adjusted by adding sulphuric acid as per the requirement.

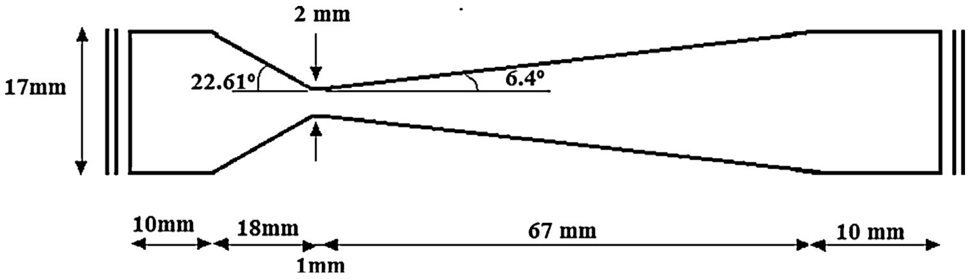

Fig. 2. Geometric specifications of a cavitating device (circular venturi).

Hydrodynamic cavitation based hybrid techniques

All the experiments were performed treating 5 L aqueous solution of imidacloprid with the initial concentration of 25 ppm. The optimum pump discharge pressure to the cavitating device of 15 bar and the optimal pH of 2.7, was used.

Fenton chemistry was employed along with hydrodynamic cavitation at the fixed molar ratio of imidacloprid:H_2O_2 as 1:40 with concentration of H_2O_2 as 3.91 mmol/L and varying molar ratio of ferrous sulphate:H_2O_2 as 1:50, 1:40, 1:30 and 1:20. Ferrous sulphate has been used as a homogeneous fenton catalyst. The degradation of imidacloprid was also performed using the conventional fenton oxidation process using a stirred reactor without hydrodynamic cavitation at the optimized ratio of imidacloprid:H_2O_2 as 1:40 and molar ratio of ferrous sulphate:H_2O_2 as 1:40 (Capacity – 2 L, 4 blade pitched impeller with diameter – 3.5 cm and angle 45°, rotating at 300 rpm).

UV assembly was placed centrally in a feed tank for UV irradiation during photofenton, photolytic, photocatalytic processes and their combination with HC. Photo-fenton and HC + photofenton processes were employed at molar ratio of imidacloprid:H_2O_2 as 1:40 and molar ratio of ferrous sulphate:H_2O_2 as 1:40. Photocatalytic and HC + photocatalytic processes were employed using niobium pentoxide (Nb_2O_5) as a photocatalyst, due to its adequate band gap of 3.4 eV and stability in acidic conditions. The catalyst was used as received from the supplier without any pretreatment such as drying, purification etc. The amount of catalyst used in all such experiments was 200 mg/L.

During AOPs such as photo-fenton, photolytic and photocatalytic processes, the flowrate of aqueous solution of imidacloprid was maintained at the same flowrate of 610 L/h (flowrate corresponding to optimal inlet pressure of 15 bar) by adjusting piston stroke length and frequency of the pump. Maintaining identical flowrate during all such experiments (with and without cavitation) ensures the identical exposure of imidacloprid to UV irradiation.

Analytical methods

Concentration of imidacloprid at any instance was determined using high pressure liquid chromatography (HPLC). HPLC instrument used comprised of UV detector (G1314B) and a Eclipse XDB-C18 column of dimensions 4.6 × 250 mm (Agilent Technologies, USA). A mixture of acetonitrile:water (30:70 v/v) was used as a mobile phase with flow rate maintained at 1 mL/min and elution was monitored using UV detector at 269 nm. In order to obtain the accurate concentration of imidacloprid at any instance, particularly in case of fenton and photofenton processes, 0.5 N sodium sulfite has been added immediately to the samples withdrawn, as a quenching agent. In case of photocatalytic process, samples withdrawn were centrifuged at 4500 rpm (5660 g relative centrifugal force) to remove the solid catalyst particles and supernatant was utilized for HPLC analyses.

In addition, some of the samples at various optimum conditions were also analyzed using total organic carbon analyzer (Shimadzu Corporation, Japan) to observe the complete mineralization of imidacloprid into end products (such as CO_2 and H_2O).

Results and discussion

Hydrodynamic cavitation

Initially, the study of degradation of imidacloprid has been carried out for the duration of 120 min using hydrodynamic cavitation for obtaining an optimal inlet pressure to the cavitating device and an optimal pH. The inlet pressure was optimized by varying the inlet pressure from 5 to 20 bar (5, 10, 12.5, 15, 17.5 and 20 bar) by adjusting piston stroke length and frequency of the pump. Similarly, the initial pH of an aqueous solution of imidacloprid was optimized by varying the pH from 2 to 7.5 (2, 2.7, 3, 4, 6, 7.5) by adding H_2SO_4 solutions as per requirement. The obtained results have been depicted in Fig. 3.

It can be seen that, the rate of degradation of imidacloprid increases with an increase in the inlet pressure till 15 bar and decreases with further increase in the inlet pressure. The results obtained are attributed to the fact that at higher inlet pressures such as 15 bar, number of cavities produced, intensity of turbulence created and intensity of cavity collapse would be higher. This condition could enhance the concentration of hydroxyl radicals and its effective utilization, which subsequently increases the possibility of the degradation of imidacloprid. However, increasing the inlet pressure beyond an optimal value leads to the formation cavity cloud which reduces the cavitational intensity. Hence, the optimal inlet pressure of 15 bar has been

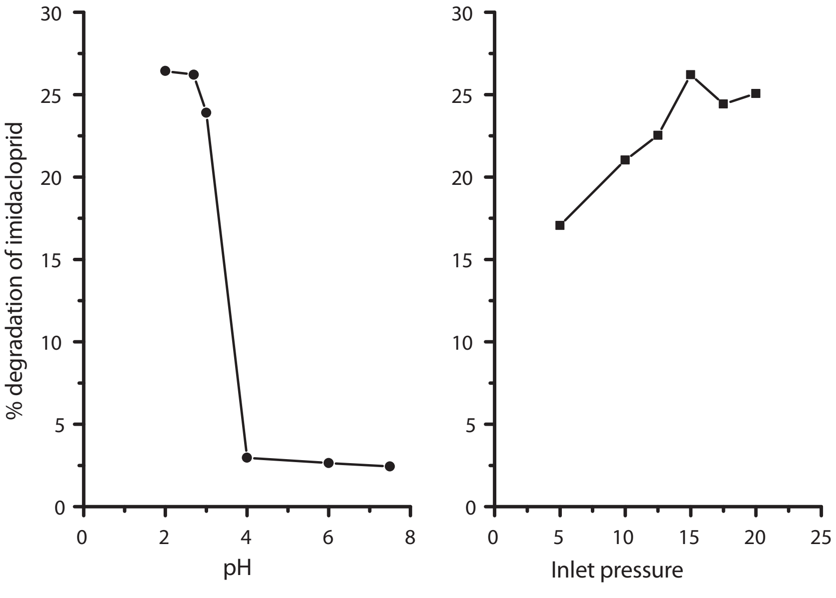

Fig. 3. Effect of inlet pressure and pH on the % degradation of imidacloprid (initial concentration of imidacloprid – 25 ppm).

used in all further experiments. In credence with these findings, Patil and Gogate [19] have also reported an increase in the extent of degradation of methyl parathion with an increase in the inlet pressure and obtained the optimal inlet pressure of 4 bar using an orifice as a cavitating device. Saharan et al. [30] have also observed that rate of degradation of reactive red 120 using hydrodynamic cavitation (venturi) increases with an increase in the inlet pressure, reaching maximum at 5 bar. These findings have indicated that an optimal inlet pressure exists, however the inlet pressure required vary greatly, since it strongly depends on the design of cavitating device and the chemical nature of target pollutant.

It has also been observed that, the extent of the degradation of imidacloprid substantially increases under the acidic conditions, when the pH of the solution has been reduced from 7.5 to 2.0. However, under strong acidic conditions at the pH of 2, marginal increase in the extent of degradation of imidacloprid has been observed. Hence, the optimal pH of 2.7 has been used in all further experiments.

Enhancement in the extent of degradation of imidacloprid at low pH is due to the fact that, under acidic conditions the oxidation potential of hydroxyl radicals increases, whereas the recombination reaction of the free radicals decreases. On the other hand, under acidic conditions the state of the imidacloprid molecule changes from ionic to molecular state, thereby causing it to locate at the cavity water interface, where the concentration of the hydroxyl radicals are high and hence the degradation rate increases.

Similar findings of an increase in the extent of degradation of pesticides under acidic conditions are also reported in the literature. Golash and Gogate [21] have also reported that the acidic condition favours the sonochemical degradation of dichlorvos. Maximum degradation of dichlorvos of 52.9% obtained at operating pH of 2 decreased to about 24% when the operating pH was increased to 8.

Hydrodynamic cavitation + fenton process

Fenton process utilizes the reactivity of hydroxyl radicals generated in acidic conditions by iron catalyzed decomposition of hydrogen peroxide (Eq. (1)) for the degradation of organic pollutant [9,11].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \tag{1}$$

Resulting Fe^{3+} ions can react with H_2O_2 (Eq. (2)) to produce the intermediate complex ($Fe\text{–}OOH^{\bullet 2+}$), which can easily get converted into Fe^{2+} and $HO_2^\bullet$ under cavitating conditions (Eq. (3)) [20].

$$Fe^{3+} + H_2O_2 \rightarrow Fe\text{–}OOH^{\bullet 2+} + H^+ \tag{2}$$

$$Fe\text{–}OOH^{\bullet 2+} \rightarrow Fe^{2+} + HO_2^\bullet \tag{3}$$

Generated Fe^{2+} ions can again react with H_2O_2 to generate even more number of hydroxyl radicals (Eq. (1)). In addition to this, some part of H_2O_2 directly decomposes to hydroxyl radicals in presence of hydrodynamic cavitation [19,20] as shown in Eq. (4)

$$H_2O_2 \rightarrow OH^\bullet + OH^\bullet \tag{4}$$

Hence, the combination of hydrodynamic cavitation and fenton process accelerates the rate of generation of hydroxyl radicals.

Effect of combination of hydrodynamic cavitation and fenton process on the extent of degradation of imidacloprid has been investigated for various molar ratios of ferrous sulphate to hydrogen peroxide. The results obtained have been depicted in Fig. 4. It has been observed that the rate of degradation of imidacloprid increases with an increase in the loading of $FeSO_4{\cdot}7H_2O$ and obeys first order degradation kinetics. First order reaction rate constants obtained have been reported in Table 1. It has been observed that 6.15% and 64.43% degradation of imidacloprid obtained after 15 min of operation using HC and conventional fenton process respectively, significantly increased to 97.77% by applying the combination of HC and fenton process. Substantial synergetic effect has been observed using HC + fenton process, since the value of reaction rate constant of $2.565 \times 10^{-3}\ min^{-1}$ and $66.711 \times 10^{-3}\ min^{-1}$ obtained in case of HC and conventional fenton process (without HC) substantially increased to $250.749 \times 10^{-3}\ min^{-1}$ when HC was combined with fenton process. The synergetic effect of combining HC with fenton process based on reaction rate constant (Eq. (5)) can be obtained as

$$\text{Synergetic index} = \frac{k_{(HC+fenton)}}{k_{HC} + k_{fenton}} = 3.636 \tag{5}$$

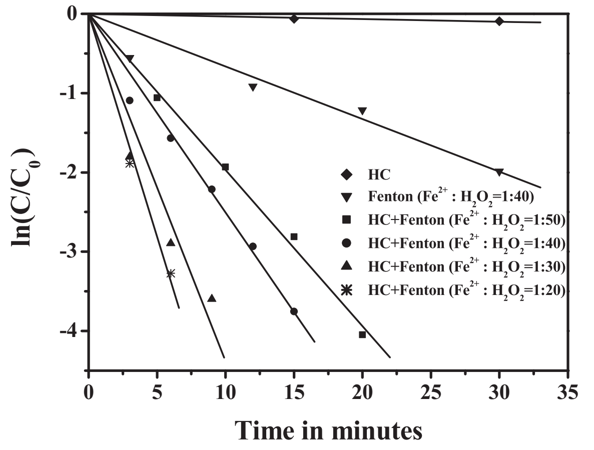

Fig. 4. First order degradation of imidacloprid using HC, Fenton and HC + fenton processes (initial concentration of imidacloprid – 25 ppm, inlet pressure – 15 bar, pH 2.7 and molar ratio of imidacloprid:H_2O_2-1:40).

Synergetic effect observed has been credited to the fact that the combination of HC and fenton process generates higher concentration of hydroxyl radicals as compared to fenton and HC processes. The increased concentration of hydroxyl radicals along with their effective utilization due to higher intensity of turbulence created by HC significantly accelerates the rate of degradation of imidacloprid. In addition, the quantity of the ferrous sulphate required as a catalyst can be reduced significantly due to the combined HC + fenton process as compared to fenton process for obtaining same extent of degradation. Hence the total dissolved solids (TDS) in the discharged liquid in the combined HC + fenton process would also be less than that in the fenton process.

Similar trends of results are reported in the literature for the degradation of other organic pollutants by applying combination of HC and fenton process. Joshi and Gogate [20] have investigated the degradation of dichlorvos using combination of hydrodynamic cavitation and fenton process and have also reported that the rate of degradation of dichlorvos increases significantly with increasing

Table 1
Effect of molar ratio of $FeSO_4{\cdot}7H_2O{:}H_2O_2$ on extent of degradation and reaction rate constant, *k*.

Process	Molar ratio of $FeSO_4{\cdot}7H_2O{:}H_2O_2$	$k \times 10^3\ min^{-1}$	% Degradation after 15 min of operation
HC	–	2.565	6.15
Fenton	1:40	66.711	64.43
HC + fenton	1:50	196.979	94.07
	1:40	250.749	97.77
	1:30	437.900	100.00
	1:20	562.169	100.00

concentrations of Fe^{2+} giving maximum degradation of 91.5% at 3:1 loading of $FeSO_4$:H_2O_2. Bremner et al. [22] have also demonstrated that the degradation of 2,4 dichlorophenoxy acetic acid can be intensified by combining hydrodynamic cavitation and advanced fenton process.

Hydrodynamic cavitation + photo-fenton process

It is well known, that under acidic conditions a part of ferrous ions would exist in the form of $Fe(OH)^{2+}$, which can easily get converted into hydroxyl radicals and Fe^{2+} under UV irradiation as indicated in Eq. (6) [10]. This can establish a cycle of reactions of generating additional hydroxyl radicals and regeneration of catalyst since Fe^{2+} ions are restored.

$$Fe(OH)^{2+} + (UV) \rightarrow Fe^{2+} + OH^{\bullet} \qquad (6)$$

Combination of hydrodynamic cavitation and photo-fenton process can further increase the concentration of hydroxyl radicals generated and hence higher rate of degradation of imidacloprid can be achieved. The results obtained giving the comparison of HC, photo-fenton and combined HC + photo-fenton processes have been shown in Fig. 5. It can be seen that the rate of degradation of imidacloprid using HC + photo-fenton process is substantially higher as compared to HC and photo-fenton processes and followed the first order degradation kinetics.

The reaction rate constants obtained have been summarized in Table 2. The value of first order reaction rate constant of $99.372 \times 10^{-3}\ \text{min}^{-1}$ for photo-fenton process has been significantly increased to $297.012 \times 10^{-3}\ \text{min}^{-1}$ by combining HC and photo-fenton process. Approximately 99.23% degradation of imidacloprid has been obtained after 15 min of operation by combining HC and photo-fenton processes as compared to only 6.15% and 81.60% degradation of imidacloprid obtained in case of HC and photo-fenton processes respectively. Hence, substantial synergistic effect has been observed in combining in HC and photo-fenton process. The synergetic index based on reaction rate constant (Eq. (7)) by combining HC with photo-fenton process can be obtained as

$$\text{Synergetic index} = \frac{k_{(\text{HC+photofenton})}}{k_{\text{HC}} + k_{\text{phootfenton}}} = 2.912 \qquad (7)$$

Synergistic effect observed can again be attributed to the effective utilization and higher generation of hydroxyl radicals, regeneration of catalyst i.e. Fe^{2+} ions and effective mixing generated by cavitation.

Table 2
Effect of combination of HC and photo-fenton process.

Type of process	$k \times 10^3\ \text{min}^{-1}$	% Degradation after 15 min of operation
HC	2.565	6.15
Photo-fenton	99.372	81.60
HC + photo-fenton	297.012	99.23

Hybrid techniques combining cavitation and photo-fenton processes have also been reported in the literature for the degradation of other organic pollutants. Torres et al. [23] have demonstrated that the simultaneous ultrasound/Fe^{2+}/light process has found to be more efficient technique for removal of bisphenol A as compared to the individual processes. Segura et al. [24] have also reported that simultaneous application of sonication and photo-fenton process resulted in the higher rate of degradation of phenol.

Hydrodynamic cavitation + photolytic process

The effect of combination of hydrodynamic cavitation (HC) and photolytic process (UV) on the rate of degradation of imidacloprid has been investigated by comparing HC, photolytic and combined HC + photolytic processes. Fig. 6 provides the comparison of these processes in terms of the rate of degradation of imidacloprid.

It can be seen that the rate of degradation of imidacloprid obtained by applying HC and photolytic processes has further enhanced by combining hydrodynamic cavitation with photolytic process. It has also been observed that the degradation of imidacloprid obeys first order degradation kinetics during these processes. Reaction rate constants and extent of degradation obtained have been summarized in Table 3. First order reaction rate constant of $2.565 \times 10^{-3}\ \text{min}^{-1}$ and $3.557 \times 10^{-3}\ \text{min}^{-1}$ obtained in case of HC and photolytic process respectively, has further enhanced to $5.034 \times 10^{-3}\ \text{min}^{-1}$ by combining HC and photolytic process. However, synergetic effect has not been observed, since the reaction rate constant obtained in case of combination of HC and photolytic process has found to be lower than the sum of the reaction rate constant obtained in case of HC and photolytic process. The results obtained might be attributed to the facts that since UV source has not been available in the

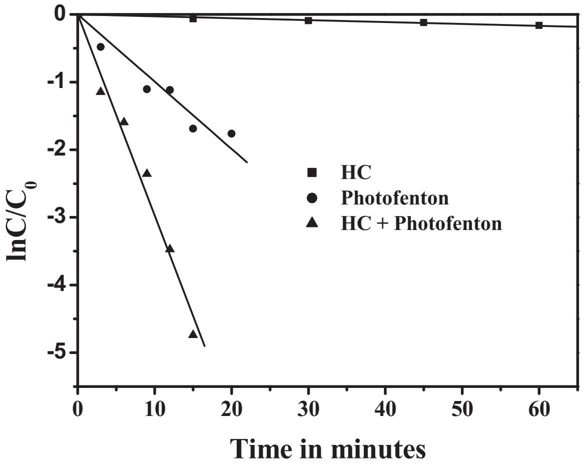

Fig. 5. First order degradation of imidacloprid using HC, photo-fenton and HC + photo-fenton processes (initial concentration of imidacloprid – 25 ppm, inlet pressure – 15 bar, pH 2.7 and molar ratio of imidacloprid:H_2O_2 – 1:40 and $FeSO_4 \cdot 7H_2O$:H_2O_2 – 1:40).

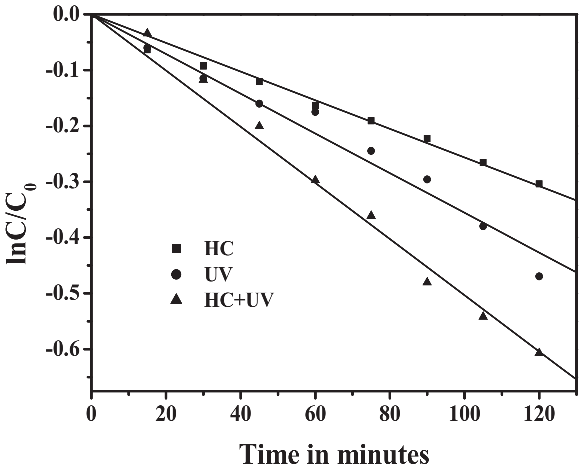

Fig. 6. First order photolytic degradation of imidacloprid using HC, UV and HC + UV processes (initial concentration of imidacloprid – 25 ppm, pH 2.7 and inlet pressure – 15 bar).

Table 3
Effect of combination of HC and photolytic process.

Type of process	$k \times 10^3$ min^{-1}	% Degradation after 120 min of operation
HC	2.565	26.24
UV	3.557	37.52
HC + UV	5.034	45.56

Table 4
Effect of combination of HC and photocatalytic process.

Type of process	$k \times 10^3$ min^{-1}	% Degradation after 120 min of operation
HC	2.565	26.24
UV + Nb_2O_5	4.871	45.99
HC + UV + Nb_2O_5	6.837	55.18

cavitating zone, in the combined HC + photolytic process the phenomena of cavitation and photolysis has not been occurring simultaneously and hence not accelerating the oxidation of imidacloprid. In fact, the combined process is actually the continuous sequential operation of UV irradiation in the feed tank followed by hydrodynamic cavitation in cavitator.

The UV source has not been placed in the cavitation zone, since the venturi was made up of brass and was not transparent. Hence, for obtaining synergetic effect an attempt can be made to apply the UV irradiation in the cavitation zone. This can be done by designing transparent cavitator and placing UV source outside the cavitator, so that these processes will occur simultaneously and could complement each other.

It has been well supported in the literature that the synergetic effect can be obtained by combining cavitation with photolytic process, when both the processes are occurring simultaneously. Khokhawala and Gogate [25] have reported the synergetic effect of the combination of ultrasound cavitation (US) and UV irradiation process occurring simultaneously for the degradation of phenol. Shirgaonkar and Pandit [27] have also obtained synergetic effect by applying simultaneous sonophotochemical process for the degradation of 2,4,6 trichlorophenol.

Hydrodynamic cavitation + photocatalytic process

Heterogeneous photocatalysis is one of the promising techniques for the degradation of various pesticides [1–3,8,15–17]. Niobium pentoxide (Nb_2O_5) has been used as a photocatalyst, since it is an emerging photocatalyst due to its stability in acidic conditions, wide band gap of 3.4 eV, and its ability to get recycled easily [31–33].

The results obtained comparing the processes such as HC, photocatalytic process and the combined HC + photocatalytic process have been shown in Fig. 7. It can be seen that the rate of degradation of imidacloprid obeys first order degradation kinetics for all the processes applied. First order reaction rate constants obtained have been summarized in Table 4. It has been observed that the first order reaction rate constant of 2.565×10^{-3} min^{-1} and 4.871×10^{-3} min^{-1} obtained by applying HC and photocatalytic processes respectively has further increased to 6.837×10^{-3} min^{-1} using combined HC + photocatalytic process. However, the synergetic effect has not been observed at a catalyst concentration of 200 mg/L, since the reaction rate constant obtained using combined HC + photocatalytic process has not been found to be higher than the sum of the reaction rate constants obtained for separate HC and photocatalytic processes. Lack of synergetic effect may be due to the fact that presence of solid particles of Nb_2O_5 during cavitation has not enhanced the cavitational phenomena. This is because even though the presence of solid particles during cavitation provides additional nuclei for the cavity bubbles, higher loading of solids may decrease the cavitational intensity since the cavity bubbles may not get adequate space for growth or their growth may be hindered due to presence of solid particles.

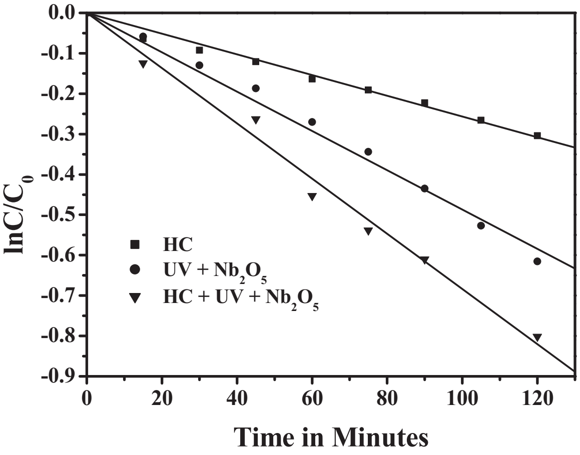

Fig. 7. First order photocatalytic degradation of imidacloprid using Nb_2O_5 with and without HC (initial concentration of imidacloprid – 25 ppm, inlet pressure – 15 bar, pH 2.7 and amount of catalyst – 200 mg/L).

In addition, high turbulence caused by cavitation might have not increased the catalytic activity of Nb_2O_5 by de-agglomerating the catalyst particles and keeping the surface of catalyst clean. This may be because the surface of Nb_2O_5 particles remains clean and do not agglomerate much even in the absence of very high turbulence [31].

It should also be noted here that, in the combined HC + photocatalytic process, HC and photocatalytic processes are not occurring simultaneously. Rather, hydrodynamic cavitation occurs in the cavitator in the presence of solid particles of Nb_2O_5 and photocatalytic process occurs in the feed tank in the presence of UV source. UV source could not be placed in the cavitating zone for making the process truly simultaneous, since the cavitator was made up of brass and was not transparent for passage of UV light.

Hence, combination of HC with photocatalytic process using concentration of catalyst as 200 mg/L does not seem to be a very promising technique under the operating conditions specified.

Cavitational yield

Cavitational yield has been calculated for various processes such as HC, HC + fenton, HC + photo-fenton, HC + photolytic and HC + photocatalytic under the optimal conditions to compare the energy efficiency of these processes and to investigate the more energy efficient process. The cavitational yield can be expressed as [34],

$$\text{Cavitational yield} = \frac{\text{Moles of imidacloprid degraded}}{\text{Energy dissipated in the system}}$$

where, power dissipated in the HC set-up = $P \times Q \times t$, P = discharge pressure of the pump = 15 bar, Q = flowrate in the main line at 15 bar pressure = 1.69×10^{-4} m^3/s, t = time of operation = 15 min.

Cavitational yield obtained by applying HC and various hybrid techniques have been depicted in Fig. 8. It can be clearly seen from the figure that the cavitational yield of 1.179×10^{-10} mol/J obtained in case of HC has substantially increased to 1.41×10^{-9} mol/J by applying the combination of HC and fenton process. Quantitatively it can be predicted that the energy

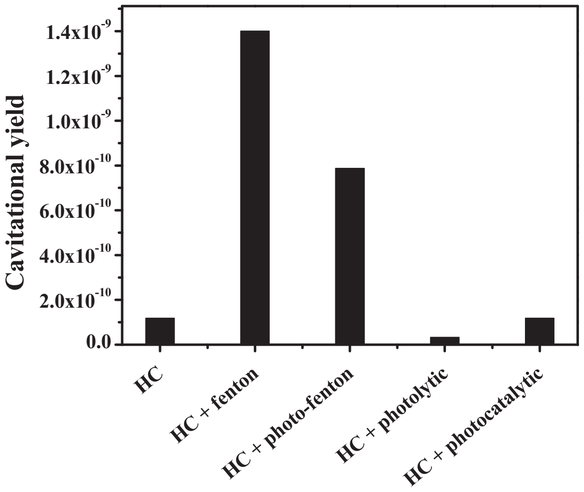

Fig. 8. Comparison of cavitational yield of various processes.

efficiency of HC + fenton process is approximately 12-folds more than that for the HC process. Similarly, the cavitational yield of 7.87×10^{-10} mol/J obtained in case of HC + photo-fenton process is approximately 6 times higher as compared to the cavitation yield for HC process.

It should also be noted here that the combination of HC with the photolytic and photocatalytic process has not increased the energy efficiency of the process since an additional energy applied for the UV irradiation has not enhanced appreciably the rate of degradation of imidacloprid in the combined process.

Hence, hybrid techniques such as HC + fenton and HC + photo-fenton have proved to be more energy efficient among all the processes.

Mineralization study

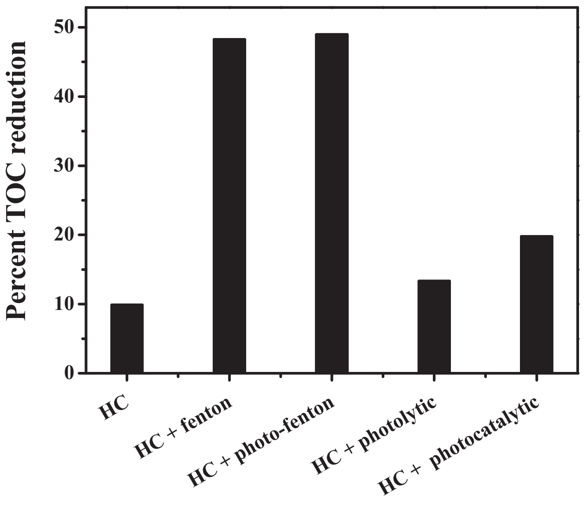

Fig. 9. Comparison of the extent of mineralization obtained during various processes.

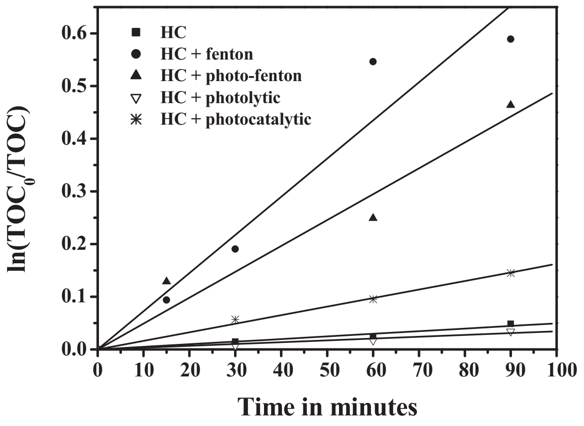

Fig. 10. Kinetics of mineralization process of imidacloprid.

Table 5
Initial rate constants and extents of mineralization obtained during various processes.

Type of process	$k' \times 10^3$ min^{-1}	% Mineralization after 180 min
HC	0.495	9.89
HC + fenton	7.246	48.25
HC + photo-fenton	4.912	48.96
HC + photolytic	0.344	13.34
HC + photocatalytic	1.624	19.78

In order to assess the extent of mineralization achieved, the decrease in the total organic carbon (TOC) has been estimated during various processes applied. The percent TOC reduction obtained during these processes have been depicted in Fig. 9 and the kinetics of mineralization of imidacloprid has been shown in Fig. 10. The results obtained have clearly indicated that HC + fenton and HC + photo-fenton processes are more effective than any other methods applied. It has been observed that initially mineralization process follows the first order mineralization kinetics for all the processes applied. The initial rate constants of mineralization along with the extent of mineralization obtained after 3 hr of operation have been summarized in Table 5. It has been observed that the percent TOC reduction of 9.89% and the initial rate constant of mineralization of 0.495×10^{-3} min^{-1} obtained in case of HC have significantly increased to 48.25% of TOC reduction and the rate constant of mineralization of 7.246×10^{-3} min^{-1} by applying the combination of HC and fenton process. In addition, higher percentage of TOC reduction has also been obtained in case of HC + photo-fenton process (% TOC reduction – 48.96).

Other processes such as HC + photolytic (% TOC reduction – 13.34) and HC + photocatalytic (% TOC reduction – 19.78) processes have resulted in only marginal increase in the extent of mineralization as compared to HC (% TOC reduction – 9.89). The results obtained are attributed to the fact that most of the end byproducts formed during photo degradation and photocatalytic degradation of imidacloprid are might be stable organic compounds, which could not be further degraded by hydrodynamic cavitation at the operating conditions (inlet pressure – 15 bar and temperature 32 ± 4 °C) used in this work. This fact may lead to reduced mineralization of imidacloprid during photolytic and photocatalytic degradation of imidacloprid.

Overall, the percent TOC reduction obtained during various processes decreased in the order of HC + photo-fenton < HC + fenton < HC + photocatalytic < HC + photolytic < HC.

Conclusions

The following important conclusions can be established for the degradation of imidacloprid.

- HC + fenton and HC + photo-fenton processes lead to almost complete degradation of imidacloprid within 15 min of operation at the molar ratio of imidacloprid:H_2O_2 as 1:40 and the molar ratio of $FeSO_4 \cdot 7H_2O:H_2O_2$ as 1:40. Significant synergetic effect has been observed since synergetic index of 3.636 and 2.912 has been obtained in case of HC + fenton and HC + photo-fenton processes respectively.

- The rate of degradation of imidacloprid obtained using the combination of HC with photolytic and photocatalytic process has found to be higher than that for the individual processes. However, combination of HC with photolytic and photocatalytic processes has not shown any synergetic effect.
- HC + fenton process has found to be the most energy efficient and effective technique for complete degradation of imidacloprid with higher extent of mineralization as compared to other processes studied.

Hence, hydrodynamic cavitation based hybrid techniques combining various AOPs can be applied successfully for the degradation of imidacloprid.

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References

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

[2] A. Zapata, I. Oller, E. Bizani, J.A. Sanchez-Perez, M.I. Maldonado, S. Malato, Evaluation of operational parameters involved in solar photo-fenton degradation of a commercial pesticide mixture, Catalysis Today 144 (2009) 94–99.

[3] N.M. Mahmoodi, M. Arami, N. Yousefi Limaee, K. Gharanjig, Photocatalytic degradation of agricultural *N*-heterocyclic organic pollutants using immobilized nanoparticles of titania, Journal of Hazardous Materials 145 (2007) 65–71.

[4] M.P. Halm, A. Rortais, G. Arnold, J.N. Tasei, S. Rault, New risk assessment approach for systemic insecticides: the case of honey bees and imidacloprid (Gaucho), Environmental Science and Technology 40 (2006) 2448–2454.

[5] P. Medrzycki, R. Montanari, L. Bortolotti, A.G. Sabatini, S. Maini, C. Porrini, Effects of imidacloprid administered in sub-lethal doses on honey bee behaviour. Laboratory tests, Bulletin of Insectology 56 (2003) 59–62.

[6] T. Tišler, A. Jemec, B. Mozetič, P. Trebše, Hazard identification of imidacloprid to aquatic environment, Chemosphere 76 (2009) 907–914.

[7] O. Malev, R.S. Klobučar, E. Fabbretti, P. Trebše, Comparative toxicity of imidacloprid and its transformation product 6-chloronicotinic acid to non-target aquatic organisms: microalgae Desmodesmus subspicatus and amphipod, Pesticide Biochemistry and Physiology 104 (2012) 178–186.

[8] S. Devipriya, S. Yesodharan, Photocatalytic degradation of pesticide contaminants in water, Solar Energy Materials and Solar Cells 86 (2005) 309–348.

[9] M.S.F. Santos, A. Alves, L.M. Madeira, Paraquat removal from water by oxidation with fenton's reagent, Chemical Engineering Journal 175 (2011) 279–290.

[10] 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, Separation and Purification Technology 61 (2008) 103–108.

[11] C. Segura, C. Zaror, H.D. Mansilla, M.A. Mondaca, Imidacloprid oxidation by photo-fenton reaction, Journal of Hazardous Materials 150 (2008) 679–686.

[12] H. Wamhoff, V. Schneider, Photodegradation of imidacloprid, Journal of Agricultural and Food Chemistry 47 (1999) 1730–1734.

[13] P.N. Moza, K. Hustert, E. Feicht, A. Kettrup, Photolysis of imidacloprid in aqueous solution, Chemosphere 36 (1998) 497–502.

[14] D. Redlich, N. Shahin, P. Ekici, A. Friess, H. Parlar, Kinetical study of the photoinduced degradation of imidacloprid in aquatic media, Clean 35 (2007) 452–458.

[15] A. Agüera, E. Almansa, S. Malato, M.I. Maldonado, A.R. Fernández-Alba, Evaluation of photocatalytic degradation of imidacloprid in industrial water by GC–MS and LC–MS, Analusis 26 (1998) 245–250.

[16] S. Malato, J. Cáceres, A. Agüera, M. Mezcua, D. Hernando, J. Vial, A.R. Fernández-Alba, Degradation of imidacloprid in water by photo-fenton and TiO_2 photocatalysis at solar pilot plant: a comparative study, Environmental Science and Technology 35 (2001) 4359–4366.

[17] R. Žabar, T. Komel, J. Fabjan, M.B. Kralj, P. Trebše, Photocatalytic degradation with immobilised TiO_2 of three selected neonicotinoid insecticides: imidacloprid, thiamethoxam and clothianidin, Chemosphere 89 (2012) 293–301.

[18] S. Malato, J. Blanco, J. Cáceres, A.R. Fernández-Alba, A. Agüera, A. Rodriguez, Photocatalytic treatment of water-soluble pesticides by photo-fenton and TiO_2 using solar energy, Catalysis Today 76 (2002) 209–220.

[19] P.N. Patil, P.R. Gogate, Degradation of methyl parathion using hydrodynamic cavitation: effect of operating parameters and intensification using additives, Separation and Purification Technology 95 (2012) 172–179.

[20] R.K. Joshi, P.R. Gogate, Degradation of dichlorvos using hydrodynamic cavitation based treatment strategies, Ultrasonics Sonochemistry 19 (2012) 532–539.

[21] N. Golash, P.R. Gogate, Degradation of dichlorvos containing wastewaters using sonochemical reactors, Ultrasonics Sonochemistry 19 (2012) 1051–1060.

[22] D.H. Bremner, S.D. Carlo, A.G. Chakinala, G. Cravotto, Mineralisation of 2,4-dichlorophenoxyacetic acid by acoustic or hydrodynamic cavitation in conjunction with the advanced fenton process, Ultrasonics Sonochemistry 15 (2008) 416–419.

[23] R.A. Torres, G. Sarantakos, E. Combet, C. Pétrier, C. Pulgarin, Sequential helio-photo-fenton and sonication processes for thetreatment of bisphenol A, Journal of Photochemistry and Photobiology A 199 (2008) 197–203.

[24] Y. Segura, R. Molina, F. Martínez, J.A. Melero, Integrated heterogeneous sono-photo fenton processes for the degradation of phenolic aqueous solutions, Ultrasonics Sonochemistry 16 (2009) 417–424.

[25] I.M. Khokhawala, P.R. Gogate, Degradation of phenol using a combination of ultrasonic and UV irradiations at pilot scale operation, Ultrasonics Sonochemistry 17 (2010) 833–838.

[26] C. Wu, X. Liu, D. Wei, J. Fan, L. Wang, Photosonochemical degradation of phenol in water, Water Research 35 (2001) 3927–3933.

[27] I.Z. Shirgaonkar, A.B. Pandit, Sonophotochemical destruction of aqueous solution of 2,4,6-trichlorophenol, Ultrasonics Sonochemistry 5 (1998) 53–61.

[28] X. Wang, J. Jia, Y. Wang, Degradation of C.I. reactive red 2 through photocatalysis coupled with water jet cavitation, Journal of Hazardous Materials 185 (2011) 315–321.

[29] Z. Cheng, X. Quan, Y. Xiong, L. Yang, Y. Huang, Synergistic degradation of methyl orange in an ultrasound intensified photocatalytic reactor, Ultrasonics Sonochemistry 19 (2012) 1027–1032.

[30] V.K. Saharan, M.P. Badve, A.B. Pandit, Degradation of reactive red 120 dye using hydrodynamic cavitation, Chemical Engineering Journal 178 (2011) 100–107.

[31] A.G.S. Prado, L.B. Bolzon, C.P. Pedroso, A.O. Moura, L.L. Costa, Nb_2O_5 as efficient and recyclable photocatalyst for indigocarmine degradation, Applied Catalysis B: Environmental 82 (2008) 219–224.

[32] B.N. Patil, D.B. Naik, V.S. Shrivastava, Photocatalytic degradation of hazardous Ponceau-S dye from industrial wastewater using nanosized niobium pentoxide with carbon, Desalination 269 (2011) 276–283.

[33] S. Ge, H. Jia, H. Zhao, Z. Zheng, L. Zhang, First observation of visible light photocatalytic activity of carbon modified Nb_2O_5 nanostructures, Journal of Materials Chemistry 20 (2010) 3052–3058.

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