

Review

# **Application of Hydrodynamic Cavitation Reactors for Treatment of Wastewater Containing Organic Pollutants: Intensification Using Hybrid Approaches**

# Pooja Thanekar<sup>D</sup> and Parag Gogate \*

Chemical Engineering Department, Institute of Chemical Technology, Matunga, Mumbai 40019, India; poojathanekar7@gmail.com

\* Correspondence: pr.gogate@ictmumbai.edu.in; Tel.: +91-22-3361-2024

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**Abstract:** The concentration of hazardous pollutants in the wastewater streams has to keep below a certain level in order to comply with the stringent environmental laws. The conventional technologies for wastewater treatment have drawbacks in terms of limited applicability and efficiency. Utilization of hydrodynamic cavitation (HC) reactors for the degradation of pollutants at large scale has shown considerable promise over last few years, due to higher energy efficiencies and low cost operation based on lower consumption of chemicals for the treatment. The present work overviews the degradation of different pollutants, such as pharmaceuticals, pesticide, phenolic derivatives and dyes, as well as the treatment of real industrial effluents using hybrid methods based on HC viz. HC/H<sub>2</sub>O<sub>2</sub>, HC/Ozone, HC/Fenton, HC/Ultraviolet irradiations (UV), and HC coupled with biological oxidation. Furthermore, based on the literature reports, recommendations for the selection of optimum operating parameters, such as inlet pressure, solution temperature, initial pH and initial pollutant concentration have been discussed in order to maximize the process intensification benefits. Moreover, hybrid methods based on HC has been demonstrated to show good synergism as compared to individual treatment approach. Overall, high energy efficient wastewater treatment can be achieved using a combined treatment approach based on HC under optimized conditions.

Keywords: wastewater; hazardous pollutants; hydrodynamic cavitation; hybrid treatment; synergism

# 1. Introduction

Over the last few years, the contamination of water has created significant environmental concerns, due to organic, as well as inorganic, substances. One of the major reasons for the concern, besides the presence of toxic contaminants, is the quantity of effluents generated, based on the fact that a huge amount of water is being utilized by many industrial, agricultural and household activities. The concerns are compounded as many emerging contaminants, such as pharmaceuticals or pesticides, have been detected in aquatic systems, due to the limitations of conventional technologies [1]. Pharmaceuticals being used for many purposes by humans and in animal husbandry are excreted in feces and/or urine as either parent compounds or as metabolites. Therefore, they can easily enter into the aquatic system via conventionally treated or even untreated wastewater discharge [2]. In the case of pesticides, the occurrence of pesticide molecules and/or their intermediates in the industrial effluent, as well as processed water from the field, is common as a huge amount is used for agricultural activities, and not all will be utilized in the intended activity [3]. The conventional techniques of wastewater treatment are not able to achieve complete conversion of the emerging contaminants to carbon dioxide and water [4]. Thus, advancement in wastewater treatment technologies and methods are targeted to meet the high standards of environmental regulations. Advanced oxidation processes



(AOPs) are one of the approaches that have been used successfully for the removal of toxic pollutants, due to the highly efficient operation and simple reactor design [5]. AOP involves the generation of highly reactive hydroxyl radicals (•OH) aimed at the degradation of pollutants. The current work concentrates on different aspects of hydrodynamic cavitation, which is one of the AOPs that can be applied for wastewater treatment applications.

Cavitational reactors, in general, have been looked as new form of multiphase reactors which are capable of generating conditions suitable for oxidation, including local hot spots and highly reactive free radicals in the system [6]. The cavitational reactors have significant potential to convert toxic/complex organic compounds like chlorinated hydrocarbons, phenolic and aromatic compounds, textile dyes, pharmaceuticals, pesticides and esters into short-chain organic acids, carbon dioxide, water and inorganic ions as final products [7]. Based on the mode of generation, cavitation is classified into four types, viz. acoustic, hydrodynamic, optic, and particle. However, only acoustic and hydrodynamic cavitation are considered efficient in different chemical processing applications [8]. In the case of acoustic cavitation, cavities are generated using ultrasound waves of frequency over the range of 16 kHz–2 MHz. Due to some limitations of acoustic cavitation, such as lower energy efficiency, lack of scale-up potential and high-cost of operation, hydrodynamic cavitation reactors are being looked as an efficient alternative to acoustic cavitation [8]. In the case of HC (hydrodynamic cavitation) reactors, cavities are generated, due to the pressure variations included in the liquid due to passage through the constriction, such as an orifice or venture [6]. Subsequently, the violent collapse of cavities results in the generation of OH radicals, as well as intense turbulence that help in intensifying the suitable physical and chemical changes [9]. For the case of wastewater treatment, many researchers [5,8] have observed that the degree of mineralization achieved using hydrodynamic cavitation alone is insufficient, due to the limited rate of generation of oxidizing radicals and the combination with other advanced oxidation processes helps in the intensification of oxidation capacity.

The efficacy of combined process for the removal of pollutants is typically higher than the individual treatment as HC generates high turbulence leading to the elimination of mass transfer limitations of the individual process especially involving chemical induced degradation of pollutant. The use of oxidizing agents, such as H<sub>2</sub>O<sub>2</sub>or ozone, and catalysts coupled with HC also results in the significant enhancement in the degradation efficiency making HC as a more effective technology for the removal of pollutants [10,11]. Many literature reports can be found confirming the effective use of combined treatment methods coupled with HC for the degradation of model pollutants, such as pesticides [12,13], pharmaceuticals [10,14], dyes [11,15], phenolic compounds [16,17], as well as real industrial effluents [18–20]. Sometimes the intermediates obtained during treatments based on HC may be more effectively treated using biological oxidation which helps in reducing the energy requirement along with the total treatment costs. Combination of HC with biological oxidation is also considered as an efficient hybrid process [21]. The current work reviews the effectiveness of the different hybrid treatment methods based on hydrodynamic cavitation for the removal of complex organic pollutants present in wastewater streams. Useful information on basics of cavitation reactor configuration, mechanisms of hybrid methods and optimum operating conditions has been provided.

### 2. Basic Aspects of Cavitation

Cavitation is the phenomenon of formation, growth, and subsequent collapse of the cavities occurring in an extremely small interval of time (microseconds) and releasing large magnitudes of energy over a very small area which generates conditions of local hotpots (temperature = 1000–15,000K; pressures = 500–5000 bar). Cavitation results in the generation of highly reactive free radicals and intense turbulence along with liquid circulation currents [22,23]. These effects are extremely suitable for the degradation of complex compounds, both organic and inorganic, including the pesticides and the emerging contaminants, such as pharmaceutical drugs [24]. In acoustic cavitation, cavities are generated using ultrasound waves with frequency ranging from16 kHz to 2 MHz which are responsible for pressure variations in the liquids [6]. The oscillating pressure field created by alternate

compression and rarefaction cycles of ultrasound waves are responsible for inducing the different stages of cavitation, such as generation of cavities, subsequent growth to a maximum size and finally violent collapse. The cavitational effects are classified into the chemical effects, such as generation of free radicals and local hot spots, and physical effects, such as intense turbulence coupled with liquid circulation that helps in reducing mass transfer resistance [25].

In the case of hydrodynamic cavitation (HC), cavities are generated, due to pressure variation in the liquids induced through geometric constrictions, such as orifice plate, venturi or throttling valve incorporated in a liquid flow. The governing principle of HC reactors is based on Bernoulli principle i.e., the alterations in the kinetic energy and local pressure. The incorporation of geometric constrictions results in an increase in the kinetic energy associated with the liquid at the expense of pressure. If the local pressure around vena contracta falls below the vapor pressure of the medium i.e., threshold pressure for cavitation, cavities are generated. Subsequently, downstream of constrictions, due to an increase in the flow area, the pressure recovers, eventually resulting in the final violent collapse, except in the case of chocked cavitation, also named supercavitation. Furthermore, a significant loss of energy in the form of permanent pressure drop at the downstream of constriction is responsible for the generation of very high intensity fluid turbulence. The intensity of the turbulence depends on the magnitude of the pressure drop, which, in turn, depends on the geometry of the constriction and the flow conditions of the liquid [26].

The intensity of cavitation obtained in the reactor is expressed in terms of the cavitation number, which is a dimensionless number [27] expressed using the following equation:

$$C_{\rm v} = \frac{p_2 - p_{\rm v}}{(1/2)\rho v_{\rm th}^2},\tag{1}$$

where,  $p_2$  = recovered pressure at downstream of the constriction,  $p_v$  = vapor pressure of the liquid,  $v_{th}$  = velocity at the throat of the constriction and  $\rho$ = density of the liquid.

The cavitation inception number,  $C_{vi}$  is the cavitation number at which the inception of cavitation occurs [28]. The cavities are typically generated at a condition of  $C_v \leq 1$  under ideal conditions, however, in many cases cavities are also generated at  $C_v>1$  due to the presence of some dissolved gases and suspended particles which provide additional nuclei for the formation of cavities. Furthermore,  $C_{vi}$  is a function of the flow geometry, increasing with the size of the constriction [5]. As per the definition of  $C_v$ , with an increase in inlet pressure that increases the flow through the main line, as well as the velocity at the throat of the constriction, a reduction in the cavitation number is obtained. Hence, a higher number of cavities are generated when the cavitation number is low, giving high intensity of cavitation. Moreover, cavitational intensity can be increased by controlling downstream pressure in the region where cavities collapse [29].

Cavitation is the typical phenomenon of rapid transformation of fluid from a liquid state to a gaseous state, forming the cavitation bubbles, their subsequent growth, and finally violent implosion. The different stages of cavitation in the different regions of hydrodynamic cavitation reactor along with the pressure profile diagram are shown in Figure 1. Bubble dynamics depicts the variation in the radius of bubble/cavity with time and helps in predicting the cavitational intensity generated. Bubble growth and trajectory is significantly affected by the operating and geometric conditions due to pressure fluctuation in the surrounding medium. Modelling of hydrodynamic cavitation process helps to understand the overall cavitation process and to investigate the effect of operating parameters and geometric conditions on the cavitational intensity. The basic bubble dynamics equation known as Rayleigh Plesset equation is given as follows:

$$R\frac{d^2R}{dt^2} + \frac{3}{2}\left(\frac{dR}{dt}\right)^2 = \frac{1}{\rho}\left[P_i - \frac{2\sigma}{R} - \frac{4\mu}{R} - \frac{dR}{dT} - P_{\infty}\right],\tag{2}$$

where,  $d^2R/dt^2$  = acceleration of the bubble/cavity, dR/dt = bubble wall velocity,  $\sigma$  = surface tension of liquid,  $\mu$  = viscosity of the medium,  $P_i$  and  $P_{\infty}$  = pressure inside the bubble and the actual pressure downstream of the constriction respectively. The solution of this equation gives an idea about radius history for a cavity (either individual or cluster of cavities), as well as collapse pressure generated after the collapse. However,  $P_{\infty}$  is the pressure that decides the bubble behavior which will change due to the flow conditions. The pressure recovery at downstream of constrictions is assumed to be linear and it can be estimated on the basis of linear pressure recovery as per the following equation:

$$P_{\text{mean}} = P_{\text{v}} + \frac{P_2 - P_{\text{v}}}{\tau},\tag{3}$$

where,  $\tau$  = pressure recovery time and  $P_{mean}$  = axial pressure downstream of the orifice to be substituted for  $P_{\infty}$  in Equation (2) when  $\tau$  =1 and also  $P_{\infty}$ , the pressure at a large distance from the inception of cavity bubble, decides the bubble behavior. Equation (3) typically explains the stable cavitation, but cannot explain the sonochemistry based effects of hydrodynamic cavitation. Due to this, an alternate equation of local fluctuating pressure  $P_t$ , is used as given below for estimating the fluctuating pressure field to be used in the Rayleigh Plesset equation [28]:

$$P_{t} = P_{v} + \frac{1}{2}\rho \left(v_{0}^{2} - v_{tn}^{2}\right) - \Delta P, \qquad (4)$$

where,  $v_{tn}$  = actual local instantaneous velocity downstream of the orifice (m/s) and  $\Delta P$  = pressure drop downstream of the orifice.



**Figure 1.** Different stages of cavitational events with a pressure profile in the hydrodynamic cavitation (HC) reactor.

## 3. Hydrodynamic Cavitation Reactors

Setups of processing systems using HC reactors usually include a recirculation type configuration consisting of a positive displacement pump, holding tank, control valves, and gauges [30], as shown in Figure 2. The suction side of the pump is connected to the bottom of the holding tank. The discharge from the pump is divided into two lines as the main line and a bypass line. The main line is equipped with the cavitation chamber, such as slit venturi, orifice valve etc. and the bypass line is equipped with the valve in order to control flow through main line. Furthermore, pressure gauges are provided in the configuration. The induction of air into the liquid is avoided by terminating both the lines below the liquid level inside the holding tank. Generally, orifices and venturi are widely used as cavitating devices in the HC reactor. Orifice plates can be with single or multiple holes. The multiple holes can be indifferent combinations of the diameter of holes and numbers, as shown in Figure 3. This variation allows obtaining different cavitational intensities using multiple holes orifice plate

as the intensity is proportional to the ratio of the perimeter of holes to its cross-sectional area [31]. Thus the orifice plate based HC reactor offers the flexibility of controlling the intensity suited for specific application in addition to the control of the inlet pressure, inlet flow rate, temperature, and, in the case of pressurized systems, the inlet, as well as downstream pressure [24]. In the case of venturi, a comparatively higher velocity at the throat is generated as compared to an orifice for a given pressure drop across the device due to its smooth converging and diverging sections (Figure 4) [26,31]. The venturi configuration can be used for milder processes (typically pressure requirement between 15 and 20 bar) and physical transformations, while, an orifice flow configuration is generally used for the intense chemical reactions [32]. However, in the field of disinfection from harmful microorganisms, it was reported that Venturi-type reactors outperform orifice plates [33].



Figure 2. Schematic representation of HC reactor.



Figure 3. Different combinations of multiple orifice plates.



Figure 4. Schematic representation of venturi.

The inlet pressure, pH of solution and temperature are major operating parameters determining the cavitational conditions and hence influencing the efficiency of the treatment. An increase in the extent of degradation of a recalcitrant pollutant can be obtained with an increase in the inlet pressure but up to a certain value of pressure, beyond which a decrease in the extent of degradation is observed, or the degradation can remain constant. Beyond the optimum inlet pressure, supercavitation occurs which reduces the cavitational intensity based on a cushioned collapse of cavity cloud thereby decreasing the extent of degradation of pollutant [34]. Therefore, it is recommended to use an optimum inlet pressure which depends on the type of HC reactor and the specific effluent to be treated. Insight to the provided discussion in terms of optimum pressure can be obtained from the literature. Kumar et al. [35] reported that the maximum decolorization of 32.32% with rate constant being  $3.41 \times 10^{-3}$  min<sup>-1</sup> was achieved for methylene blue dye at an optimum pressure of 5 bar in 120 min. Beyond the optimum pressure of 5 bar, chocked cavitation occurred, due to the generation of vaporous cavities that lowers the generation rate of OH radicals, which was reported to reduce the rate of decolorization for further increase of pressure. Saharan et al. [11] also confirmed the cavity cloud formation beyond the optimum value of pressure of 5 bar by performing photographic analysis for the degradation of reactive red 120 dye. The actual extent of decolorization was reported to be lower at higher pressures beyond 5 bar.

The pH of the solution plays a vital role in deciding the extent of degradation. Acidic pH of the solution favors the generation of OH radical also offering higher oxidation potential and the lower rate of recombination of OH radicals. Hence, a higher density of OH radicals is available under acidic conditions for the degradation process, which ultimately increases the extent of degradation. Additionally, the extent of degradation depends on the state of the pollutant molecule i.e., whether it is present in the molecular state or ionic state. Considering these two effects, an optimum pH may also be observed. The optimum pH value is typically dependent on the specific pollutant's dissociation constant (pKa) which decides whether the pollutant is present in the molecular state or ionic state. Gogate and Patil [36] investigated the effect of pH on the extent of degradation of triazophos by varying pH from 2.5 to 8. The maximum extent of degradation about 50% was reported at optimum pH 3. Cai et al. [37] also reported the existence of optimum pH of 2 for the decolorization of azo dye, Orange G using the approach ofHC combined with heterogeneous Fenton process. The maximum decolorization of 98.8% was achieved at pH of 2 whereas, only 12.3% of decolorization was achieved at neutral pH confirming a very strong dependence on pH.

The effect of temperature on the extent of degradation in HC reactor is typically specific for the pollutant. An increase in temperature in the initial stages results in an increased degradation rate due to the enhanced cavitational intensity based on the formation of a number of cavitation bubbles in the reactor and favorable kinetics. Significant increase in the temperature results in the generation of vaporous cavities which lowers the intensity of cavitation, meaning optimum temperature may be observed. There is also a need to compare the observed benefits in terms of degradation rates against

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the higher operating costs incurred due to additional heating [36]. Wang and Zhang [38] reported 40 °C as the optimum temperature for the degradation of alachlor in aqueous solution, using HC. The maximum degradation rate of  $4.90 \times 10^{-2} \text{ min}^{-1}$  was obtained at 40 °C. It was observed that with an increasing temperature from 30 °C to 40 °C resulted in an increased degradation rates from  $4.04 \times 10^{-2} \text{ min}^{-1}$  to  $4.90 \times 10^{-2} \text{ min}^{-1}$  whereas, a decrease in the degradation rates were observed beyond the temperature of 40 °C ( $3.23 \times 10^{-2} \text{ min}^{-1}$ ). In another work, the maximum extent of degradation of 12.4% was reported at an optimized temperature of 35 °C, the maximum extent of degradation of 12.4% with rate constant  $1.2 \times 10^{-3} \text{ min}^{-1}$  was obtained. The different illustrations for the effect of operating conditions of HC reactor revealed that the optimum value of each parameter is different for different pollutants and reactor configurations, thereby confirming the necessity of detailed investigation of each parameter for different pollutants. Establishing the optimum is very important in achieving an energy efficient operation of the HC reactor with maximum efficacy.

# 4. Review of Hybrid Methods Based on HC for Treatment of Wastewater

## 4.1. Combination of HC with $H_2O_2$

The main driving mechanism for the degradation of a pollutant based on HC is the formation and subsequent attack of hydroxyl radicals.  $H_2O_2$  acts as a supplementary source of hydroxyl radicals which can intensify the process of degradation using the HC treatment. It is important to note that  $H_2O_2$  can also act as scavenger especially at higher loadings which ultimately reduces the extent of degradation [40]. Under the cavitational effect, dissociation of  $H_2O_2$  into OH radicals occurs due to extreme conditions generated in the HC reactor, such as local hot spots with high temperature and high pressure. The following chain of reactions occur during the combined treatment of HC and  $H_2O_2$  [41].

$$\begin{split} H_2O_2 &\rightarrow OH + OH, \\ OH + H_2O_2 &\rightarrow HO_2 + H_2O, \\ OH + HO_2 &\rightarrow H_2O + O_2, \\ HO_2 + H_2O_2 &\rightarrow OH + H_2O + O_2, \end{split}$$

Pollutant + OH  $\rightarrow$  CO<sub>2</sub> + H<sub>2</sub>O + degradation intermediates.

It has been reported that the extent of degradation increases with an increase in  $H_2O_2$  loading up to an optimum value, beyond which it generally decreases due to scavenging effect, or remains constant [35]. Rajoriya et al. [30] studied the effect of  $H_2O_2$  addition on the extent of decolorization of reactive blue 13 using slit venturi as a cavitating device. It was reported that the rate of decolorization increased significantly with the addition of  $H_2O_2$  till an optimum molar ratio of dye: $H_2O_2$  as 1:10 (initial concentration of dye =30ppm) whereas with a further increase in the molar ratio, the extent of decolorization remained constant. But the maximum extent of decolorization of 91% with rate constant of 4.66  $\times$  10<sup>-2</sup> min<sup>-1</sup>was obtained at the molar ratio of dye:H<sub>2</sub>O<sub>2</sub> as 1:20 which was selected as optimum molar ratio for the decolorization of reactive blue 13. Sayyaadi [42] studied the application of the combined approach of HC and H<sub>2</sub>O<sub>2</sub> described as enhanced cavitation–oxidation process (ECOP) for the degradation of non-volatile organic compound VOC containing solution (2-Chlorophenol) using circular venturi. The effect of the cavitation number, quantity of  $H_2O_2$  injection, as well as injection duration on the degradation rate of 2-Chlorophenol was studied. It was reported that the rate of reaction increases with the injected amount of H2O2, as well as and also when the injection duration was shortened. The maximum efficiency of about 0.1317 mg kJ<sup>-1</sup> was obtained when H<sub>2</sub>O<sub>2</sub> loading of 1000 ppm was injected in one time (injection duration =1 s) at cavitation number of 0.36. Comparatively lower efficiency as 0.0736 mg kJ<sup>-1</sup> was obtained when the same quantity of H<sub>2</sub>O<sub>2</sub> (1000 ppm) was injected over a longer duration of injection of about 30 min

Raut–Jadhav et al. [43] reported the optimal molar ratio of methomyl to  $H_2O_2$  as 1:30 for the extent of degradation of methomyl, whereas, beyond the optimum ratio of 1:30, decreased rate of degradation was observed using circular venturi as a cavitating device where the initial concentration of dye was 25 ppm. The individual treatment of  $H_2O_2$  and HC resulted in 2.86% and 13.9% of decolorization respectively whereas, the combination of HC and H<sub>2</sub>O<sub>2</sub> resulted in 97.5% of decolorization at optimum loading, which confirmed the significant synergism arising from the hybrid application. The optimum ratio of atrazine:  $H_2O_2$  as 1:5 was reported for the study of treatment of wastewater containing atrazine [44]. Bagal and Gogate [45] investigated the effect of varying H<sub>2</sub>O<sub>2</sub> loading over the range of 0.05–0.3 g/L on the degradation of diclofenac sodium at the initial concentration of atrazine as 20 ppm using the combined process of HC/Ultraviolet irradiations  $(UV)/TiO_2/H_2O_2$  using slit venturi as a cavitating device. It was reported that at an optimum loading of  $H_2O_2$  as 0.2 g/L, about 95% as the extent of degradation and 76% of total organic carbon (TOC) removal was obtained. Based on the literature reports, it can be concluded that the optimum loading of H<sub>2</sub>O<sub>2</sub> is different for the specific pollutant, confirming the necessity of the investigations related to the optimum loading of  $H_2O_2$ . It is also important that the extent of intensification obtained due to the use of  $H_2O_2$  also depends on the specific pollutant.

## 4.2. Combination of HC with $O_3$

Ozonation offers an effective treatment approach due to the high oxidation potential of 2.08 V [46] for the degradation of pollutants like dyes [47] and pesticides [48]. The combination of HC and ozone can be effective as under the cavitational effect, the ozone gets easily dissociated into molecular  $O_2$  and nascent oxygen (O) which form hydroxyl radicals due to reaction with water [30]. The following chain of reactions occurs during the combined operation of HC and  $O_3$  [15,49]

$$H_2O \rightarrow H + OH,$$
  
 $O_3 \rightarrow O_2 + O,$   
 $O + H_2O \rightarrow 2OH,$ 

Pollutant + OH  $\rightarrow$  CO<sub>2</sub>+H<sub>2</sub>O+ degradation intermediates.

Gore et al. [49] investigated the degradation of reactive orange 4 dye using the combination of HC with ozone under conditions of varying ozone flow rate over the range of 1 to 8 g/h using circular venturi. It was reported that with an increase in the ozone feed rate from 1 to 3 g/h, the rate of mineralization also increased, but with a further increase in the flow beyond 3 g/h the rate of mineralization remained constant. About 76.25% of TOC reduction with rate constant of  $2.06 \times 10^{-2}$  min<sup>-1</sup> was obtained using the combined process of HC with ozone at ozone feed rate of 3 g/h. The lower extent of TOC reduction of the individual treatment of HC and ozone as 14.67% and 20.75% were obtained for HC and ozone at the same ozone feed rate operated individually. The synergetic index was calculated based on the degradation rate constants as follows:

Synergetic coefficent = 
$$\frac{k_{HC} + O_3}{k_{HC} + k_{o3}} = \frac{20.6 \times 10^{-3}}{2.4 \times 10^{-3} + 4.4 \times 10^{-3}} = 3.03.$$
 (5)

The combination of HC and ozone showed synergism (synergetic coefficient of 3.03) making the approach efficient for the degradation of reactive orange 4 dye. The treatment of the effluent obtained from the textile dyeing industries using HC in combination with ozonation was investigated by Rajoriya et al. [19]. The combined process of HC and ozone was reported to give 48% of TOC reduction, 22.72% of COD reduction and a rate constant of  $6.4 \times 10^{-3} \text{ min}^{-1}$  when the ozone was injected at the throat of a cavitating device as slit venturi. Lower TOC reduction of 41% and 12% of COD reduction was obtained when the ozone was injected directly into the solution tank in combination with HC. Gogate and Patil [36] also studied the ozonation process coupled with HC for the degradation of

triazophos using orifice as a cavitating device. The effect of ozone on the extent of degradation of triazophos was studied by injecting ozone at a flow rate of 0.576 g/h directly into the holding tank, as well as at the orifice plate. The obtained degradation rate constant of  $5.826 \times 10^{-2} \text{ min}^{-1}$  by injecting ozone in solution was higher as compared to the rate constant obtained for the case of ozone injected at the orifice  $(4.695 \times 10^{-2} \text{ min}^{-1})$ . The lower degradation obtained with ozone introduced at orifice plate can be attributed to the fact that the induced back pressure lowers the flow rate of water which ultimately reduces the passes of liquid leading to the lower degradation rates. The different literature reports revealed that the degree of synergism is dependent on the specific type of the pollutant. Hence, detailed investigations specific for each pollutant related to the optimum ozone flow rates, as well as the injection point, is necessary in order to achieve higher degradation rates for the specific pollutant in question.

Wu et al. [50] studied the application of the hybrid method of HC and ozonation for the removal of blue green algae suspension using orifice plate as a cavitating device. It was reported that about 15% removal of algae was obtained using hydrodynamic cavitation and 35% by ozone treatment, whereas the combined method of hydrodynamic cavitation and ozonation resulted in 99% removal of algae within only 10 min.

## 4.3. Combination of HC with Fenton

Fenton's reagent is a combination of ferrous sulfate and hydrogen peroxide that is used for the oxidation of organic pollutants. Many researchers have used Fenton reagent in combination with HC for the treatment of wastewater [18,19]. The combined process of HC with Fenton has been found to be more efficient due to the regeneration of Fe<sup>2+</sup> which intensifies the production of OH radicals. Furthermore, H<sub>2</sub>O<sub>2</sub> is more effectively utilized giving more OH radicals for the oxidation of pollutant [34]. Typically, with an increase in the dosage of ferrous sulfate(till the optimum), the extent of degradation also increases. In order to increase the effectiveness of the Fenton's process, the loading of ferrous sulfate and hydrogen peroxide needs to be optimized for specific pollutant as any excess addition leads to an increase in the TDS, as well as COD content of the effluent [5]. The two major disadvantages associated with Fenton's process are the requirement of pH of the solution to be in acidic range (usually between 2 and 4) and disposal of the sludge generated during the treatment [51]. Nevertheless, Fenton's process has been applied (especially in combination mode, including with HC) for the treatment of wastewater effluent containing complex organics with satisfactory results. Rajoriya et al. [19] studied the approach of HC combined with Fenton's reagent for the treatment of textile dyeing industry (TDI) effluent using slit venturi as a cavitating device. The effect of different loadings of Fenton's reagent on the basis of ratios of FeSO<sub>4</sub>.7H<sub>2</sub>O to H<sub>2</sub>O<sub>2</sub> as 1:1 to 1:10 was studied at a fixed concentration of  $H_2O_2$  as 5 mL/L of effluent. The maximum extent of TOC reduction of 48.4%, decolorization of 97.7% and COD reduction of 38% were reported at an optimum ratio of FeSO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub> as 1:5. However, a different optimum ratio of FeSO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub> as 1:30 was reported by Kumar et al. [18] for the treatment of ternary dye wastewater for the same approach of HC combined with Fenton's reagent. The maximum extent of decolorization of 98.86% with rate constant being  $0.203 \text{ min}^{-1}$  was reported using the combination of HC with Fenton within 20 min using orifice as a cavitating device. Furthermore, the obtained synergetic index (6.285) showed the better effectiveness of combination HC with Fenton than the individual approach of HC or Fenton. Joshi and Gogate [52] also investigated the combination of HC with Fenton's process for the degradation of dichlorvos and reported that the maximum extent of degradation of 91.5% was obtained at the optimum loading of FeSO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub> as 3:1 at the initial concentration of dichlorvos as 20 ppm. Cai et al. [37] investigated the decolorization of orange G (OG) dye using the hybrid treatment method involving HC and advanced Fenton process (AFP). The HC set up used consisted of 1.25 L capacity feed vessel tank, a vortex pump, valves and orifice plate as a cavitating device. Initially, the effect of inlet pressure, initial concentration of OG, loading of H<sub>2</sub>O<sub>2</sub> and zero valent iron (ZVI), position of ZVI (distance away from cavitating device), and pH of solution on the extent of decolorization was studied. Under the optimized operating

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conditions, such as temperature of 25 °C, fluid flow rate as 0.55 L/s, and pH as 3.0, the extent of decolorization for HC alone, HC +  $H_2O_2$ , and HC + AFP was 25.6%, 99.5%, and 99.8% respectively within 2 h of treatment. The decolorization rate was found to be strongly dependent on the position of ZVI, as well as dosing of  $H_2O_2$  and initial concentration of dye. Better results were obtained for the combination approach as compared to the individual approaches.

The studied literature reports revealed that the optimum ratio of FeSO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub> is different for different systems, justifying the need for detailed investigations related to specific pollutants.

## 4.4. Combination of HC with UV Photolysis

The combined operation of HC and UV can result in the enhanced generation of the higher quantity of hydroxyl radicals than the individual approach of HC or UV, which ultimately can increase the extent of degradation of pollutant [8]. The cavitational effects result in the generation of hydroxyl radicals, while UV irradiations initiate the photolysis of water molecule, thus contributing to the availability of hydroxyl radicals for the degradation of pollutant. Bagal and Gogate [45] investigated the efficacy of the combined operation of HC with UV for the degradation of diclofenac sodium by inserting UV lamp of 250 W inside the holding tank of the HC reactor. The combination of HC/UV process was reported to give 65.5% of degradation whereas only 26.8% and 43% as the extent of degradation was achieved in an individual approach of HC and UV process respectively.

Barik and Gogate [17,53] studied the degradation of 4-chloro 2-aminophenol using the combined process of Ultrasound (US) and HC with UV of wavelength 254 nm. In the case of the combined approach of the US with UV, the maximum degradation of 88.42% was reported whereas, the individual approach of US and UV resulted in degradation of 24.17% and 80.8% as the degradation respectively. The combined approach of HC and UV was reported to result in 79.3% of degradation whereas the individual approach of HC and UV resulted in degradation of 21.89% and 68.89% respectively using orifice plate as a cavitating device.

Similar enhancement in the extent of degradation for the removal of atrazine using the combined approach of HC and UV was reported by Jawale et al. [44]. The maximum extent of degradation of 44.44% with rate constant as  $1.16 \times 10^{-2}$  min<sup>-1</sup> was reported to be obtained using the combined approach of HC and UV (16 W) of wavelength 235 nm for the removal of atrazine using slit venturi as a cavitating device. Cehovin et al. [54] investigated the scale up potential of HC reactor in order to quantify the dissolved oxygen concentration (DOC) removal efficiency for the treatment of drinking water using orifice plate as a cavitating device. The hybrid treatment approaches of  $O_3$ ,  $H_2O_2/O_3$ ,  $H_2O_2/UV$  and  $O_3/UV$  alone and in combination with HC was investigated for the DOC removal efficiency of drinking water. It was reported that HC can significantly increase the DOC removal by 2–15% in combination with  $O_3$ ,  $H_2O_2/O_3$ , and  $H_2O_2/UV$  except  $O_3/UV$ . It was also reported that the combination of  $H_2O_2 + UV + HC$  and  $O_3 + UV + HC$  resulted in the DOC removal of 30.8% and 23.5% respectively when the concentrations of  $H_2O_2$  as 4 mg L<sup>-1</sup>,  $O_3$  as 2 mg L<sup>-1</sup> and intensity of UV irradiations as 300 mJ/cm<sup>2</sup> and wavelength of 254 nm were used. Furthermore, the formation of disinfection by-products was studied for the different AOPs combinations and it was reported that the combined process of HC coupled with  $H_2O_2$  and UV resulted in the higher concentration of intermediates, such as trihalomethanes (THMs), halogenated acetic acids (HAAs) and absorbable organic halogens as compared to the treatment of approach  $H_2O_2 + UV$ .

Based on the literature analysis, it can be concluded that the extent of degradation for combined treatment approach changes with the type of pollutant and hence, the selection of any combined treatment method is strongly dependent on the initial investigations for the specific pollutant.

## 4.5. Combination of HC with Photocatalysis

The heterogeneous photocatalysis has been widely applied as an efficient degradation process for the removal of recalcitrant pollutants, especially phenolic compounds. Photocatalysis involves the acceleration of the photoreaction in the presence of semiconductor photocatalyst [41]. Titanium dioxide

(TiO<sub>2</sub>) is a widely used photocatalyst that absorbs a photon energy equal to, or higher than the band gap energy, resulting in the transfer of an electron (e-) from the valence band to the conduction band, as well as at the same time, leaving a hole in valence bond. Subsequently, the generated electron-hole pair results in the formation of OH radicals based on the reaction with water or with oxygen [42]. The cavitation effects contribute to the enhancement in the OH radical formation by accelerating the transfer of an electron from the valence band to the conduction band, as well as turbulence generated by cavitation helps in continuous cleaning of catalysts allowing efficient photocatalytic activity for longer irradiation times [43]. Bethi et al. [55] studied the decolorization of crystal violet dye using the hybrid method involving HC and undoped, as well as doped TiO<sub>2</sub> catalyst using circular venturi as a cavitating device. It was reported that the combination of HC and Fe-doped  $TiO_2$  (0.8% Fe) in the presence of UV lamp (125 W) resulted in 98% decolorization whereas, the combination of HC and Ce-doped  $TiO_2$ (0.8% Ce) resulted in 84% of decolorization for catalyst loading of 0.6 g/L. The combination of HC with undoped TiO<sub>2</sub> in the presence of UV lamp (125 W) resulted in 94% of decolorization whereas, only HC, only UV and combination of UV + TiO<sub>2</sub> resulted in the extent of decolorization as 20%, 44.5%, and 37.6% respectively in 60 min treatment time. Wang et al. [10] also studied the degradation of tetracycline using the combination of HC and photocatalysis (TiO<sub>2</sub>). The venturi tube of inner diameter 2 mm was used as a cavitating device. It was reported that the approach of HC +  $TiO_2$  resulted in 78.2% of degradation, however, the individual approach of HC and TiO<sub>2</sub> resulted in only 12.2%, and 28.1% of degradation respectively within 90 min of treatment time for TiO<sub>2</sub> dosage of 100 mg/L. The effect using different catalysts, such as ZnO (2.57  $\mu$ m as the mean particle size), CuO(8.81  $\mu$ m) and TiO<sub>2</sub> (11.37 µm) with HC has been investigated for degradation of atrazine [44]. The reported best-combined approach for degradation of atrazine was HC + ZnO giving higher degradation of 43.16% with the kinetic constant being  $1.41 \times 10^{-2}$  min<sup>-1</sup> as compared to combination with other catalysts. Caliskan et al. [56] studied the pilot scale degradation of concentrated azo dye solutions using HC coupled with photocatalysis. The hybrid reactor consisting of photocatalysis reactor coupled with HC unit was used for the decolorization, as well as mineralization of RR180 dye solutions. The photoreactor consisted of 6 UVA types lamps with wavelength of about 315–400 nm located equally in a sealed tube. HC unit consisted of a circular venturi as the cavitating device having a throat diameter of about 7 mm. Different hybrid methods, such as HC, HC + UV, and HC + UV + ZnO were studied in order to quantify the synergism at an optimized inlet pressure of 5 bar, flow rate as  $4.1 \text{ m}^3/\text{h}$  and 180 min of treatment time. It was reported that the combination of HC + photolysis (UV) resulted in the enhanced decolorization from 4.6% to 16.4% within 180 min. However, the combination of HC + photocatalysis (UV + ZnO) resulted in 95% of decolorization, 77% of COD removal and 66% of TOC removal within 90 min at an optimized loading of ZnO as 1 g/L. Furthermore, the synergetic coefficients for the combination of HC and photocatalysis were obtained as 1.48 and 1.17 for COD and TOC reduction respectively. Overall, the hybrid process of HC +photocatalysis (ZnO) was established as a promising treatment method for the removal of recalcitrant textile dye effluents.

It can be concluded the best catalyst treatment approach (both in terms of type and loading of catalyst) varies with pollutant type. Hence, there is a need for detailed investigations for establishing the suitable combination method for treatment of the specific pollutant.

#### 5. Review of Hybrid Treatment Approaches Studied Involving HC and Other AOPs

Some of the recently depicted work based on hydrodynamic cavitation for the degradation of toxic pollutants, as well as the treatment of real industrial effluent, has been highlighted in this section illustrating the effectiveness of hybrid methods based on hydrodynamic cavitation. Moreover, analysis of the few literature reports related to the application of HC and AOPs for wastewater treatment has been represented in tabular form (Table 1).

Montusiewicz et al. [57] studied the effect hydrodynamic cavitation on the biodegradability and composition of suspended brewery spent grain (BSG) diluted by municipal wastewater obtained from wastewater treatment plant in Lublin (Poland). The HC device used consisted of a transparent glass

tube for observation of cavitation phenomenon, an orifice plate as a cavitating device and a pump of 16 bar maximum operating pressure and power rating of 2.2 kW. The mechanically pretreated (pre-settled) BSG samples were subjected to cavitation treatment and analyzed for biodegradability index. Biodegradability index is the ratio of biological oxidation demand (BOD): Chemical oxidation demand (COD) which measures the extent of biodegradation of wastewater. The enhancement in the biodegradability index from 0.074 to 0.091 was observed when the effluent was passed through the cavitation zone for 30 cycles at an inlet pressure of 7 bar. After the HC treatment, the observed reduction in COD, as well as TS and VS content confirmed the destruction of complex organic compounds due to cavitation. Moreover, 25.5% of hemicellulose and 87% of monosaccharides removal confirmed the solubilization of carbohydrates under the cavitation effect.

Wang and Zhang [38] investigated the degradation of alachlor, a widely used herbicide present in aqueous solution, using HC. The HC reactor set up consisted of a closed loop consisting of a swirling cavitation chamber, holding tank of capacity 40 L and a centrifugal pump. The effect of operating parameters, such as pressure, temperature, solution pH, and initial concentration on the extent of degradation of alachlor was investigated. It was reported that with an increase in the pressure, the degradation rate also increased, whereas rate decreased with an increase in the concentration of alachlor. It was also reported that the reaction followed the pseudo first order kinetics with rate constant being  $4.90 \times 10^{-2} \text{ min}^{-1}$  at 0.6 MPa pressure and 40 °C temperature.

Jung et al. [58] investigated the approach of electric field assisted HC using graphite electrodes in combination with H<sub>2</sub>O<sub>2</sub> for decolorization of acid orange 7 (AO-7). The two different orifice plates, one of 2 mm diameter hole as conventional orifice (C) and another type of modified orifice (M) consisting of a crisscrossed pipe (20 mm diameter; 40 mm length) placed before the 2 mm diameter orifice, were used as a cavitating devices in HC reactor. The two graphite electrodes of equal sizes (distance between electrodes = 15 cm) were immersed in the HC circulation. The different treatment approaches involving C-HC, M-HC, electric field-assisted modified orifice plate (EFM-HC), electric field-assisted conventional orifice plate (EFC-HC) were compared in terms of the decolorization efficiency at the fixed concentration of AO-7 as 10 mg/L and the pH of the dye solution maintained as  $6.5 \pm 0.7$ . It was reported that the decolorization of about 39.5% and 51% was achieved after the addition of H<sub>2</sub>O<sub>2</sub> to C-HC and M-HC system respectively whereas, individual systems of C-HC and M-HC resulted in comparatively lower decolorization of about 15.42% and 22.06% respectively. In the case of electric field assisted systems (EFM-HC and EFC-HC), the higher extent of decolorization was observed as a result of generation of strong oxidants, such as HOCl and OCl<sup>-</sup> in the presence of electric field, as well as cavitation effect. The higher decolorization in EFM-HC system as compared to EFC-HC was observed due to generation of intense shock waves at the throat of crisscrossed pipe, which ultimately breaks the molecular bonds. Moreover, it was reported that the addition of H<sub>2</sub>O<sub>2</sub>in electric field assisted systems resulted in decreased rate of decolorization due to a reduction in the regeneration reactions of Cl<sub>2</sub> and HOCl due to the combination of OH and HO<sub>2</sub> in presence of  $H_2O_2$ . The combined approach of EFM-HC (without the addition of  $H_2O_2$ ) resulted in the complete decolorization of AO-7.

Li et al. [59] studied the decolorization of methyl orange using HC in combination with zero-valent metal nanoparticles. It was reported that the HC alone and use of  $Cu^0$  nanoparticles alone resulted in the lower extent of decolorization as only 6.8% and 20% respectively whereas, enhanced decolorization efficiency of about 83% was achieved using the combined approach of  $Cu^0/HC$  at a fixed dosage of  $Cu^0$  nanoparticles as 40 mg/L. Furthermore, the obtained synergetic index (4.25) for the combined approach of  $Cu^0/HC$  confirmed the better efficiency than the individual approach. The study related to the effect of operating parameters, such as inlet pressure, pH and concentration of  $Cu^0$  on the extent of decolorization established that the maximum decolorization was achieved at an optimum pressure of 0.4 MPa, acidic condition of pH as 3, and loading of  $Cu^0$  as 200 mg L<sup>-1</sup>.

Boczkaj et al. [60] studied the treatment of industrial effluent obtained from the production of bitumen using HC in combination with  $O_3$ ,  $H_2O_2$  and Peroxone using venturi tube as a cavitating

device. All the experiments were performed using 5 L solution at the temperature maintained of  $40 \pm 2$  °C. The effectiveness of HC aided by H<sub>2</sub>O<sub>2</sub> on the COD reduction was investigated and it was reported that the HC aided by H<sub>2</sub>O<sub>2</sub> resulted in 20% of COD reduction whereas, HC alone resulted in 13% of COD reduction at the H<sub>2</sub>O<sub>2</sub> loading of 1.0 mL/min. Furthermore, HC aided by ozonation process was studied using ozone flow rate of 9.41 g/h and it was reported that about 40% of COD and 50% of BOD reduction was achieved. Comparatively lower COD and BOD reduction, as 13% and 18%, respectively, was obtained for HC aided peroxone within 360 min of treatment. The individual treatment approach of O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and peroxone gave COD reduction of 20.1%, 6.8%, and 37% respectively. Maximum treatment efficiency was obtained using the combined approach of HC and ozone.

Raut-Jadhav et al. [61] investigated the treatment of effluent obtained from the pesticide industry using HC and its combination with  $H_2O_2$ , as well as ozone. The effect of dilution of the effluent on the extent of mineralization was initially studied at no dilution, 1:5 dilution and 1:10, at constant inlet pressure to the venturi as 6 bar and 90min of treatment time. It was reported that with an increase in the dilution of the effluent, the COD reduction also increased. As the dilution increases, the total volume of the pollutant that is to be treated also increases, hence the use of much diluted effluent may not be beneficial. All the experiments were performed using five times diluted effluent as the optimized condition. The hybrid method of HC coupled with ozonation was investigated at varying ozone flow rate from 0.5 to 3 g/h. It was reported that the extent of mineralization increases significantly with increased ozone flow rate up to 0.75 g/h, whereas, a further increase in the ozone flow rate beyond 0.75 g/h resulted in only marginal increase in COD and TOC reduction. For HC and ozonation treatment, the maximum extent of COD reduction and rate constant as 25.69% and 2.47  $\times$  10<sup>-3</sup> min<sup>-1</sup> respectively were obtained at optimum ozone loading of 0.75 g/h. The biodegradability index was enhanced from 0.123 to 0.324 for the hybrid method of HC and ozone (3 g/h) after 2 h of treatment. Significantly lower extent of COD reduction and rate constant of 14.77% and 1.38  $\times$  10<sup>-3</sup> min<sup>-1</sup> respectively were obtained using HC alone. The combination of HC and  $H_2O_2$  (10 g/L) resulted in enhanced COD and TOC reduction as 60.29% and 54.87% respectively as compared to HC alone. Overall, the combination of HC and  $H_2O_2$  (10 g/L) was reported as an energy efficient and cost effective treatment as the cost incurred during combined HC and H<sub>2</sub>O<sub>2</sub>was almost 4 times lower (1951.63 Rs./m<sup>3</sup>) than that required during HC alone (10,250.99 Rs./m<sup>3</sup>). Furthermore, it was reported that the energy efficiency obtained for the combination of HC and  $H_2O_2$  was higher (6.01  $\times$  10<sup>-9</sup> mol/J) as compared to the energy efficiency obtained for the combination of HC and ozone  $(2.2 \times 10^{-9} \text{mol/J})$ for the treatment of pesticide effluent.

Saxena et al. [62] studied the possible enhancement in mineralization and biodegradability using hydrodynamic and acoustic cavitation along with alum coagulation for the case of treatment of tannery waste effluent. The slit venturi was used as a cavitating device in HC reactor. Two different coagulation methods (one with adjustment of solution pH at 7 and other without adjustment of pH of the solution) were used (M1 and M2) and the supernatant collected was further subjected to HC and US treatment. The effect of inlet pressure on the extent of mineralization of effluents obtained from coagulation processes (M1 and M2) was studied by varying inlet pressure over the range of 5 to 10 bars. It was reported that at an optimum inlet pressure of 5 bar, the effluent obtained from M1, resulted in higher COD and TOC reduction as 35.6% and 43.9% in the HC treatment respectively as compared to that obtained from M2 (16.5% and 18.2% respectively). It was also reported that the biodegradability index was also enhanced from 0.14 to 0.57 after 120 min treatment of HC. Coagulation followed by US resulted in lesser enhancement in the biodegradability index from 0.10 to 0.41. It was also reported that the coagulation followed by HC treatment was almost 6 times more energy efficient than the treatment of coagulation followed by US.

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| Sr. No. | Type of Wastewater                  | <b>Treatment Methods</b>   | <b>Operating Conditions</b>   | Results   | Comments   | Reference |
|---------|-------------------------------------|--|---|---|--|-----------|
| 1       | Textile dyeing industry<br>effluent | HC, HC + Oxygen,<br>HC + O <sub>3</sub> , HC + Fenton                        | HC reactor:<br>Inlet pressure of 5 bar; reaction<br>volume of 6 L; pH as 6.8; treatment<br>time of 120 min<br>HC + Oxygen (2 L/min as O <sub>2</sub><br>flow rate);<br>HC + O <sub>3</sub> (3g/h as ozone flow rate);<br>HC + Fenton (molar ratio of<br>FeSO <sub>4</sub> ·7H <sub>2</sub> O:H <sub>2</sub> O <sub>2</sub> as 1:5)  | HC alone resulted in 17% of total<br>organic carbon (TOC)and 12% of<br>chemical oxidation demand<br>(COD)reduction with 25% of<br>decolorization<br>HC + Fenton resulted in 48% of TOC<br>and 38% of COD reduction with 98%<br>of decolorization<br>HC + Oxygen resulted in 48% of<br>TOC, 33% of COD, 62% of<br>decolorization<br>HC + O <sub>3</sub> resulted in 48% of TOC,<br>23% of COD and 88% of<br>decolorization   | HC + Fenton's reagent resulted in<br>highest reduction in TOC, COD,<br>and color as compared to other<br>hybrid processes  | [19]      |
| 2       | Reactive Orange 4 (RO4)             | HC, HC + H <sub>2</sub> O <sub>2</sub> ,<br>HC + O <sub>3</sub>              | HC reactor:<br>Inlet pressure of 5 bar; Initial<br>concentration as 40 ppm; pH as 5;<br>Reaction volume of 6 L; Reaction<br>time as 120 min;<br>HC + H <sub>2</sub> O <sub>2</sub> (molar ratio of<br>RO4:H <sub>2</sub> O <sub>2</sub> as 1:1:30); HC + O <sub>3</sub> (O <sub>3</sub> as<br>3 g/h)  | Extent of mineralization for HC alone as 14.67%; HC + $H_2O_2$ as 31.90%; HC + $O_3$ as 76.25%  | HC coupled with ozone found to be<br>the most energy efficient method for<br>the degradation of RO4  | [56]      |
| 3       | Methomyl                            | HC, HC + H <sub>2</sub> O <sub>2</sub> ,<br>HC + Fenton, HC + O <sub>3</sub> | HC reactor:<br>Inlet pressure of 5 bar; Initial<br>concentration as 25 ppm; Reaction<br>volume of 5 L; Reaction time as<br>120 min; pH as 2.5;<br>HC + H <sub>2</sub> O <sub>2</sub> (mole ratio of<br>methomyl:4H <sub>2</sub> O <sub>2</sub> as 1:05);<br>HC + Fe0nton (mole ratio of<br>Fe <sup>2+</sup> :H <sub>2</sub> O <sub>2</sub> as 1:20;<br>HC + O <sub>3</sub> = (2 g/h as ozone flow rate) | Extent of degradation for HC alone<br>as 13.9%, HC + H <sub>2</sub> O <sub>2</sub> as 59.86% in<br>60 min treatment; HC + Fenton as<br>100% in 30 min, HC + O <sub>3</sub> as 69.87%<br>Extent of TOC reduction for HC<br>alone as 5.45%, HC + H <sub>2</sub> O <sub>2</sub> as 15.4%,<br>HC + Fenton as 35.79% and HC + O <sub>3</sub><br>as 70.79%<br>Synergetic coefficient for HC + H <sub>2</sub> O <sub>2</sub> ,<br>HC + Fenton, HC + O <sub>3</sub> was found to<br>be 5.8, 13.41 and 47.6 respectively | The combined method of HC + $O_3$<br>found to be the most effective<br>process as it resulted in highest<br>synergetic coefficient, energy<br>efficiency and the extent of<br>mineralization                                     | [43]      |
| 4       | Tetracycline                        | HC, HC + Photocatalysis  | HC reactor:<br>Initial concentration as 30 mg/L;<br>Reaction volume of 4 L; Reaction<br>time 90 min; pH as 4.2; TiO <sub>2</sub> loading<br>as 100 mg L <sup><math>-1</math></sup> ; UV254 lamp   | The rate constant obtained for HC alone was $1.4 \times 10^{-3} \text{ min}^{-1}$ and for HC + Photocatalysis as $1.67 \times 10^{-2} \text{ min}^{-1}$ as the rate constant  | The rate constant obtained for<br>photocatalysis coupled with HC was<br>found to be 1.5–3.7 times of the sum<br>of the individual processes<br>The degradation of Tetracycline was<br>pH-dependent and favored at<br>alkaline pH | [10]      |

# Table 1. Overview of work done on the treatment of wastewater using HC combined with advanced oxidation processes (AOPs).

| Sr. No. | Type of Wastewater      | Treatment Methods   | <b>Operating Conditions</b>   | Results   | Comments  | Reference |
|---------|-------------------------|---|---|---|---|-----------|
| 5       | Imidacloprid            | HC, HC + H <sub>2</sub> O <sub>2</sub>  | HC reactor:<br>Inlet pressure of 15 bar; Temperature<br>as $32 \pm 4$ °C; pH as 2.7;<br>Initial concentration as 25 mg/L;<br>Reaction volume of 5 L;<br>HC + H <sub>2</sub> O <sub>2</sub> (Molar ratio of<br>Imidacloprid:H <sub>2</sub> O <sub>2</sub> as 1:40)   | HC alone resulted in 26.5% of<br>degradation with rate constant being<br>$2.565 \times 10^{-3}$ min <sup>-1</sup><br>For HC + H <sub>2</sub> O <sub>2</sub> , 100% degradation<br>was achieved in 45 min with rate<br>constant of 0.122216 min <sup>-1</sup> and TOC<br>reduction of 36.1%  | The combined method of<br>HC + $H_2O_2$ was found as an efficient<br>process due to higher synergetic<br>index obtained as 22.79 for<br>degradation of imidacloprid           | [63]      |
| 6       | Methylene blue (MB)     | HC, HC + H <sub>2</sub> O <sub>2</sub> ,<br>HC + Photocatalysis                                       | HC reactor:<br>Inlet pressure of 5 bar; pH as 2;<br>treatment time of 120 min; initial<br>concentration as 50 ppm<br>HC + $H_2O_2$ (MB: $H_2O_2$ as 1:20);<br>HC + Photocatalyst (Bismuth doped<br>Ti $O_2$ at loading of 200 mg/L)   | Extent of decolorization for HC<br>alone as 32.32%, HC + Photocatalyst<br>as 64.58%, HC + H <sub>2</sub> O <sub>2</sub> as 100%<br>Extent of mineralization for HC<br>alone as 9.46%, HC + photocatalysis<br>as 12.68%, HC + H <sub>2</sub> O <sub>2</sub> as 18.41%  | The combined method of<br>HC + photocatalytic oxidation<br>shows the synergy but it is less<br>efficient compared to combined<br>method of HC + H <sub>2</sub> O <sub>2</sub> | [35]      |
| 7       | Phenol                  | HC, HC + heterogeneous<br>AFP   | HC generated using liquid whistle<br>reactor (LWR):<br>Inlet pressure of 1500 psi; Reaction<br>volume as 4 L; Temperature as<br>$35 \pm 3$ °C; pH of solution as 2.5;<br>H <sub>2</sub> O <sub>2</sub> concentration as 2000 mg/L;<br>iron 80 g (50 pieces of 1 cm × 2 cm,<br>thickness of 0.10 cm); Orifice as a<br>cavitating device and orifice area<br>0.012 in. <sup>2</sup>   | TOC removal of about 50–60%<br>obtained within 105 min of<br>treatment time with the modified<br>AFP combined with HC   | The modified AFP combined with<br>HC found be a promising technology<br>for treatment of wastewaters<br>containing high organic content                                       | [64]      |
| 8       | Reactive blue 13 (RB13) | HC, HC + Oxygen,<br>HC + H <sub>2</sub> O <sub>2</sub> , HC + ferrous<br>sulfate, HC + O <sub>3</sub> | HC reactor:<br>Inlet pressure of 0.4 MPa; Solution<br>pH as 2; Initial concentration as<br>30 ppm; Reaction volume of 6 L;<br>temperature as 30 °C; Reaction time<br>of 120 min;<br>Combined method:<br>HC + H <sub>2</sub> O <sub>2</sub> (molar ratio of<br>RB13:H <sub>2</sub> O <sub>2</sub> as 1:20); HC + Oxygen<br>(oxygen flow rate as 2 L/min);<br>HC + ferrous sulfate (molar ratio of<br>H <sub>2</sub> O <sub>2</sub> :FeSO <sub>4</sub> .7H <sub>2</sub> O as 1:3); HC + O <sub>3</sub><br>(O <sub>3</sub> flow rate as 3 g/h) | Extent of decolorization for HC<br>alone as $47\%$ , HC + Oxygen as 66%,<br>HC + H <sub>2</sub> O <sub>2</sub> as 91%, HC + ferrous<br>sulfate as 66.3%, HC + O <sub>3</sub> as 100%<br>Extent of TOC reduction for HC<br>alone as 19.06%, HC + Oxygen as<br>18.10%, HC + H <sub>2</sub> O <sub>2</sub> as 24.65%,<br>HC + ferrous sulfate as 66.3%,<br>HC + O <sub>3</sub> as 71.76% | HC + ozone process established as<br>best treatment approach for the<br>decolorization and mineralization<br>of RB13  | [30]      |

| Sr. No. | Type of Wastewater   | Treatment Methods  | <b>Operating Conditions</b>   | Results  | Comments  | Reference |
|---------|--|--|---|--|---|-----------|
| 9       | Tannery dye wastewater<br>(Synthetically prepared<br>mixture of Methylene<br>blue, Methyl orange,<br>Rhodamine-B)    | HC, HC + H <sub>2</sub> O <sub>2</sub> ,<br>HC + Fenton, HC + photo<br>Fenton<br>HC + photolytic,<br>HC + photocatalytic | HC reactor:<br>Inlet pressure of 6 bar; pH as 3;<br>Reaction volume of 5 L; initial<br>concentration as 30 ppm; orifice as<br>a cavitating device; temperature as<br>30 °C<br>Hybrid methods:<br>HC + H <sub>2</sub> O <sub>2</sub> (Molar ration of<br>dye:H <sub>2</sub> O <sub>2</sub> as 1:40); HC + Fenton<br>(Molar ration of FeSO <sub>4</sub> ·7H <sub>2</sub> O:H <sub>2</sub> O <sub>2</sub><br>as 1:30); HC + photo Fenton<br>(Ultraviolet irradiations (UV)<br>wavelength 350-750 nm);<br>HC + photocatalytic (TiO <sub>2</sub> loading of<br>200 mg/L) | Extent of TOC removal obtained for<br>HC alone as 8.53%; HC + $H_2O_2$ as<br>16.95%; HC + Fenton as 38.42%;<br>HC + photo Fenton as 41.28%;<br>HC + photolytic as 14.01%;<br>HC + photocatalytic as 15.63%   | The method of HC + $H_2O_2$ was<br>found as the best combination for<br>the removal of dye from aqueous<br>solution as the complete<br>decolorization was obtained along<br>with higher synergetic index as<br>28.974 | [18]      |
| 10      | 2,4-dichlorophenoxyacetic<br>acid  | US, US + AFP<br>HC, HC + AFP   | US reactor:<br>Frequency of 20 kHz, operating in a<br>pulse mode of 4 s on and 2 s off;<br>Initial concentration as 0.235 g/L,<br>Temperature as $22 \pm 2$ °C; Treatment<br>time of 60 min; hydrogen peroxide<br>(30% H <sub>2</sub> O <sub>2</sub> at loading of 1.7 mL);<br>powdered iron (at loading of 0.12 g)<br>HC reactor:<br>orifice as a cavitating device, Inlet<br>pressure of 1500 psi, Initial<br>concentration as 0.235 g/L, Reaction<br>volume of 8 L, Temperature as<br>$18 \pm 2$ °C, flow rate as 5.2 L/min;<br>Treatment time of 90 min         | US alone resulted in 11% of TOC<br>reduction; addition of iron powder<br>(0.12 g) resulted in TOC removal as<br>18%; Ultrasound + advanced Fenton<br>process resulted in about 60% TOC<br>reduction<br>HC + advanced Fenton process<br>resulted in about 70% TOC removal | HC was found to be more suitable<br>for treating effluent at a much larger<br>scale of operation as compared to<br>acoustic cavitation treatment method   | [65]      |
| 11      | Industrial effluent 1<br>containing substituted<br>phenolic compounds<br>Industrial effluent 2<br>dyestuffs solution | HC + Advanced Fenton<br>process (AFP)  | HC generated using liquid whistle<br>reactor (LWR):<br>Reaction volume as 4 L, time 150 min   | For industrial effluent 1, 60% TOC<br>reduction; For industrial effluent 2,<br>70% of TOC reduction was obtained   | HC in combination with AFP was<br>found as effective treatment<br>approach reducing TOC by about<br>60% to 70%  | [66]      |

| Sr. No. | Type of Wastewater        | Treatment Methods   | <b>Operating Conditions</b>  | Results  | Comments  | Reference |
|---------|---------------------------|---|--|--|---|-----------|
| 12      | Crystal violet            | HC + hydro gels packed<br>bed adsorption  | HC reactor:<br>Inlet pressure of 3 bar, Initial<br>concentration as 500 mg/L, Reaction<br>volume as 2 L, orifice as a cavitating<br>device, Poly-acrylic acid bentonite<br>nano composite hydro gel loading as<br>0.5 wt % (30 g as the quantity)  | HC alone resulted in 20%<br>decolorization and 17% of TOC<br>reduction; HC + hydro gels packed<br>bed adsorption resulted in 96%<br>decolorization and 70% of TOC<br>reduction at pH 2.3; synergetic index<br>for HC + hydro gels packed bed<br>adsorption was found to be 1.2 | HC followed by hydro gel<br>adsorption was found to be an<br>efficient hybrid technology for the<br>treatment of textile industry<br>wastewater containing dyes   | [67]      |
| 13      | Real pesticide wastewater | НС  | HC reactor:<br>Temperature as 28 °C, treatment<br>time of 150 min  | About 90.55% COD and 83.21% color removal was achieved   | HC was found to be ecofriendly<br>solution for the treatment of the<br>wastewater. Also, generation of<br>sludge after treatment was very less  | [68]      |
| 14      | 2,4-dinitrophenol (DNP)   | HC, HC/H <sub>2</sub> O <sub>2</sub> ,<br>HC/Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> /FeSO <sub>4</sub> ,<br>HC/FeSO <sub>4</sub> /H <sub>2</sub> O <sub>2</sub><br>HC/Fe/H <sub>2</sub> O <sub>2</sub><br>HC/CuO/H <sub>2</sub> O <sub>2</sub> | HC reactor:<br>Inlet pressure of 4 bar; pH as 4;<br>Temperature as 35 °C; initial<br>concentration as 20 ppm; treatment<br>time of 120 min;<br>HC/H <sub>2</sub> O <sub>2</sub> (DNP:H <sub>2</sub> O <sub>2</sub> ratio of 1:5);<br>HC/Fenton (0.3 g/L H <sub>2</sub> O <sub>2</sub> + 0.6 g/L<br>FeSO <sub>4</sub> );<br>HC/advanced Fenton (0.4 g/L H <sub>2</sub> O <sub>2</sub><br>+ 0.6 g/L Fe);<br>HC/CuO/H <sub>2</sub> O <sub>2</sub> (H <sub>2</sub> O <sub>2</sub> :CuO ratio of<br>1:6);<br>HC/Ferrous activated persulfate<br>(0.08 g/L FeSO <sub>4</sub> + 0.16 g/L<br>Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ) | Extent of degradation for HC alone<br>as 12.4%, HC/H <sub>2</sub> O <sub>2</sub> as 21.3%,<br>HC/Fenton as 100%, HC/advanced<br>Fenton as 54.1%, HC/CuO/H <sub>2</sub> O <sub>2</sub> as<br>29.80%, and HC/Ferrous activated<br>persulfate as 55.30%                           | The maximum cavitational yield $5.81 \times 10^{-6}$ min <sup>-1</sup> mg/J was obtained for HC/Ferrous activated persulfate approach   | [39]      |
| 15      | Orange-G                  | НС  | HC reactor:<br>Inlet pressure of 5 bar, Reaction<br>volume as 6 L, time of 2 h,<br>temperature as $32 \pm 2$ °C<br>Cavitating devices used: Orifice<br>plate, circular venturi and slit<br>venturi   | TOC reduction obtained using HC<br>with slit venturi as 37%, circular<br>venturi was 28%, orifice was 14%  | The maximum degradation was<br>obtained (almost 50% higher) using<br>HC with slit venturi. Also, the power<br>dissipated into the system and hence<br>the energy transfer efficiency was<br>found to be higher as compared to<br>circular venturi and orifice plate | [69]      |

| Sr. No. | Type of Wastewater | Treatment Methods                                     | <b>Operating Conditions</b>  | Results  | Comments  | Reference |
|---------|--------------------|---|--|--|---|-----------|
| 16      | 4-acetamidophenol  | HC, US,<br>HC + photocatalysis<br>US + Photocatalysis | Photo catalytic reactor:<br>UV lamp of 300 W; Wavelength >400<br>nm; irradiation intensity as<br>2.47 W/cm <sup>2</sup> ; TiO <sub>2</sub> catalyst loading<br>as 2 g/L<br>HC reactor:<br>inlet pressure of 5 bar; slit venturi as<br>a cavitating device; pH as 6.8;<br>US horn:<br>Frequency as 20 kHz, input power<br>750 W                             | Photocatalytic oxidation resulted in<br>almost 50% removal with rate<br>constant of $4.4 \times 10^{-3}$ min <sup>-1</sup> ;<br>Sm and N doped TiO <sub>2</sub> resulted in<br>about 60% and 63% degradation<br>respectively<br>Extent of degradation for US +<br>photocatalysis was 87%,<br>HC + photocatalysis was 91%   | HC + photocatalytic oxidation was<br>found to be energy efficient process<br>$(9.0 \times 10^{-6} \text{ mg/J})$ with almost 9 fold<br>than the US + photocatalytic process             | [70]      |
| 17      | Ibuprofen          | НС  | HC reactor:<br>Inlet pressure of 0.35 MPa; initial<br>concentration as 200 μg/L; pH as 6;<br>Temperature as 25 °C  | About 60% of ibuprofen was<br>degraded within 60 min with an<br>electrical energy per order of<br>10.77 kWhm <sup>-3</sup>   | HC alone was found as the effective<br>method for degradation of ibuprofen<br>both in the neutral and dissociated<br>form of ibuprofen  | [71]      |
| 18      | Carbamazepine      | HC  HC + UV  HC + H2O2  HC + O3  HC + H2O2 + O3       | HC reactor:<br>Inlet pressure of 4 bar; pH of<br>solution as 4; Initial concentration as<br>10 ppm; Reaction volume of 4 L;<br>reaction time as 120 min;<br>HC + UV (UV power as 16 W)<br>HC + H <sub>2</sub> O <sub>2</sub> (molar ratio of CBZ:<br>H <sub>2</sub> O <sub>2</sub> as 1:5);<br>HC + O <sub>3</sub> (O <sub>3</sub> flow rate as 400 mg/h); | Extent of degradation for<br>HC + H <sub>2</sub> O <sub>2</sub> + O <sub>3</sub> was 100%;<br>HC + O <sub>3</sub> was 91.4%, HC + H <sub>2</sub> O <sub>2</sub> was<br>58.3%, and HC + UV was 52.9%<br>Synergetic index obtained for<br>HC + H <sub>2</sub> O <sub>2</sub> + O <sub>3</sub> was 3.2, HC + O <sub>3</sub><br>was 2.2, HC + H <sub>2</sub> O <sub>2</sub> was 1.01,<br>and HC + UV was 0.9 | The combined method of<br>HC + $H_2O_2 + O_3$ established as the<br>most effective treatment for the<br>removal of CBZ from wastewater<br>due to low cost of treatment as<br>0.29 Rs./L | [14]      |

Barik and Gogate [16] studied the degradation of 2,4,6-trichlorophenol (2,4,6 TCP) using hybrid methods based on HC. The cavitational effects are generated using slit venturi as a cavitating device. The hybrid method of HC + O<sub>3</sub> and HC + H<sub>2</sub>O<sub>2</sub> were investigated by varying ozone flow rate from 100 to 400 mg/h and using different loadings of H<sub>2</sub>O<sub>2</sub> (2,4,6-TCP: H<sub>2</sub>O<sub>2</sub>, 1:1–1:7) at an initial concentration of 2,4,6 TCP as 20 ppm under the optimized inlet pressure of 4 bar and pH as 7. For the hybrid method of HC + H<sub>2</sub>O<sub>2</sub>, the maximum extent of degradation and rate constant of 62.07% and  $8 \times 10^{-3}$  min<sup>-1</sup> respectively were obtained at the optimum ratio of TCP:H<sub>2</sub>O<sub>2</sub> as 1:5 whereas, only H<sub>2</sub>O<sub>2</sub> and only HC resulted in comparatively much lower extent of degradation of 17.4% and 24.34% respectively at the same ratio (1:5) in the case of only H<sub>2</sub>O<sub>2</sub>. The effect of combined approaches of O<sub>3</sub> + H<sub>2</sub>O<sub>2</sub>, HC + O<sub>3</sub>, HC + O<sub>3</sub> + H<sub>2</sub>O<sub>2</sub> on the extent of degradation, COD, and TOC removal was also investigated under the optimized conditions of HC reactor. The combined approach of HC + O<sub>3</sub> + H<sub>2</sub>O<sub>2</sub> was reported as the most efficient approach as the extent of degradation, COD and TOC reduction of 100%, 95.6%, and 80.9% respectively were much higher as compared to other approaches.

Thanekar et al. [12] used the HC as the pretreatment for the biological oxidation of dichlorvos present in the aqueous solution using slit venturi as a cavitating device. Under the optimized set of operating parameters of HC reactor as inlet pressure of 5 bar and pH of 4, the effect of HC alone and the combination of HC +  $O_3$  on the removal of dichlorvos was investigated. It was reported that the HC alone gave 41.4% of degradation and 27.9% of TOC reduction whereas HC +  $O_3$  gave 84.8% of degradation and 39.4% of TOC reduction. Subsequently, the effluents obtained after treatment of HC alone, as well as HC +  $O_3$  method were subjected to biological oxidation. The maximum TOC reduction of 86.1% was achieved using HC +  $O_3$  as pretreatment to biological oxidation whereas, HC alone combined with biological oxidation resulted in 50.6% of TOC reduction. Only 14.4% of TOC reduction was obtained using direct biological oxidation (without any pretreatment). It was thus demonstrated that the combined method of HC +  $O_3$  followed by biological oxidation is the most efficient treatment approach for the degradation of dichlorvos.

## Discussion Related to Selection of Optimum Conditions

The purpose of the literature analysis was to understand the important information regarding the selection of operating conditions of the HC reactors when operated individually or in combination with other AOPs. The recommended optimum inlet pressure is typically within the range of 4–7 bar beyond which the possible onset of supercavitation could lower the degradation rate.

Furthermore, pH of the solution is found to be an important operating parameter, which affects the efficacy of hydrodynamic cavitation. The recommended value of optimum pH lies usually within the acidic range of 3–5. However, it also depends on the specific pollutant's dissociation constant (pKa) which decides whether the pollutant is present in the molecular state or ionic state. Moreover, in order to avoid additional treatment costs and maintenance of reactor under acidic conditions, the wastewater treatment should be carried out at natural pH of the effluent especially when the intensification in the extent of degradation obtained under acidic conditions is marginal.

Similarly, although the degradation rate increases with an increase in temperature, the additional heating cost would be incurred and hence optimization is required.

Based on the literature, the individual operation of hydrodynamic cavitation is less effective for the destruction of complex pollutant. Hybrid methods, such as HC coupled with  $H_2O_2$ ,  $O_3$ , Fenton's process, photocatalysts etc. result in better efficiency for the treatment of wastewater than the HC operated alone. In order to achieve the maximum efficiency in terms of the degradation rates, the optimum loading of additives needs to be considered, which ultimately depends on the type of pollutant. Moreover, the synergetic index can be calculated for different combinations using the degradation kinetics, based on which the suitable treatment approach for the specific pollutant needs to be established.

# 6. Conclusions

The hydrodynamic cavitation reactors offer 100% scale up potential as compared to the ultrasonic reactors for the destruction of complex pollutants. The combination of HC with other AOPs is found to be more efficient than the individual technique, as the combination generates more OH radicals, thus intensifying the degradation.

The operating parameters of HC, such as inlet pressure, pH of the solution, temperature etc. play a crucial role in deciding the effectiveness of treatment and final obtained extent of degradation. It is recommended to perform the hydrodynamic cavitation treatment at the available temperature in order to reduce the additional heating cost. Although the acidic conditions favor the cavitation based treatment, the obtained benefits need to be weighed against the operating cost of the process as the pH adjustment requires an additional chemical cost.

The review mainly focused on the different aspects of hydrodynamic cavitation combined with AOPs, such as  $H_2O_2$ ,  $O_3$ , UV irradiation, photocatalysis, and Fenton's treatment for the removal of pollutants present in the aqueous form. It was demonstrated that, in order to achieve the maximum benefits in terms of the complete mineralization, the selection of optimum loading of the additives is necessary and need to be established using the detailed investigations specific for that pollutant. Overall, it can be said that HC reactors offer a substantial promise as an efficient wastewater treatment method.

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## Abbreviations

- COD Chemical oxidation demand
- BOD Biological oxidation demand
- TOC Total organic carbon
- DOC Dissolved oxygen concentration
- TDS Total dissolved solids

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