

# A Review on Hydrodynamic Cavitation as a Treatment Option for Refractory Organics Removal

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**Abstract:** Effluents from different industries such as pharmaceutical, pesticides, dyes and dye intermediates are increasing day by day. Different Advanced Oxidation Processes such as Fenton, photo catalytic, hydrodynamic, acoustic cavitation processes, etc. are used to mineralize complex molecules of these effluents which are not easily biodegradable. Among these processes, Hydrodynamic Cavitation has emerged as a new energy-efficient technology for the treatment of various bio-refractory pollutants present in aqueous effluent. Hydrodynamic Cavitation involves the use of a cavitating device for the treatment of wastewater. In present work, the current status of Hydrodynamic Cavitation reactors has been reviewed discussing cavitation yield. Operating parameters like pH, temperature, pressure, flow rate are also varied. Also, Cavitation reactors are compared with Sonochemical reactors and hydrodynamic cavitation reactors found to be more efficient. There are various advantages of combining Hydrodynamic Cavitation with other oxidants and other Advanced Oxidation Processes such as H<sub>2</sub>O<sub>2</sub>, ozone, and photocatalytic process have been discussed with some recommendation for large-scale operation.

Keywords : Hydrodynamic Cavitation, Oxidation, pharmaceutical, pesticides, dyes and dye intermediates

## 1. Introduction:

The treatment of wastewater containing refractory pollutants from various industries has been a serious environmental issue. Water is polluted by industrial and commercial actions, agriculture practices and by various human activities. Human health is affected by water pollution mainly due to the contamination of drinking water from waste streams. Several industries such as pesticides, pharmaceuticals, dyes, textiles, etc are continuously polluting water as they contain large quantities of organic pollutants. These organic molecules are bio-refractory or very toxic to microorganisms. Hence, conventional biological methods are not capable of completely degrading such complex compounds due to high toxicity and carcinogenicity. Advanced Oxidation Processes involve generation of Hydroxyl radicals to degrade refractory compounds into carbon dioxide and water. Cavitation is defined as the phenomenon of formation of vapour bubbles of a flowing liquid in a region where the pressure of liquid falls below its vapour pressure and then the sudden collapsing of these bubbles in a region of high pressure. Cavitation includes formation of vapour bubbles of the flowing liquid and collapsing of the vapour bubbles. When the pressure of the flowing liquid is less than its vapour pressure, the liquid starts boiling and formation of bubbles take place. These bubbles are carried along with the liquid to higher pressure zones where these bubbles collapse. Hydrodynamic Cavitation is an Advanced Oxidation

Process that is simply generated by the passage of liquid through a cavitating device which is a constriction such as throttling valve, orifice plate, venturi etc. when the liquid passes through the cavitating device, the kinetic energy or the velocity of the liquid increases. Due to throttling, the pressure around the point of vena.

A Review on Hydrodynamic Cavitation as a treatment option for Refractory Organics removal contracta falls below the threshold pressure which is also known as vapor pressure of the medium at operating temperature for cavitation, millions of cavities are generated. And when the liquid jet expands, pressure recovers and the cavities collapse. According to Sunil Rajoriya and AniruddhaPandit, below is the schematic representation for a typical Hydrodynamic Cavitation Reactor, which includes control valves, pressure gauges, storage tank, cavitation generating unit and a centrifugal pump:

### 1.1 Acoustic Cavitation:

In Acoustic Cavitation, Cavities are created by passing the sound waves through the liquid medium. The range of sonic spectrum is 20 kHz to 10 MHz, which is subdivided into three main sections as low-frequency and high-power ultrasound (20– 100 kHz), high-frequency and medium-power ultrasound (100 kHz to 1 MHz), and high-frequency and low-power ultrasound (1–10 MHz). The ultrasound range for chemical and biological applications can be 20 kHz to 1 MHz, while the range of spectrum from 1 to 10 MHz must be used for medical and diagnostic purposes. Ultrasonic waves consist of a rarefaction (expansion) and compression cycles; when these waves are transmitted through a liquid, cavities are formed, followed by a rapid growth and finally the collapse of these generated cavities. The average distance between the liquid molecules is larger in rarefaction cycle but smaller in the compression cycle. Cavitation occurs in rarefaction cycles where negative acoustic pressure is sufficiently large to pull apart the liquid molecules from each other, and the distance between the adjacent molecules can exceed the critical molecular distance. At that moment, the void is created in the liquid, which causes the formation of cavities. Subsequently, in the compression cycle of the sound wave, acoustic pressure is positive, which pushes the molecules together. The cavities will compress (decrease in size) during the compression cycle of ultrasonic wave, and few of them may collapse in a very small time interval. The final collapse phase is adiabatic in nature, thus producing high local temperatures and pressures. Acoustic cavitation has also been employed to degrade bio-refractory pollutants in aqueous solution. However, it was found that the design of acoustic devices and its large scale of operation have a major problem because of higher cost of op-

eration and low energy efficiencies. In recent years, Hydrodynamic Cavitation process is found to be a good alternative to the Acoustic Cavitation for the degradation of complex molecules from wastewater. Also, it has been proved energy efficient in destroying of bio-refractory pollutants, has better prospects for scale-up, is cost-effective, and has higher cavitation activity.

## 1.2 Hydrodynamic Cavitation:

Hydrodynamic cavitation can be produced by the passage of liquid through a constriction such as venturi. When the liquid is allowed to pass through the cavitating device, the kinetic energy/velocity of the liquid increases at the expense of the pressure. The pressure at the throat or vena-contracta of the constriction drops below or equals the vapor pressure of the liquid, the liquid gets vaporized, thus creating a number of vaporous cavities, and these cavities are further collapsed when the pressure recovers downstream of the mechanical constriction. The cavity collapse causes the creation of hot spots.

A Review on Hydrodynamic Cavitation as a treatment option for Refractory Organics removal releasing highly reactive free radicals due to thermal breakdown of molecules and intensification in mass transfer rates. The collapse of bubbles/cavities generates confined "hot spots" where the temperatures can reach up to 10,000 K and pressures of about 1000 atm (Sivakumar and Pandit 2002). In HC, a dimensionless parameter known as cavitation number ( $C_v$ ) is used to characterize the condition of cavitation inside a cavitating device (Saharan et al. 2011). It is defined as the ratio of the pressure drop between the throat and extreme downstream section of the cavitating device to the kinetic head at the throat. A very low value of cavitation number may also result in the condition of choked cavitation and super cavitation which have no practical utility. Thus, the cavitating device should always be operated at an optimum value.

Hydrodynamic Cavitation is capable of generating hot spots, and thus any molecules which are trapped inside the cavities or located itself near the cavity-liquid interface gets thermally broken down into smaller molecules and highly reactive free radicals. In case of wastewater solution subjected to HC, the water molecules will get dissociated into hydroxyl radicals ( $\bullet\text{OH}$ ) under extreme temperature and pressure conditions. These hydroxyl radicals having high oxidation potential can oxidize any organic molecules present in wastewater solution and thereby mineralize such compounds. There are two main mechanisms involved in the destruction of organic pollutants by cavitation, i.e. first, thermal decomposition/pyrolysis of the volatile pollutant molecule entrapped inside the collapsing cavity and second, the reaction of  $\bullet\text{OH}$  radicals with the pollutants. Both mechanisms can take place in the core of cavity, at the interface of cavity, and in bulk liquid medium. Sometimes, the mechanical effects are also significant in destruction of such pollutants. In some cases, the high intensity of shock-waves (which is generated by the collapsing cavity) can break molecular bonds especially the complex large-molecular-weight compounds. The broken down intermediates are more vulnerable to  $\bullet\text{OH}$  attack as well as biological oxidation, and thus it is feasible to increase the rate of mineralization/oxidation of such compounds using HC as a pretreatment

method. This review work provides a detailed overview of generation and mechanism of hydrodynamically generated cavities and also emphasizes the geometrical and designing aspects of the cavitating devices which play a crucial role in degradation of various water pollutants. The accountability and effect of other operating and geometrical parameters on the performance of the cavitating devices is discussed. The importance and advantage of combining HC with other AOPs have also been discussed. The recent findings on synergetic effects of HC in coupling with other AOPs to improve the efficiency of individual AOPs have been discussed.

## 2. Optimum design parameters for hydrodynamic cavitation:

The important parameters which decide the efficiency and the overall cavitation yield in the case of hydrodynamic cavitation reactors are:

1. Inlet pressure into the system;
2. Physicochemical properties of liquid and initial radius of the nuclei;
3. Diameter of the constriction used for the generation of cavities, e.g. hole on the orifice plate; and
4. Percentage free area offered for the flow.

The effect of the various design parameters mentioned above has been studied extensively in terms of the collapse pressures.

### 2.1 Inlet pressure into the system:

It is observed that the spectacular effects of cavitation are predominantly observed only after a particular pressure or operating speed which is defined as the cavitation inception threshold value. Further increase in the inlet pressure increases the collapse pressure due to collapse of single cavities where as the number of cavities goes on decreasing thereby resulting in an optimum inlet pressure in the hydrodynamic cavitation set-up. Thus it can be said that higher operating pressures in the system are preferred up a Review on Hydrodynamic Cavitation as a treatment option for Refractory Organics removal to an optimum value which is a strong function of the geometry of the system.

### 2.2 Physico-chemical properties of liquid and initial size of the nuclei:

By far the liquid properties is one of the very important aspects that affect the cavitation processes, though the magnitude of the effect of all the liquid variables may not be the same. Most of the liquid properties affect cavitation in more than one way. For example, while an increase in the surface tension of the liquid increases the threshold pressure for cavitation making generation of cavitation more difficult, the collapse of cavities is more violent. The opposing effect of liquid properties gives ample scope for optimization. It should also be noted that the physico-chemical properties of the liquid also decide the initial size of the nuclei and the effect of initial radius must also be considered while choosing a particular liquid medium and the process conditions. Gogate and Pandit have clearly shown that the collapse pressure is inversely proportional to the initial size of the nuclei and hence conditions resulting in smaller cavities will be preferred.

### 2.3. Effect of the geometry of the constriction:

The geometry of the constriction has a crucial effect on both the number of the cavitation events and also the pressure pulse generated due to the collapse of a single cavity. Moreover, the geometry affects the pressure distribution and pressure recovery profile downstream of the constriction and hence the active cavitation volume, which is very important considering global effects of the hydrodynamic cavitation reactor. In the case of orifice plate set-up, the free area offered for the flow and also the distribution of the same free area in terms of number and diameter of the holes is important. The diameter of the constriction used affects the inception of cavitation and cavitation inception number increases with increase in the diameter of the hole. Thus for larger diameter holes, the cavitation starts at a higher cavitation number; therefore the extent and intensity of cavitation also increases for the same cavitation number in the system as long as it is below the cavitation inception number. It has also been confirmed that as the diameter of the hole increases, the collapse pressure generated for a single cavity increases. However, there is a downside associated with an increase in the diameter of the hole at constant free area. For the same free area, as one increases the diameter of the hole, the number of holes decreases thereby decreasing the number of cavities generated.

### 2.4 Percentage free area offered for the flow:

The effect of free area on the cavitation intensity and hence the yield has been well studied both on the basis of theoretical analysis of the bubble dynamics behavior. It has been shown that the collapse pressure generated by the collapse of cavities decreases with an increase in the percentage free area offered by the holes in the orifice plates. It is confirmed that the enhanced cavitation effects at lower free areas offered for the flow experimentally. Thus lower free areas offered for the flow are preferred when designing hydrodynamic cavitation reactors.

### 3. Applications of Hydrodynamic Cavitation to wastewater treatment:

Parag Gogate have mentioned about the destruction of p-nitrophenol in recirculating flow loops using a variety of cavitating jet configurations and operating conditions and have shown that, indeed, hydrodynamic cavitation degraded p-nitrophenol. Submerged cavitating liquid jets were found to generate a two orders of magnitude increase in energy efficiency compared to the ultrasonic method.

Sunil Rajoriya and Aniruddha B. Pandit has carried a study to examine the efficacy of Hydrodynamic Cavitation in treating an industrial effluent from Common Effluent Treatment Plant after treatment from Upflow Anaerobic Sludge Blanket due to high COD than the discharge limits. 47% COD was reduced in first 10 passes only and afterwards COD reduction marginally increased. Also TOC reduction of 22% was found in case of using slit venturi.

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Sivakumar and Pandit have first reported the degradation of colored pollutant present in water using HC. They have used

various configurations of orifice plates for the degradation of Rhodamine B dye as a model pollutant. The maximum degradation was obtained at 30 psig using the optimized geometry of orifice plate. They have also concluded that the orifice-based devices can degrade such kinds of pollutants as orifice can generate the higher number of transient cavities with high collapse intensity for producing the desirable changes. They have reported that orifice plate hydrodynamic cavitation set-up can be used for the destruction of the rhodamine B complex in an efficient way as compared to acoustic cavitation.

Manickam have also mentioned about the degradation of orange-G dye using orifice, slit, and circular venturi as cavitating device. They have reported that Hydrodynamic Cavitation alone can efficiently degrade almost 92% of the dye using slit venturi at an optimum pressure of 3 bar. This study has shown a higher output using venturi compared to orifice for the degradation of orange-G dye. The cavitation formed in a venturi is stable and produces greater number of cavities than the orifice plate. In venturi, the pressure recovers smoothly, which leads to the maximum growth of cavities and thus results into a large magnitude of cavity collapse pressure.

D. G. Aseev and A. A. Batoeva have studied the effect of addition of Hydrogen Peroxide in Hydrodynamic Cavitation and they found that hydrogen peroxide causes formation of OH radicals at low pressure. The extra OH radicals formed optimizes the treatment and enhances the degradation rate.

### 4. Conclusion:

Acoustic and hydrodynamic cavitation generate conditions of high temperature and pressure along with release of active radicals which results in many of the chemical transformations under much less severe conditions. The important parameters that affect the collapse pressures generated and hence the overall cavitation yield in the case of hydrodynamic cavitation are found to be inlet pressure, speed of rotation, physico-chemical properties of the liquid medium, constituents of the liquid, geometry of the holes number and diameter of the holes on the orifice plate and initial radius of the nuclei.

An orifice flow is necessary only for intense chemical reactions whereas for milder processes and physical transformations, a venturi flow is recommended.

Hydrodynamic cavitation reactor with lower free area for the flow is recommended.

It was shown that hydrogen peroxide causes the formation of free OH radicals upon hydrodynamic cavitation generated by a low pressure jet device. The main preconditions for the intensification of oxidative destruction processes of organic pollutants with additional cavitation stimulus were determined.

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