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Harnessing hydroxyl radicals generated by hydrodynamic cavitation reactor in simultaneous removal of chlorpyrifos pesticide and COD from aqueous solution

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ABSTRACT

Harmful recalcitrant compound such as chlorpyrifos, an organophosphate pesticide is present in different environmental matrices due to its wide spectrum application throughout the world. To deal with or remove such compound, various different approaches are adopted and employed. But, in doing so, problems such as efficiency, large scale application, economical aspects, by-product generation, compatibility, etc are raised. Hydrodynamic cavitation (HC) is a cleaner technical process, have ability to produce strong Hydroxyl radicals that can take care of all above said problems. Present work focuses on application of HC reactor in simultaneous removal of model pollutant chlorpyrifos pesticide and chemical oxygen demand (COD) from aqueous solution. Kinetic parameters relating to HC were studied and found that optimum inlet pressure of 5 bars gave 100% chlorpyrifos and 46.7% COD removal. Study relating to number of passes for economical operation reveals that 53 passes were optimum for 56.2% COD removal and 100% chlorpyrifos degradation, acidic pH 4 is more efficient with 55.1% COD removal than alkaline pH 10 with 32.4% COD removal efficiency and has no significant effects on the extent of degradation of chlorpyrifos. Contact time of 2 h yielded maximum COD removal of around 55%.This paper illustrates the HC process, which can be effectively used in field application, with both organic matter in form of COD and recalcitrant compound chlorpyrifos can be treated simultaneously.

Keywords: Chlorpyrifos; Chemical oxygen demand (COD); Degradation; Hydrodynamic cavitation; Efficiency

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1. Introduction

Chlorpyrifos, O,O-diethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate ($C_9H_{11}C_{13}NO_3PS$) (CPF), is a well-known organo phosphorothioate pesticide that is used in agricultural and nonagricultural areas and is available in various formulations under the trade names such as Lorsban, Pyrinex, Spannit, Tricel, Dursban, Piridane, Silrifos, and Talon [1–4]. It is widely used to control a large variety of pests (for example, Coleoptera, Diptera, Homoptera and Lepidoptera families) in agricultural and animal farms [5,6]. It acts as a synaptic poison having a broad spectrum of insecticidal activity which is used to control insects attacking corn, cotton, citrus, fruits, nut crops, potato, beets, pulses, etc. [7]. This compound was first developed by DOW chemical company in 1965 and is applied in over 100 countries across the world. Chlorpyrifos has become the largest organophosphate insecticide worldwide in both volume and value. Sales volume of CPF in 2007 was reported to rank first in USA amongst all organophosphate insecticides [8,9]. The extensive usage of organophosphates pesticide particularly chlorpyrifos for pest control and the potential toxicity in human body have raised serious public concerns in regard of human health, environment and food safety [3,10]. Even at very low concentrations of few parts per trillion, CPF can kill fish, birds, etc. Hyperglycemia is observed on exposure to CPF [7].

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Due to its long half life (60–120 d) and high residual concentrations (0.01–0.62 mg kg^{-1}), it has contaminated aquatic and terrestrial ecosystems and posed risk to public health [3,11]. The insecticide inhibits acetyl cholinesterase in an irreversible manner and causes insect death [7,12]. Compound resists biodegradation and have potential toxicity towards humans and animals [13]. It interferes with the normal functioning of the central nervous system, including the brain. Chlorpyrifos enter in to the human body via inhalation, ingestion and through skin contact and inhibits acetylcholine esterase enzyme in the central nervous system [14]. Harmful effects of chlorpyrifos include twitching of muscles, skin irritation, depression, respiratory failures, convulsion, and death [7].

Inappropriate use, storage, spillage, handling and disposal are responsible factors for water [15], land [16], soil and environmental [17] contamination. Degradation of CPF in water is of high significance due to its high toxicity to aquatic life and persistent metabolites with complex nature [18,19]. Conventional treatment methods such as Photochemical methods [15,20,21]; Ozone Treatment [22]; Bioremediation [23]; Electrolysis [24], etc are relatively expensive, ineffective or involve only the transfer of contaminants from one media to another, creating secondary pollution [25,26]. Thus, advanced pesticide removal methods are usually needed to meet environmental quality requirements and improve the ecological system [27].

One of the most promising new approaches, controlled hydrodynamic cavitation (HC) is defined as the phenomena of the formation, growth and subsequent collapse of micro-bubbles or cavities occurring in extremely small timeframes (milliseconds) while releasing large magnitudes of energy [28,29]. Cavitation-based AOPs have been widely developed as a promising and efficient method for the removal of azo dyes [30], microbial disinfection of seawater [31], pharmaceuticals [32], biorefractory compounds [29], pesticide effluent treatment [33] and degradation [33], etc. and are classified as acoustic cavitation (AC), hydrodynamic cavitation (HC), optic cavitation and steam bubble cavitation [30,32]. Although cavitation can be induced by many ways, hydrodynamic cavitation has been reported to be the most cost effective, scalable [34] and efficient way of inducing the cavitation [33]. The mechanism of water treatment due to cavitation has been mainly attributed to the mechanical (e.g., generation of turbulence, liquid circulation currents and shear stresses), chemical (generation of active free radicals) and heat effects (generation of local hot spots i.e., condition of very high temperature and pressure locally) [28]. When local pressure falls below the vapor pressure of the fluid, cavities are created [35]. The radicals produced from hydrodynamic cavitation such as ·H and ·OH can react with pollutants in water to promote degradation of pollutants [36]. OH· radicals generation is documented by different researchers as given below. Studies done by [37] states that with collapse of bubble, water along with hydrogen peroxide dissociates and gives the reaction:

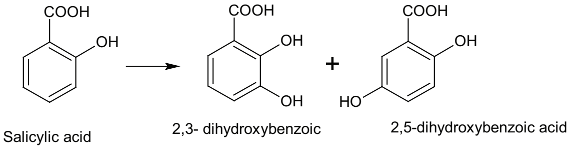
$$H_2O \rightarrow HO\cdot + H\cdot \quad (1)$$

$$H_2O_2 \rightarrow HO\cdot + HO\cdot \quad (2)$$

$$H_2O_2 + HO\cdot \rightarrow H_2O + HO_2 \quad (3)$$

Similarly, [38] studied the optimization of HC in generation of OH· radicals [Eq. (4)] and used salicylic acid to trap the hydroxyl radical, forming 2,3-dihydroxybenzoic acid and 2,5-dihydroxybenzoic acid [Eq. (4)] to quantify amount of OH· radical generation in HC. Reactions involved in this process is as below:

$$H_2O \rightarrow HO\cdot{+}H\cdot \quad (4)$$



(5)

Present paper focuses on degradation of organophosphate pesticide chlorpyrifos as model pollutant and COD simultaneously in aqueous solution by hydrodynamic cavitation method, illustrating its efficiency, various factors affecting efficiency. This study is first attempt to simultaneous removal of both chlorpyrifos and COD in aqueous solution, as no literature is cited till date regarding application of HC regarding this and its practical applicability in the field.

2. Materials

An artificial aqueous solution was prepared of desired chlorpyrifos concentration of 0.3 ± 0.01 mg/l and COD 7000 ± 200 mg/L in laboratory. The combination and concentrations of CPF used in this study were adapted from actual field conditions based on industrial batch composition. This combination is specifically prepared to study and evaluate simultaneous removal of both from aqueous solution, study the feasibility of HC process in treating chlorpyrifos compound and its orientation in industrial application (first of its kind as no literature is cited which shows simultaneous removal of both COD and chlorpyrifos by HC till date). The chemicals used were analytical grade namely potassium hydroxide pellets, sulphuric acid, NaOH (to maintain pH of aqueous solution), methanol. Aqueous solution was specifically prepared of desired concentrations to meet practical problems arising such as; sufficient quantity of 8 litres for each specific run, which will take care of sufficient quantity of effluent that should be available for continuous recirculation in reactor and analysis.

3. Experimental setup

Reactor was connected to centrifugal pump (2900 rpm, 1.1 kW), holding/collection tank (having cooling arrangement) with 20 L capacity in a loop system with high density poly ethylene (HDPE) pipes network as shown in Fig. 1. Bottom of holding/collection tank was connected to suction side of pump having valve (V_1). Delivery side of pump is diverged into two lines namely main line and by-pass lines.

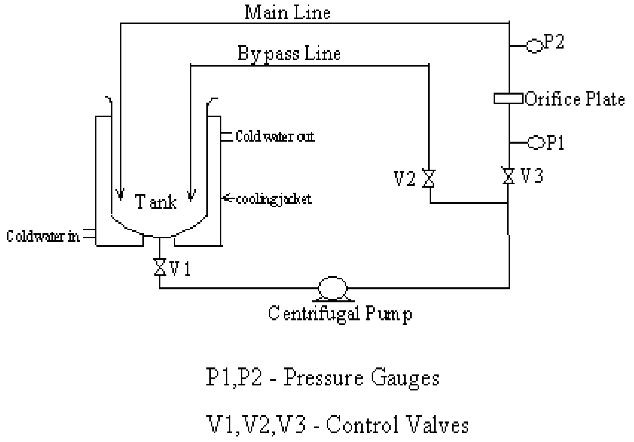


Fig. 1. Hydrodynamic cavitation reactor setup.

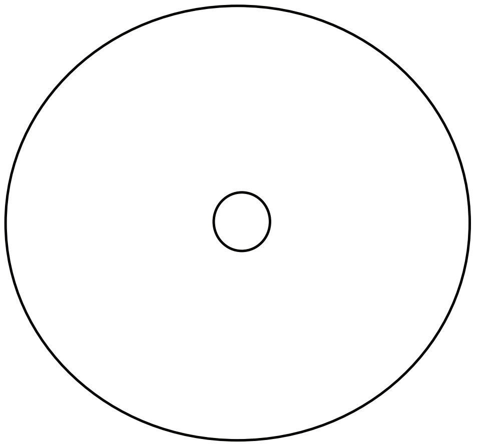


Fig. 2. Orifice plate with 2mm Ø single hole.

Main line consists of adjustable pressure valve (V_3), cavitating device as orifice plate, inlet pressure gauge (P_1) and fully recovered downstream pressure gauge (P_2). Cavitating device used here is orifice plate placed between flanges and joined with nut and bolt fastening arrangement along with rubber packing for prevention against any leakage. Orifice plate dimensions are as shown in Fig. 2. Aqueous solution was feed into collection tank and pump is started with all valves open. Inlet pressure is maintained at any desired value by operating/ closing by-pass valve (V_2) in by-pass line and is shown by pressure gauge P_1 in main line. Discharge from main line is measured and used to calculate the dimensionless cavitation number. Both main line and by-pass line is allowed to terminate well below liquid level in collection tank to prevent entry of any gas due to plunging liquid jets. Temperature in holding/collection tank is maintained in range of 36 ± 1°C by circulating cold water around the circumference of tank. Samples are withdrawn at given specific time and analyzed.

4. Analysis

HPLC analysis was done to find the chlorpyrifos content in aqueous solution after the treatment at any specific time. HPLC instrument used consists of HPLC pump [Serial dual plunger, micro volume (10 µL on primary side, 5 µL on secondary)] with UV detector having wavelength range between 190–600 nm and lichrospher (5 µm) analytical column. Acetonitrile and water were used as mobile phase (85:15) with a flow rate of 1 mL/min and the detection was effected at a wavelength of 230 nm. All experimental samples were analyzed with the same HPLC parameters. Along with this, chemical oxygen demand (COD) concentration was analyzed with standard operating procedure. All the experiments were conducted for three replicates to ensure any error and change in results.

5. Flow characteristics of orifice plate and cavitation number

Table 1 shows flow characteristics of orifice plate as cavitating device.

The primary parameter for determining the presence and intensity of cavitation is the cavitation number. It is derived from pressure–velocity relationship of flowing liquid explained from Bernoulli's theorem [39–41]. It is defined as ratio of pressure head and velocity head [42] given as:

$$C_N = \frac{Pressure\ Head}{Velocity\ Head} \tag{6}$$

$$C_N = \frac{P_2 - P_V}{0.5\rho V_0^2} \tag{7}$$

where C_N =cavitation number; P_2 = downstream pressure; P_V = vapor pressure of liquid; V_0 = velocity at constriction.

Cavitation number is a non-dimensional number, which is defined as the difference between the system and vapour pressure (at the system temperature) divided by the dynamic pressure. Decreasing the cavitation number results in a higher probability of cavitation occurrence or in an increase in the magnitude of the already present cavitation [32]. But, as per [43] describing cavitation conditions solely by the value of the cavitation number is inappropriate and misleading. Observations obtained states that every flow, either cavitating or not, can be attributed by a cavitation number and its value depends on the geometry, fluid, fluid temperature and the velocity of the flow.

6. Sample calculation for number of passes for 30 min at 5 bar and cavitation yield

*6.1. Number of passes = (volumetric flow rate/total volume) * time of operation.*

$$= \frac{3.57 lpm}{8l} * 30 \qquad = 13.4 \sim 14\ nos$$

6.2. Cavitation yield $= \dfrac{\text{extent of degradation of the pollutant}(\text{mg})}{\text{total energy supplied}(\text{J})}$

$$= \frac{7360 - 4200}{1260000}$$

$$= 0.00025\ mg / J$$

Table 1
Flow characteristics of orifice plate as cavitating device

Plate dimensions: 2 mm Ø single hole					
Inlet pressure (bar)	Mainline flow rate (L/s)	Mainline flow (volumetric flow) (lpm)	Orifice velocity, V_0 (m/s)	Cavitational number, C_v (@ 37°C)	Cavitational number, C_v (@ 35°C)
2	0.0398	2.388	12.61	1.19	1.20
3	0.0483	2.898	15.41	0.8	0.8
4	0.0540	3.24	17.21	0.64	0.65
5	0.0596	3.576	19.0	0.52	0.53
6	0.0636	3.816	20.28	0.46	0.46
7	0.0686	4.116	21.84	0.39	0.40
8	0.0737	4.422	23.47	0.34	0.35

7. Results and discussion

7.1. Effect of inlet pressure

In the case of hydrodynamic cavitation, inlet pressure is an indication of the quantum of energy supplied for the cavitation events [44]. As stated by [45], increase in upstream/inlet pressure increases the downstream pressure and the pressure recovery rate. This is to be kept at optimum level as collapse of the cavity depends on the rate of pressure recovery in the expansion section. To study the effect on percent degradation of Chlorpyrifos and removal of COD, Inlet Pressure was varied from 2 to 7 bar. Fig. 3 and Fig. 4 illustrate the effect of upstream pressure on percent degradation of Chlorpyrifos and simultaneous removal of COD with respect to one hour treatment time from aqueous solution. Kinetics rates constants are described in Table 2. The results obtained shows that maximum degradation (100%) of Chlorpyrifos takes place at inlet pressure of 5 bar. Similarly, percent COD reduction increases with increase in inlet pressure and reaches to maximum of 46.7% at 5 bar inlet pressure, decreasing further to 29.34% with increase in inlet pressure to 6 bars. As seen in Table 2, maximum degradation of 46.7% and 100% of COD and chlorpyrifos pesticide respectively, with maximum kinetic rates of 0.010 min^{-1} and 0.133 min^{-1} respectively is obtained at 5 bar inlet pressure. From this it can be said optimum inlet pressure of 5 bar exists in this study. At this optimum inlet pressure, generations of OH· radicals are at maximum and result into maximum efficiency of the reactor. Excess inlet pressure after optimum pressure, lead to super cavitation resulting in vapor locking and no cavitational collapse; thus reducing the efficiency [44]. Hence, 5 bar optimum pressure was taken to study the different parameters in further study.

7.2. Effect of number of passes

The extent of degradation increases with increasing number of passes. However, it is essential to optimize the number of passes for economical operation as higher number of passes directly reflects higher cost of treatment. Thus, this factor is crucial in determining the cost of operation, less number of passes- lower the cost. This, again depends on the nature of effluent, especially that for real industrial

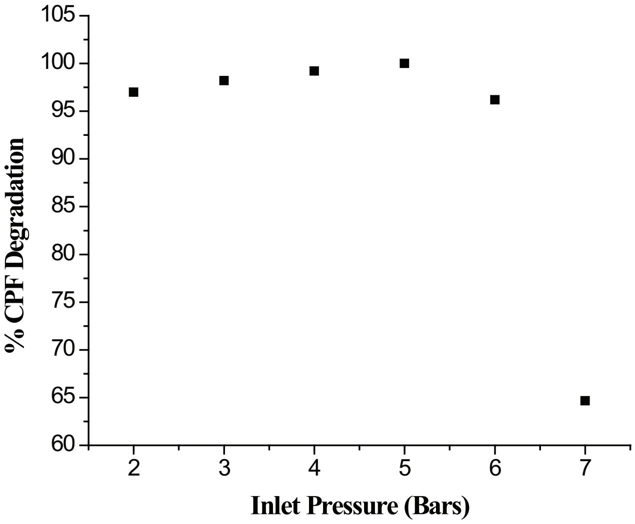


Fig. 3. Effect of inlet pressure in degradation of chlorpyrifos.

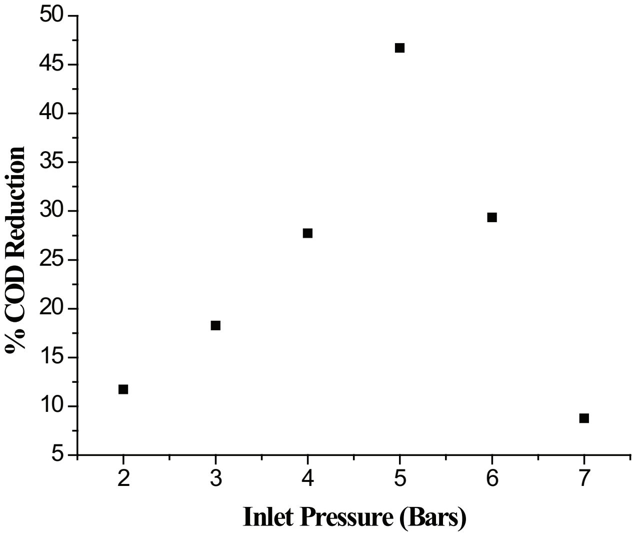


Fig. 4. Effect of inlet pressure in COD removal.

Table 2
Effect of inlet pressure on extent of degradation of COD and chlorpyrifos and first order rate constant

Sr. No	Inlet Pressure (bars)	Extent of degradation (%)		Rate constant k (min^{-1})	
		COD	Chlorpyrifos	COD	Chlorpyrifos
01	2	11.62	97	0.0020	0.058
02	3	17.82	98.4	0.0033	0.068
03	4	27.71	99.3	0.0054	0.015
04	5	46.72	100	0.010	0.133
05	6	29.34	94.33	0.0057	0.056
06	7	8.97	64.67	0.0015	0.017

effluent for which characteristics such as COD, presence of metals, TDS/TSS are varying in most cases. To study the effect of number of passes, aqueous solution was treated till 3 h duration with continuous passes. Fig. 5 shows that as number of pass increased, COD removal efficiency also increased till around 53 numbers of passes. But, above that, as number of passes increases, there is no significant increase in COD removal efficiency. Thus, in present case, 53 numbers of passes is most appropriate, which gave COD removal efficiency of 56.52%, after which COD removal efficiency is very negligible. If further passes are continued, it will only consume electricity without giving good cavitational yield. Cavitational yield is defined as the observed extent of degradation of the pollutant per unit energy supplied to the system. In this study, the cavitational yield for COD is reduced from 1.388 × 10^{-4} mg/J at 53 numbers of passes to 0.5 × 10^{-4} mg/J thereafter. Considering degradation of Chlorpyrifos, it was found that at around 26 number of passes, 100% degradation took place, hence 26 number of passes are sufficient or optimum in degrading CPF.

7.3. Effect of pH

Initial pH is an important parameter solution pH is an important factor in determining the physical and chemical properties of the solution and influencing the treatment efficiency. In order to study the effect of pH on COD reduction efficiency, experiments were conducted at basic/alkaline (pH 10) and acidic (pH 4) conditions. Experiments were performed at optimum inlet pressure of 5 bar and at maximum 52 number of passes and contact period of 2 h. The obtained results are as shown in Fig. 6. Results shows that trend lines illustrating rate of efficiency for COD removal is always more for acidic pH than basic pH. It may be due to the fact that oxidation capacity of hydroxyl radicals is higher under acidic conditions when used with cavitational reactors either operated alone or in combination [45–48]. Acidic pH gave maximum COD removal efficiency of 55.1% as compared to 32.4% for basic pH range with hydrodynamic cavitation treatment. For chlorpyrifos degradation, it is found that variation of pH has no significant effect on the extent of degradation and results found to be less than the extent of error associated with each experiment. In present case, the singular reason pH did not affect the degradation of chlorpyrifos is, the rate of hydrolysis is constant in acidic to neutral waters, but increases in alkaline waters [49].

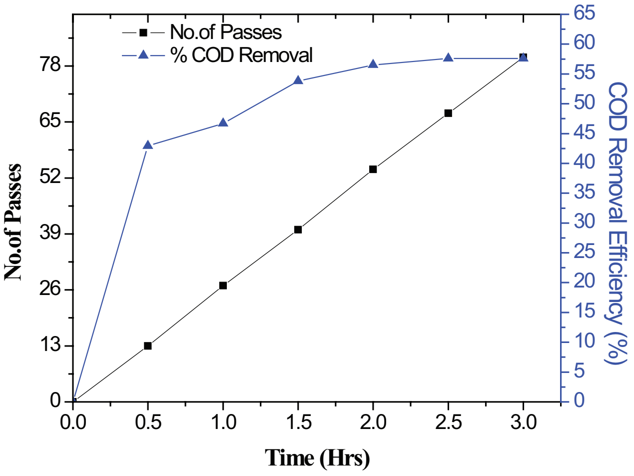


Fig. 5. Effect of number of passes in COD removal.

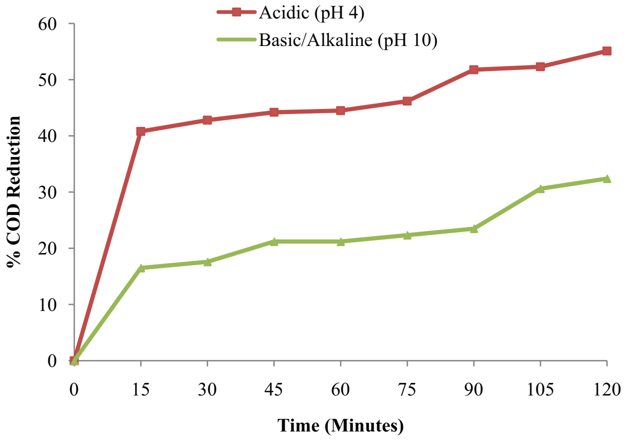


Fig. 6. Effect of pH on %COD reduction.

Table 3
Effect of pH on extent of degradation of COD and chlorpyrifos and first order rate constants

Sr. No	pH	Extent of degradation (%)		Rate constant k (min^{-1})	
		COD	Chlorpyrifos	COD	Chlorpyrifos
01	4 (Acidic)	55.1	100	0.0066	0.066
02	10 (Basic)	32.4	100	0.0032	0.066

7.4. Effect of contact/reaction time

Reaction/contact time can be defined as stipulated time necessary for any contaminant to degrade or reduce in its concentration. To study the effect of contact time, experiments were performed at different time intervals with optimum pressure of 5 bar, 53 number of passes as maximum and acidic medium (pH 4). Fig. 7. illustrates effect of contact

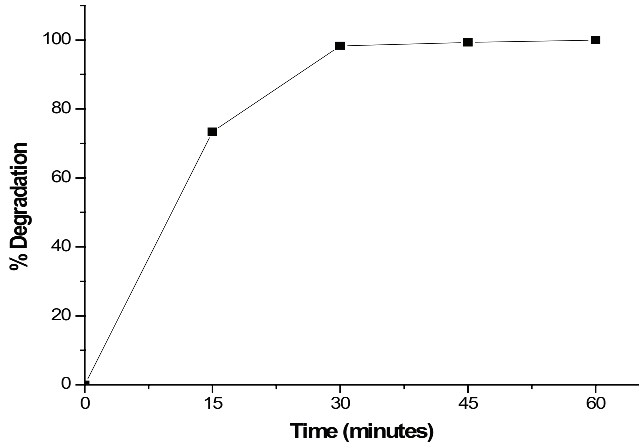


Fig. 7. Effect of contact/ reaction time on degradation of chlorpyrifos.

time for degradation of chlorpyrifos in aqueous solution. It can be seen from a result that at 15 min contact time degradation of 73.4% is obtained. With increase in contact time to 60 min, it increases to 100% degradation of chlorpyrifos. Also for COD removal, contact time plays an important role. It can be seen from results as depicted in Fig. 9 which shows that removal of COD increases with increase in contact time of 30 min from 42.93% to 56.52% at 2 h. This can be attributed to continuous generation of OH· radicals and minimum time required for degradation of pollutant. Similar studies by [36] for an herbicide named alachlor [2-Chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide] which belong to chloroacetanilide family found that its concentration in water decreased exponentially with-reaction time. In the degradation of auramine O [4-(dimethylamino) phenyl methaniminium chloride] an dye used as fluorescent strain by vortex diode; it was found that the concentration of auramine O in water decreased exponen-

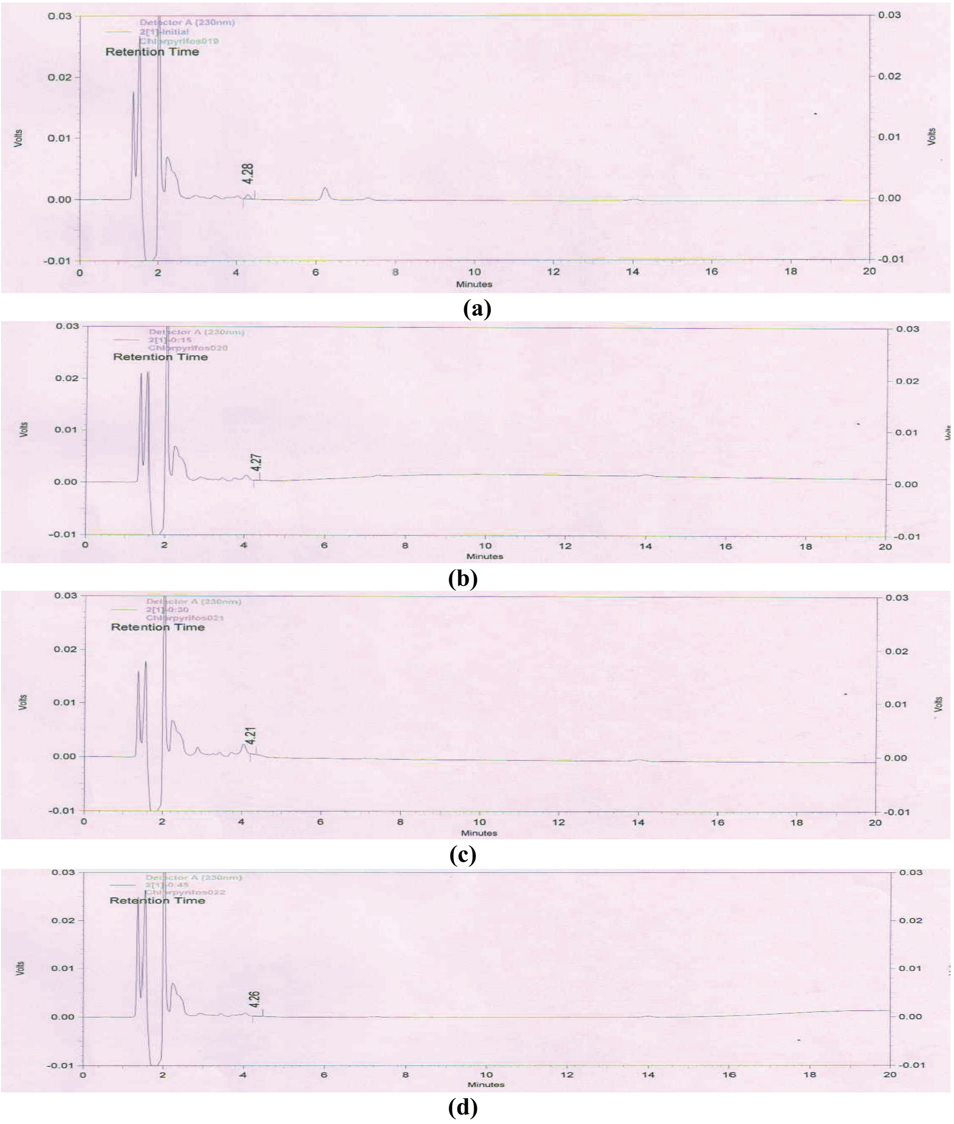


Fig. 8. Peaks of Chlorpyrifos degraded by HC process at (a) initial time (b) 15 min (c) 30 min (d) 45 min of contact time/reaction time.

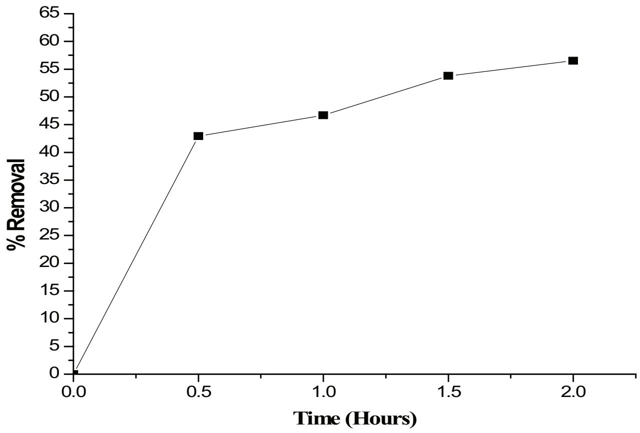


Fig. 9. Effect of contact/reaction time on % COD removal.

tially with reaction time [50]. Reaction time requirement for hydrodynamic cavitation is marginally more as compared to the conventional approach for intensification of synthesis of methyl esters from sustainable feedstock [51].

8. Cost estimation and recommendations for up-scaling of HC

For any system to be successfully implemented in large scale or industrial applications it has to be technically feasible and economical. Considering this study and earlier published literature, HC reactor is found to be technically feasible to treat various recalcitrant compounds. In HC process, operational cost in terms of energy efficiency is lower [52], along with advantage of more flexibility and higher potential for scale-up [30,53]. Considering the economic aspects; HC should be able to effectively convert the electrical energy supplied into the system to other form, i.e formation of cavities and its collapse [54]. There is significant energy loss in fluid pumping process depending on flow rate and pressure level [54]. With energy requirement for pumping and recirculation, the operating cost of the HC can be reduced if the wastewater effluent is available at considerable hydrostatic heads or pressures. In that case treatment cost of HC can be reduced by designing the pressure reduction devices in such a way that they will work in a hydrodynamic cavitation mode, without supply of any additional energy [33]. With serious limitation of low degradation or mineralization rates when applied individually for the treatment of complex wastewater [33,55] or up-scaling, its cost efficiency can be remarkably improved by using different intensifying additives which can enhance $OH^{\cdot}$ radical generation in same energy supplied and improving the cavitational yield. Generally, in case of HC cost estimation is done on basis of energy consumption by system (in terms of cavitational yield) [33,45,56–58]. In present study, using HC and treatment time of 1 h, extent of degradation of 0.3 mg/l chlorpyrifos is 100% and thus the cavitational yield has been obtained to be equal to 9.8×10^{-8} mg/J. Similarly, extent of degradation of 7000 ± 200 mg/l COD is minimum 40% in 2 h treatment time, its cavitational yield is 4.71×10^{-4} mg/J.

9. Conclusions

Present work states that utilizing HC for simultaneous removal of both organic matter in terms of COD and recalcitrant compound chlorpyrifos is a sustainable, environmental protection and solution to mitigate health and disposal issues with no by-product generation, higher removal efficiencies and ease of operation. It was found that HC alone gave more than 40% COD removal efficiencies with each case of optimum inlet pressure 5 bar, contact time 2 h, 53 number of passes and acidic pH range. It was seen that Chlorpyrifos needed just 1 h of treatment for optimum pressure of 5 bar; at around 26 number of passes, 100% degradation took place, hence 26 number of passes are sufficient or optimum in degrading CPF. It is also found that variation of pH has no significant effects on the extent of degradation and results are found to be less than the extent of error associated with each experiment. This can be very helpful in field applications during shock loadings of extreme pH difference. At 15 min contact time, Chlorpyrifos degradation percent of 73.4% is obtained and with increase in contact time to 60 min, it increases to 100% degradation. Thus, to remove maximum concentration of pollutant, sufficient contact time/ reaction time is essential. The present study proved that the developed HC pilot plant is one of its kind a success and can be effectively scaled up for large scale operation.

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