

## Cavitation based processes for water and wastewater treatment

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**Abstract** Cavitation based on advanced oxidation processes (Cav-AOPs) is interesting alternatives for already implemented wastewater treatment technologies. Destructive and strongly undesirable phenomena in the industry, i.e., cavitation, revealed to be useful in a positive manner as a source of energy for chemical reactions. During the implosion of cavitation bubbles, focused energy and resulting high temperature and pressure allows to effectively degrade many chemical compounds present in the cavitated liquid phase. The main reactions taking place in the cavitation zone are the thermal decomposition of chemical moieties as well as oxidation with dissolved oxygen and hydroxyl radicals produced during the implosion of cavitation bubbles. Great interest on this topic is supported by an increased number of publications dedicated to several aspects

relating to the formation of cavitation phenomena and its application for water and wastewater treatment as well as hybrid processes based on external oxidants providing effective formation of radical species in cavitation conditions. In this chapter, a state-of-the-art of cavitation-based water treatment technologies, including AOPs, as well as recent trends in this field are discussed. The principles of cavitation combined with AOPs are presented, followed by the evaluation of their effectiveness in the oxidation of organic contaminants. A comparison of hydrodynamic and acoustic cavitation processes for the same type of pollutants has been discussed. For example, the sanitization (disinfection) of water, as well as the degradation of pollutants including sulfide ions and several groups of organic compounds such as sulfur, nitrogen, and oxygen-containing organic compounds, aromatic hydrocarbons, dyes, and pharmaceuticals, have been taken into account while comparing the different cavitation processes.

*Keywords: cavitation; advanced oxidation processes; radicals; wastewater treatment; ozonation; persulfates*

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## 1. Introduction

Cavitation is defined as a phenomenon of formation, growth, and subsequent collapse of microbubbles in extremely short time intervals (milliseconds), which generates large amounts of energy focused in small space. It must also be noted that although energy is released over a very small pocket, cavitation occurs simultaneously in several reactor locations (some indication of the number of cavities in the reactor can be obtained by using theoretical modeling of dynamic bubble equations even if the exact number of cavitation events is difficult to be quantified). Cavitation is generally categorized into four types according to its generation method:

1. Acoustic cavitation: Pressure differences inside the fluid are achieved using sound waves, generally ultrasounds, which relates to a frequency range of 16 kHz to 100 MHz. The chemical modifications resulted from cavitation induced by the passage of sound waves are generally known as sonochemistry (Tzanakis et al., 2017; Yusof et al., 2016).
2. Hydrodynamic cavitation: Cavitation is generated by fluctuations in pressure caused by the fluid flow through different system geometry. For example, a restricted aperture, Venturi flow in the pipe, etc. can be used to achieve an interchange of pressure and kinetic energy (Gagol et al., 2018a; Yi et al., 2018).
3. Optical cavitation: Cavitation is generated by photons of high intensity (laser) light rupturing the fluid (Gagol et al., 2018a).
4. Particle cavitation: Cavitation is produced by any other type of beam of elementary particles such as protons, which ruptures a liquid, as in a bubble chamber (Gagol et al., 2018a).

Acoustic and hydrodynamic cavitation is of scientific and industrial interest among the numerous ways of producing cavitation. In the last few years, acoustic cavitation/sonochemistry has been extensively studied. However, despite extensive research, the lack of expertise in various areas such as materials science, acoustics, chemical engineering, and others to scale up the successfully developed in the lab-scale processes, it cannot be said that these solutions are ready for implementation in chemical processing performed at the manufacturing level. Some attempts of the scale upended successfully. Similarly, the cavitation phenomenon can be generated readily and identified in hydraulic machinery involving liquid transportation. The researchers in the field of hydraulics were aware of cavitation and studied the effects of cavitation in hydraulic machinery (Luo et al., 2016). There were several attempts made to understand the

physiochemical effects of the cavitation phenomenon. Few research groups later explored the distinctive properties, mechanisms, and physical/chemical transformation of materials under the influence of the cavitation phenomenon. Up to now, several studies proved the potential of cavitation technology as an alternative energy-saving tool for various applications like wastewater treatment, process industries, etc. (Gregersen et al., 2019; Li et al., 2018).

## **2. Acoustic cavitation**

Acoustic cavitation is a physical phenomenon in a fluid medium characterized by the growth and collapse of bubbles or cavities under the influence of ultrasounds. Generally, sound waves with frequency ranging from 16 kHz to 100 MHz are used for acoustic cavitation. The ultrasound waves in the liquid medium, causing vibration inside of the liquid, promote the generation of cavities or bubbles. The continuous propagation of ultrasounds leads to the expansion of bubbles, followed by their collapse. The collapse of bubbles under the influence of ultrasound generates several physical effects such as turbulence, shock waves, microjets, etc. Also, the bubble collapse releases extreme energy resulting in a rapid increase in temperature and pressure for a short period named hot spots. It has been observed that under these extreme conditions, highly reactive radicals are generated and used for various applications such as degradation of complex compounds, synthesis of medicines, etc. (Gogate, 2002; Ashokumar, 2011; Yosuf et al., 2016; Gagol et al., 2018).

### **2.1 Optimum design parameters for maximizing the effects of acoustic cavitation**

The important parameters affecting the intensity of collapse and hence the yields from the reactors are:

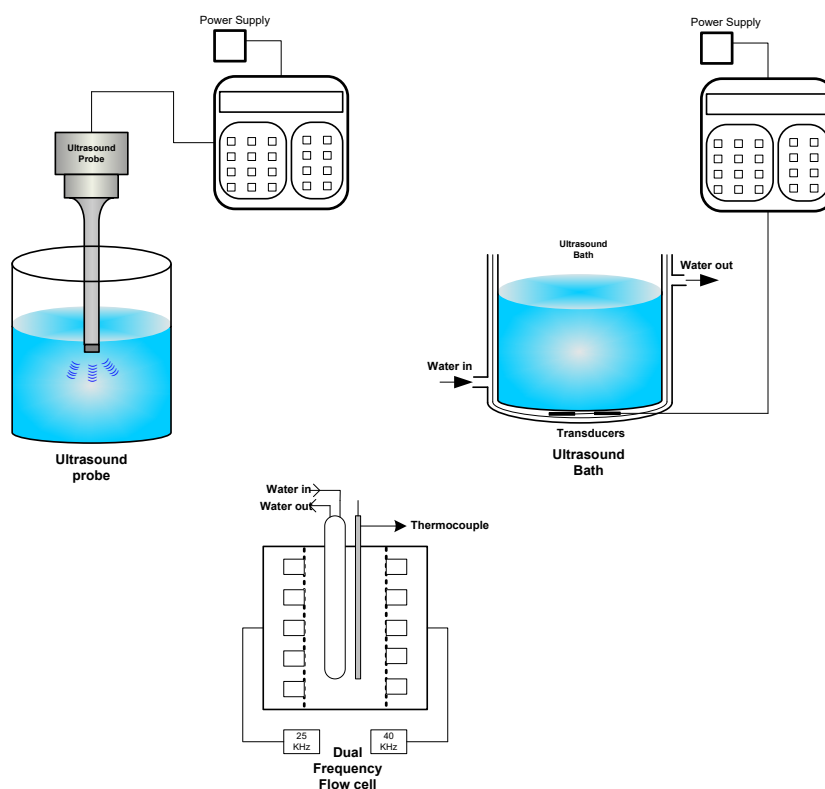
1. The intensity of irradiation;
2. Frequency of irradiation;
3. Initial radius of the nuclei.

#### **2.1.1 Intensity of irradiation**

The ratio of power introduced to the device and the energy dissipated in the medium is described as the intensity of the ultrasonic equipment. Thus, the intensity of irradiation can be

varied by either altering the system power input or by transmission technique where two transducers are placed opposite to each other in the system.

Different types of equipment to induce acoustic cavitation are presented in **Fig 1**. In ultrasonic probes (horns), the vibrations are emitted radially in all directions into the solution from the surface of the probe. In ultrasonic bath type systems, the transducers are placed under the bottom of the reactor such that the ultrasound waves are transmitted through the bottom wall of the bath. The equipment with multiple frequency or transducers is supplied to improve the energy dissipation.



**Fig.1** Various type of sonocavitation reactors

The pressure increase created by a collapse of single-cavity reduces with a rise in irradiation intensity. However, certain key points are needed to be considered. Firstly, the positive impacts of cavitation begin to happen at a critical intensity (the optimum range of intensity varied from 10 to 300 W/cm<sup>2</sup>). It follows the chemical reactions induced by cavitation, which result from the creation of a relatively small amount of free radicals. This amount of free

radicals relies on the intensity and amount of cavitation events that, in turn, depend on the intensity of the radiation.

The change in intensity of irradiation plays an essential role in cavitation behavior. This change can be done either by varying the power input to the system or by providing multiple transducers where energy dissipation is increased. If the intensity is increased by raising the system's power input ( $P/V$ ), there is a rise in the number of cavitation events and an increase in the cumulative pressure pulse (number of produced cavities multiplied by single bubble collapse pressure). In this situation, because of the larger magnitude of the released pressure energy, the degradation rate will be greater. Further increase in energy input enhances the number of cavities causing its coalescence, which results in lowering the degradation rate (Carpenter and Saharan, 2017). At a lower intensity, the change in the transmittance area of ultrasound equipment means that the same energy dissipation happens in a wider area, which results in uniform dispersion, with a greater active region of cavities resulting in increased cavitation output. Thus, the change in transmittance area of ultrasound equipment at lower intensity gives higher cavitation yield. The studies on emulsion characteristics of an oil-water system revealed that, although the power input to the ultrasound bath and horns are virtually identical, bath showed better emulsification effect. In the case of the ultrasound bath, the energy is dispersed over a wider transmission area comparing to the ultrasound horn (Hamidi et al., 2015).

It can be inferred that a gain in intensity increases the cavitation effect up to an optimum level. The maximum cavitation yield can be obtained at a lower intensity with a large transmittance area of ultrasound equipment. Campbell and Hoffmann (2016) observed that there is a deviation from the increasing trend of cavitation effect when the intensity is increased beyond the optimum value of 250 W/L. At higher intensity, the decreasing effect was attributed to the loss of energy in the form of heat, as well as the increase in bubble coalescence, which ends in a lower intensity of bubble collapse, lowered mass transport, and reaction kinetics.

### **2.1.2 Frequency of irradiation**

The produced collapse pressure has already been shown to increase with a rise of radiation intensity in the frequency range typically studied (20-200 kHz frequently observed in ultrasonic applications) using theoretical simulations of Rayleigh-Plesset equations governing the bubble dynamics (Kanthale et al., 2008; Gogate et al., 2001). Higher irradiation frequencies will,





therefore, be preferred in the wastewater treatment systems to degrade chemical pollutants (Matafonova and Batoev, 2019). The enhanced sonochemical effects at higher frequencies can be attributed to reduced cavity dimensions (also leading to greater pressure effects during bubble collapse) and the greater region to volume ratio (improved spreading and mass transfer of liquid-phase reactants to vapor phase when pyrolytic degradation occurs). Moreover, at a higher frequency, the generated bubbles go through fewer acoustic cycles before reaching the required resonant dimension for collapse. Therefore, more bubbles at higher frequencies promote diffusion at a faster rate before a transient bubble collapse takes place. The frequency of ultrasound equipment cannot be changed over a variety of ranges since the transducer gives the highest transmission effectiveness at its resonating frequency. The range of frequencies usually used for physical effects is between 20 and 200 kHz, while greater frequencies are still used effectively for some cases.

The liquid inside the reactor is irradiated by immersion type transducer (ultrasound probe/sonotrode/horn) or the transducers placed at the bottom (ultrasound bath). The active regions under the influence of ultrasound waves are localized mostly near the surface of the transducer. To overcome these limitations, two or more transducers with similar or different frequencies are used. Transducers are mostly used in series of few to several pieces localized in a line parallel to the axis of the reaction chamber (often localized vice-versa on both sides of reaction chamber) – but sometimes also other geometries of transducers placing are used. In the case of the immersion type transducer, the irradiation is strongly localized in the place of sonotrode immersion. The irradiation intensity decreases along with the distance of sonotrode.

In the ultrasound reactor, there is a possibility of acoustic standing waves formation with consecutive positive and negative pressure phases from the different medium interface or reflection of waves from the reactor wall (Luo et al., 2018). Due to the standing waves, big bubbles tend to coalesce, and thus, the energy is not evenly dissipated, leading to a reduction in reactor efficiency (Hallez et al., 2007). To overcome these limitations, the use of a dual-frequency processor or a parallel plate ultrasonic processor is a viable alternative. The attenuation of the sound would be decreased when the plates are positioned close together and result in the interference pattern of waves, minimizing standing waves and improving the cavitation process. The use of multiple frequency acoustic cavitation showed a four-fold increase in cavitation yield when compared with the single frequency. These multiple frequency modes (dual-

frequency (17 kHz + 33 kHz)) has been employed in the treatment of large volume of wastewater (about 50 L) containing bacteria subtilis (concentration of approximately  $10^4$  CFU/mL) resulted in 85.25% efficiency (to reduce bacteria contamination) of treatment in 30 minutes while the single frequency mode (33 kHz) gave only 30.26% (Zou and Wang, 2017).

### **2.1.3 Initial size of the nuclei**

The growth and collapse of bubbles from small-sized nuclei are more intense. Therefore, the reduction of the initial bubble size promotes a better cavitation effect. The physical properties such as viscosity, surface tension, and vapor pressure of the fluid influence the behavioral characteristics of bubbles produced (Sharma et al., 2008; Gogate and Pandit, 2000). The threshold pressure required for bubble collapse increases with the increase in viscosity due to cohesive forces. Thus, the liquid medium with lower viscosity promotes a better cavitation effect. The use of a high vapor pressure medium instantly increases the vapor content inside the bubble, which results in a lesser cavitation effect due to the condensation process. Hence, liquid medium with low vapor pressure is preferred for higher bubble collapse intensity, which will lead to a higher cavitation effect. The surface tension of the liquid medium is directly proportional to the bubble formation and collapse pressure intensity because higher surface tension medium increases bubble contraction. The bubble collapse causes extremely high-pressure increase near the place of collapse; therefore, high surface tension media give higher preference when cavitation is used for treatment applications like disinfection of bacteria, milk process, etc. (Brennen, 2014).

## **3. Hydrodynamic Cavitation**

Hydrodynamic cavitation is a rapid transformation in the liquid when the liquid passes through a constriction such as a Venturi tube or orifice. In the place of constriction, the linear velocity of the liquid significantly increases at the cost of pressure drop – often below the vapor pressure of the liquid– leading to the formation of cavitation bubbles (Tao et al., 2016). After the constriction, the diameter of the tubing gets back to normal value, the linear velocity of the liquid falls, and the static pressure recovers, which results in the collapse of the cavities. Turbulence intensity in the cavitation and collapse zones has a high impact on the intensity of cavitation. Thus, by varying the geometric and operating conditions of the reactor, the cavitation intensity is optimized concerning the degradation effects of target pollutants present in the treated medium.



To link flow conditions with the strength of cavitation, a dimensionless number, known as cavitation number ( $C_v$ ), is used (equation 1):

$$C_v = \frac{P_2 - P_v}{\frac{1}{2} \rho v^2} \quad \text{Eq. 1.}$$

where  $P_2$  is the fully recovered downstream pressure,  $P_v$  is the vapor pressure of the liquid/medium,  $\rho$  is the liquid density, and  $v$  is the velocity of the liquid at the throat of the constriction (Gogate, 2002).

Ideally, the initiation of cavitation happens at  $C_v = 1$ , and important cavitation impacts occur at  $C_v$  values below 1. When  $C_v$  reaches zero value, supercavitation takes place. At this condition, a cavitation cloud is formed, which strongly minimizes the effect of the bubbles collapse due to the coalescence of the bubbles.

The major advantages of hydrodynamic cavitation are as follows:

1. Reactions that require moderately rigorous conditions can be carried out under the surrounding conditions, which is the main benefit of the hydrodynamic cavitation.
2. It is the cheapest and most energy-efficient method of a cavitation generation.
3. The construction of cavitational equipment is relatively simple.
4. Such reactors are easy and cheap in maintenance.
5. It is relatively simple to scale up such processes.

It should be noted that, in terms of temperature and pressure, hydrodynamic cavitation provides a significantly lower intensity of collapse than acoustic cavitation. However, the simplicity and potential for implementation of hydrodynamic cavitation in the industry make it of high interest both in scientific work as well as real scenario applications.

### **3.1 Optimum design parameters for hydrodynamic cavitation**

Three aspects are commonly included in the studies for a full understanding of the hydrodynamic phenomenon:

1. Cavitation number.
2. Physico-chemical properties of the liquid and initial size of the nuclei.
3. Type of cavitating reactor and its design details.

In terms of bubble collapse, pressure-based upon numerical simulation using bubble dynamics equations and studies in separate reactors, the impact of the multiple design parameters

listed above is widely examined. It is worth noting that there has been thorough research about the impacts of multiple design parameters on the efficiency of hydrodynamic cavitation-reactors, and only guidance on the selection of a certain parameter has been provided with fundamental discussions.

### **3.1.1 Cavitation number**

Cavitation number is one of the most important parameters for measuring the efficiency of the cavitation treatment process. This parameter is mutually interrelated with system inlet pressure. The required pressure on the fluid induces velocity via the cavitation system. With the increasing operating pressures, the flow velocity is increased across the throat, and the number of cavitation is decreased. The lower cavitation number generates more cavities as a result of high-pressure input, resulting in more hydroxyl radicals helping in maximum degradation of the pollutant compound. Many research studies found that the cavitation number ranging from 0.14 to 0.29 with operating inlet pressure 3-5 bar gave maximum efficiency in treatment processes (Boczka et al., 2018).

### **3.1.2 Physico-chemical properties of the liquid and initial size of the nuclei**

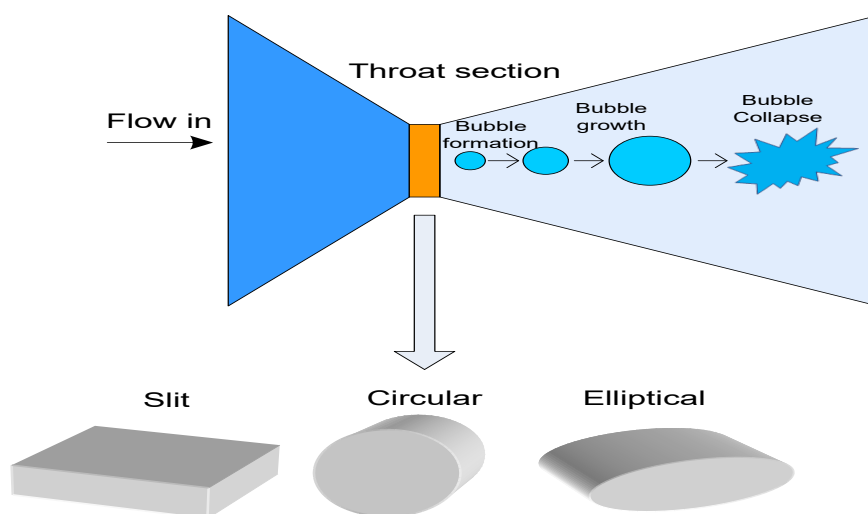
Similar to acoustic cavitation, the degradation process of hydrodynamic cavitation can be influenced by physicochemical properties of the aqueous medium such as liquid vapor pressure, density, viscosity, surface tension, dissolved gas in the liquid, etc. Cavitation takes place in a liquid medium when the cohesive forces are overcome. Thus, liquids with high viscosity have a much lower cavitation effect than liquids with low viscosity. As a result, the maximum cavitation effect can be achieved in liquids with low viscosity, such as water. For non-Newtonian fluids, the effect of viscosity on cavitation effectiveness is even more pronounced. The vapor pressure of the liquid medium also affects the efficiency of the cavitation. The production of cavities increases with the increase in the vapor pressure of the liquid medium. The cavities produced from high vapor pressure medium have lower cavitation intensity, which can efficiently degrade only simple organic compounds. While the lower vapor pressure medium generates cavities with a higher cavitation intensity, which is needed to degrade persistent organic compounds efficiently. The liquid medium with high surface tension has the most powerful cavitation effect (relating to the energy of bubble collapse). The nature of the contaminant molecule in the liquid medium also influences the efficiency of degradation with



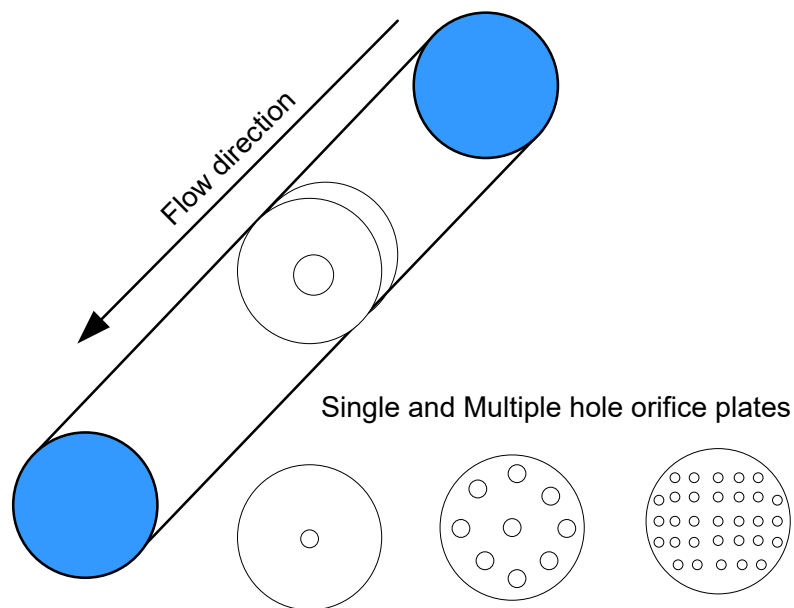
hydrodynamic cavitation. When the pollutant molecules are hydrophobic, they diffuse to the gas-water interface; thus, they are near the collapse of cavities. This results in the direct attack of  $\cdot\text{OH}$  radicals formed during bubble collapse and thus increases the degradation efficiency. If the pollutant molecules are hydrophilic, the molecules remain in the liquid medium and are not affected by the cavities collapse. The radical species need some time to reach these compounds.

### 3.1.2 Type of cavitating reactor

Hydrodynamic cavitation can be generated when the liquid is passed through a constriction. The kinetic energy and velocity of the liquid passing through a constriction increase. At the same time, the static pressure falls to fulfill the Bernoulli equation. Cavitation occurs when the static pressure becomes lower than the vapor pressure of the liquid. Simply, it could be said that under this condition, “the liquid starts to boil.” The phenomenon of cavitation generation can take place at an orifice plate, in the throat of the Venturi tube, as well as near the surface of the high-speed rotor or high-speed homogenizer. Orifice and Venturi-based systems are efficient in generating cavitation for chemical reactions. Among orifice and Venturi, the cavitation generation is stable in Venturi-based hydrodynamic cavitation (HC) devices and, therefore, is mostly preferred for water treatment applications. The different types of Venturi-based and orifice-based HC devices are presented in **Figures 2 and 3**.

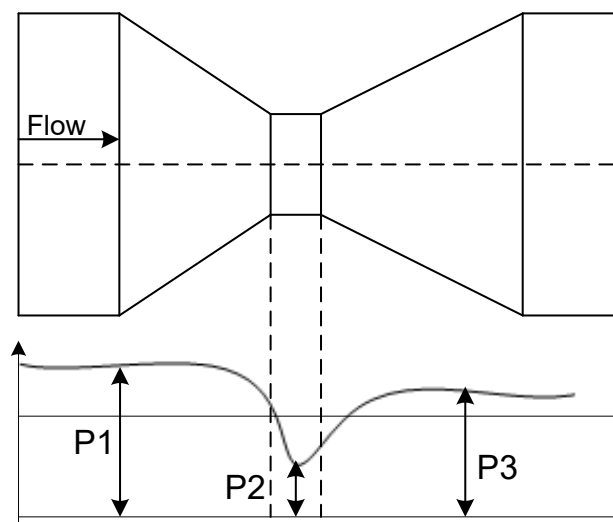


**Fig.2** Venturi-based cavitating device



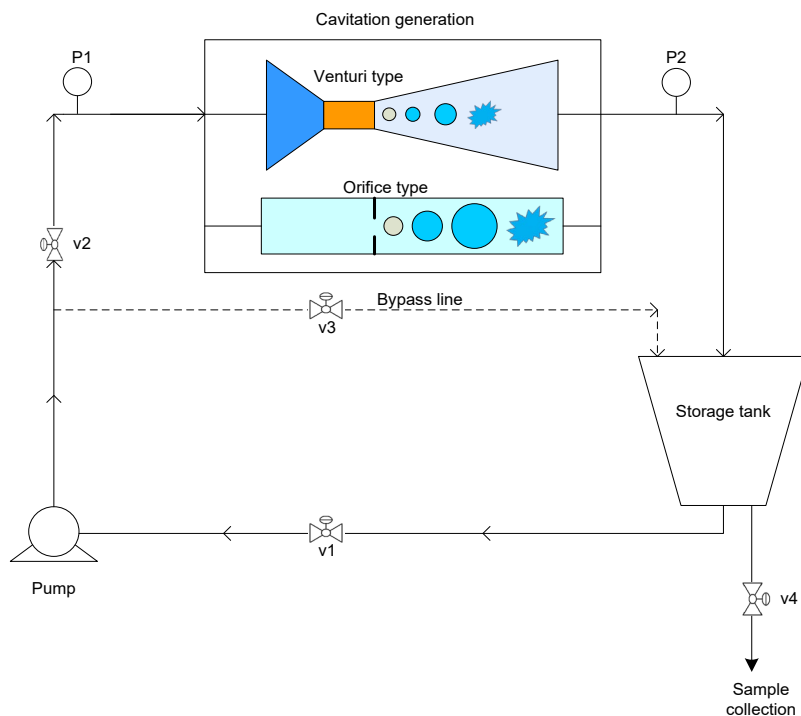
**Fig.3** Different types of orifice-based HC device

The constriction can have a form of a throat (Venturi system, it can have a circular shape or other like elliptical or a slit type), i.e., a short length of Venturi, between the convergence and divergence sections, having much smaller diameter compared to the diameter of the inlet and outlet of the Venturi. In the case of the orifice, a plate placed inside of the orifice has one or more holes having a small diameter. In each system (throat or orifice), the small internal diameter region is responsible to “speed up” the liquid to a linear velocity allowing to (according to Bernoulli equation) obtain an effective increase of dynamic pressure and a corresponding decrease of static pressure causing the formation of cavitation bubbles (equation 1 - cavitation number below 1 and – value P2) **Figure 4**.



**Fig. 4** Scheme of static pressure profile in the Venturi – P1 pressure before, P2 pressure at the throat, P3 – pressure after the throat

A schematic arrangement of the hydrodynamic cavitation reactor is illustrated in Figure 5 where a Venturi tube is used to generate a cavitation effect. The set-up consists of a closed circuit with a storage tank, a pump, and a cavitating device (Venturi tube). The pump discharge is divided into 2 sections. The primary first line consists of a Venturi or orifice (cavitating device). The pressure gauge (P1) is mounted near the inlet of the Venturi or orifice, another one (P2) is attached to the outlet or discharge line from the Venturi or orifice. The fluid flow rate through the cavitation device is regulated by the pump total flow rate and a bypass line. The bypass line allows the use of optimal rotation speed of the pump and to split the stream to the desired flow rate into the cavitation system, and the remaining volume passed through the bypass. The flow rate through the mainline is regulated at the appropriate places using regulation valves. The application of the bypass is used mainly for research purposes. It allows using one pump with the regulator of the flow rate, which along with the bypass line, allows optimizing the cavitation conditions with respect to cavitation number (affected directly by the volumetric flow rate by the resulting linear velocity through the constriction). The flow rate splitting is not economically feasible; thus, it is not used in industrial practice. Furthermore, this feature should be included in economic analysis performed in research papers for adequate calculation of energy demand for optimized cavitation numbers.



**Fig.5** Schematic representation of hydrodynamic cavitation reactor setup

## 4. Cavitation based Advanced Oxidation Processes (Cav-AOPs)

### 4.1. Formation of radical species under cavitation conditions

The energy associated with physical phenomena can be used for intensification of chemical processes, which helps in developing novel solutions in various industries. Thus, the energy released during the cavitation phenomenon can be used to accelerate the formation of reactive radicals used in advanced oxidation processes (AOPs). AOPs have shown significant potential in the removal of organic pollutants over the past few decades. AOPs are defined as a class of techniques involving strong oxidizing species such as hydroxyl radicals ( $\text{HO}^\bullet$ ) to degrade the pollutants. Having a high capability for destruction of pollutants,  $\text{HO}^\bullet$  are generated and used in a majority of AOPs. Various types of AOPs were explored to decompose or mineralize even the refractory organic molecules which possess recalcitrance to be conventional and biological water treatment technologies. As effective treatment technologies, AOPs can be applied as a single treatment process or incorporated into conventional treatment schemes depending on



properties of the pollutant, wastewater origin, water matrix, pH, etc. Despite the high efficiency demonstrated in lab-scale experiments, AOPs found limited use in industrial-scale, mainly due to the high cost of the treatments as well as maintenance (Gogate and Pandit, 2004).

This effect of cavitation is often used in effluent treatment technologies because it ensures the disruption of bacterial cultures, decomposition of persistent organic compounds and dissociation of water molecules into a variety of radical species, including  $H^{\bullet}$ ,  $HO^{\bullet}$ ,  $HO_2^{\bullet-}$ ,  $HOO^{\bullet}$  (Gagol et al., 2018a; Gagol et al., 2018b). The generated radicals are extremely unstable and reactive due to their high redox potential. The reaction between organic contaminants and these reactive radicals is extremely fast and non-selective, mainly controlled by the production yield of radicals and mass transfer processes between radicals and pollutants. According to recent reports, cavitation is effective in the degradation of organic pollutants present in a variety of water matrices such as tap water, groundwater, and industrial effluents. When applied individually, cavitation was often reported to give a low rate of degradation, which ranges from 20 to 50%. Comparably, high degradation rates were obtained when cavitation was combined with hydrogen peroxide, ozone, and/or peroxone, often leading to 100% removal efficiency (Gagol et al., 2018a).

#### **4.2. Effect of external oxidants –oxygen, ozone, hydrogen peroxide, persulfates – hybrid processes**

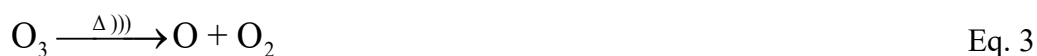
A combination of cavitation with an AOP is a physicochemical technique, recently adopted for wastewater treatments. As a hybrid water treatment technique, the combination of cavitational methods with various AOPs has been reported in the literature for the degradation of many organic pollutants (Boczkaj et al., 2017; Gagol et al., 2018b; Gagol et al., 2019). Obtained results indicated a considerable increase in degradation rates of pollutants, which was attributed to the intensification of the production of radicals and their facilitated diffusion into the liquid. It is widely recognized that the enhancement is a result of synergism between cavitation and AOP due to the similarity in the mechanism of pollutant degradation and jointly overcome drawbacks (Bagal and Gogate, 2014a). To measure the improvement obtained in the hybrid technique, the index of synergy ( $\mathcal{E}$ ) can be calculated using equation 2. Its value indicates the degree of synergism between the combined techniques in the observed experiment or its absence if the calculated value of the synergy index is below 1.

$$\varepsilon = \frac{k_{Cav/AOPs}}{k_{Cav} + k_{AOPs}} \quad \text{Eq. 2}$$

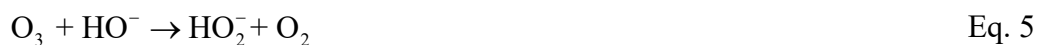
Typical hybrid approaches include hydrodynamic and acoustic cavitation at optimum operational conditions coupled with AOPs based on external oxidants, UV irradiation, photocatalysis, electrochemical oxidation, and Fenton's reaction. Most of the typically used external oxidants (oxygen, ozone, hydrogen peroxide, persulfate) were already tested in Cav-AOPs.

#### 4.2.1 Hybrid processes based on ozone and cavitation phenomenon

Appreciable insights on the decomposition of methyl tert-butyl ether have been gained by acoustic cavitation in the presence of ozone (Kang and Hoffmann, 1998). In this study, the combination of ozone (0.30 mM) with ultrasonic irradiation (205 kHz, 200 W) compared to sole ultrasonic treatment increased the observed first-order rate constant of methyl tert-butyl ether from  $8.5 \times 10^{-4}$  to  $33.2 \times 10^{-4} \text{ s}^{-1}$ . It was concluded that the increase in kinetic rates was caused by enhanced direct reaction of the substrate with ozone at the cavitation bubble interface or due to indirect reactions with ozone decomposition products. Further studies of the ozone effect on the formation rate of hydrogen peroxide provided a more plausible explanation for the observed reactions (Kang and Hoffmann, 1998). Thus, in the coupled process of ozone and ultrasound, ozone molecules were proposed to undergo thermal decomposition in the gas phase of the cavitation bubble to yield molecular and atomic oxygen. A wide variety of radical reactions may occur initiated by an unstable oxygen atom, including the formation of hydroxyl radicals ( $\text{HO}^\bullet$ ) (Gagol et al., 2018a):



At the interfacial zone, ozone reacts with hydroxide ion  $\text{HO}^-$  and the conjugate base of  $\text{H}_2\text{O}_2$  ( $\text{HO}_2^-$ ) to generate hydroperoxyl ( $\text{HO}_2^\bullet$ ) and hydroxyl radical ( $\text{HO}^\bullet$ ) in accordance of reactions (5) and (6).



$\text{HO}_2^-$  can be formed not only as a product of the reaction between ozone and  $\text{HO}^\bullet$  but also as a result of  $\text{H}_2\text{O}_2$  disassociation (reaction (7)):





Substantial enhancement in the degradation of methyl tert-butyl ether was achieved by the combined process of ozonation plus ultrasound compared to the sole use of ozonation or ultrasound. The enhanced degradation was attributed to the significant contribution of the direct reaction of ozone with the pollutant. This reaction is almost negligible at ambient conditions but accelerated due to zones of high temperature at the interfacial regions of the cavitation bubbles and can be illustrated as follows:



During the ozonation-ultrasound process,  $\text{H}_2\text{O}_2$  was reported to play a crucial role. Being readily formed by sonolysis of water, it also reacts with ozone (reaction (9)) contributing to the overall removal of pollutants:



Reaction (9) initiates a chain of radical reactions, which leads to the decomposition of ozone and the formation of reactive radicals ( $\text{HO}^\bullet$  and  $\text{HO}_2^\bullet$ ). On the other hand, the accumulation of  $\text{H}_2\text{O}_2$  quenches radical species, thus terminating the radical chain reactions. The combination of reactive radicals to form stable products could be considered as chain-termination reactions (e.g., Eqs. 10 and 11):



Similarly, the higher removal efficiency of organic contaminants has been reported for ozonation, coupled with hydrodynamic cavitation (Gore et al., 2014). Enhancement of mass transfer of ozone along with the accelerated formation of  $\text{HO}^\bullet$  and atomic oxygen induced by cavitation were highlighted as the main advantages of the coupled process. The mineralization degree of reactive orange 4 dye was significantly increased when hydrodynamic cavitation was coupled with ozonation. TOC removal of 14.67% was obtained in the sole hydrodynamic cavitation process, which increased to 76.25% by combining ozone with hydrodynamic cavitation (Gore et al., 2014). The synergy index of 3.03 was estimated based on the mineralization rate and indicates that the hybrid process of hydrodynamic cavitation with ozone is better as compared to individual processes (Gore et al., 2014). Similar observations were made for the degradation of methyl tert-butyl ether by ultrasound coupled with ozonation and phenol under suction-cavitation

in the presence of ozone using orifice as cavitation unit (Kang and Hoffmann, 1998; Wu et al., 2011). Studies on the degradation of triazophos revealed the superiority in the effectiveness of ozonation combined with hydrodynamic cavitation over ozonation alone. The Pseudo-first order rate constant of  $41.3 \times 10^{-3} \text{ min}^{-1}$  observed in ozonation alone was increased to  $58.26 \times 10^{-3} \text{ min}^{-1}$  for the combined process. TOC removal of 96% was achieved in 60 min when ozone loading of 1.95 g/h was injected directly into the solution tank. The introduction of ozone into the solution tank instead of at orifice improved the degradation rate of triazophos by 8%. This was attributed to the effect of a drop-in inlet pressure of the medium before the orifice plate resulting from the introduction of ozone and thus the limitation of the cavitation phenomenon. At the same time, amounts of oxidants in the system become limited due to decreased solubility of ozone and oxygen caused by the lowered pressure. The introduction of ozone at the orifice plate dropped the flow rate of water from 290 L/h to 120 L/h at 5 bar pressure. A lowered flow rate leads to a decrease in the number of passes of the liquid in the reactor, thus affecting the dissociation of water and ozone-producing reactive radical species (Gogate and Patil, 2015).

Another example of the application of the ozonation, coupled with hydrodynamic cavitation, is the treatment of organic pollutants present in the effluents from bitumen production. Oxygenated organic compounds such as 1-propanal, 2-pentanone, furfural, 1-hexanol, phenol, m-cresol present in the complex composition of real industrial effluent were almost completely degraded by hydrodynamic cavitation aided with ozone after 180 min of treatment. Studies on COD and BOD profiles of the effluent revealed a 40% and 50% reduction of these parameters describing changes in total pollutants load – which in terms of industrial, highly polluted effluents confirms the applicability of this technology for effective pre-treatment of such effluents before biological treatment stage (Boczkaj et al., 2017). Ozonation combined with hydrodynamic cavitation was suggested as a potentially effective approach to lower the content of toxic organic compounds, especially phenols, its derivatives, as well as other oxygen-containing compounds that are known to be toxic to activated sludge used in biological treatment of refinery effluents. Furthermore, this process is sufficient to simultaneously decolorize, disinfect, and reduce malodorousness of the effluent.



#### 4.2.2 Hybrid processes based on hydrogen peroxide and cavitation phenomenon

The aqueous solution of hydrogen peroxide is an effective and green oxidizing agent commonly used in various technologies. Having  $pK_a = 11.69$ , hydrogen peroxide is considered a weak acid, and its properties strongly depend on the pH value of the reaction medium. At acidic conditions, hydrogen peroxide shows an oxidation potential of 1.80 V, while this value drops to 0.87 V at pH 14. Under alkaline conditions, reactions with hydroxyl ions induce an increasing tendency of decomposition of  $H_2O_2$  resulting in the formation of per hydroxyl anion and water (Eq. 12) (Spalek et al., 1982):



Low stability of  $H_2O_2$  in alkaline media is the main disadvantage, which limits its practical use as a sole oxidizing agent. As a sole oxidant,  $H_2O_2$  is used in industrial processes involving direct oxidation of carboxylic acids, polycyclic aromatic hydrocarbons, and haloalkenes at acidic conditions. Extreme conditions of collapsing gas bubbles during hydrodynamic and acoustic cavitation, lead to the thermal dissociation of  $H_2O_2$  into  $HO^\bullet$ , which is capable of decomposing a wide range of organic contaminants in water and wastewater:



Once generated,  $HO^\bullet$  initiate radical chain reactions and amplify oxidation of organic contaminants, which are reduced or degraded completely. Despite numerous studies, the detailed mechanism of oxidation reactions has not yet been fully elucidated. Nevertheless, it has been established that the oxidation of halogenated organic compounds involves abstraction of halogen atom followed by the addition of oxygen to the formed organic radical. This step results in the formation of the corresponding intermediates, such as aldehydes, ketones, carboxylic acids, etc. which are subsequently converted to  $CO_2$ ,  $H_2O$ , and halogen anions in the final step.

Both hydrodynamic (HC) and acoustic cavitation (AC), in combination with  $H_2O_2$ , showed an enhanced degradation efficiency for a variety of pollutants. The improvement in the degradation efficiency was concluded as a result of the intensification of  $HO^\bullet$  production in treated medium (Gagol et al., 2018a; Pradhan and Gogate, 2010; Patil et al., 2014). For example, organosulfur compounds (2-ethylthiophene, dibutyl sulfide, di-tert butyl sulfide) were degraded above 80% under HC induced by Venturi tube ( $C_v = 0.14$ , inlet pressure 8 bar). Phenol and its derivatives (4-ethylphenol, m-cresol, o-cresol) were completely degraded in 360 min (Gagol et

al., 2018a). After 180 min of the treatment, the lowest oxidation degree was observed for 2-nitrophenol (66.9% – AC + H<sub>2</sub>O<sub>2</sub>, 62.9% – HC + H<sub>2</sub>O<sub>2</sub>). In this case, the lower degradation rate was attributed to the formation of intermediate products, which compete for HO• due to its non-selective nature. Comparable results in degradation of 2-nitrophenol were obtained by AC + H<sub>2</sub>O<sub>2</sub> under acidic conditions (59% in 90 min at pH 3.7, C<sub>0</sub> = 1%, V = 7 L, T = 28 °C, [H<sub>2</sub>O<sub>2</sub>] = 5 g L<sup>-1</sup>, AC = 25 kHz, 1 W). Complete degradation of imidacloprid was obtained for hydrodynamic cavitation aided with H<sub>2</sub>O<sub>2</sub> in 120 min in acidic media (pH 3, C<sub>0</sub> = 20 ppm, V = 4 L, T = 34 °C, [H<sub>2</sub>O<sub>2</sub>] = 80 ppm, inlet pressure = 4 bar, C<sub>v</sub> = 0.37). When comparing two different cavitating devices (hydrodynamic and acoustic) aided with H<sub>2</sub>O<sub>2</sub> in terms of the degradation efficiency, an improvement of 5-10% was observed for hydrodynamic cavitation. It was suggested that the reactor of hydrodynamic cavitation with a cavitation number of 0.14 possesses a higher cavitation intensity and provides a longer residence time in the cavitation zone, increasing the probability of the reaction with HO• comparing to an acoustic cavitation system based on 25 kHz frequency ultrasonic transducers. According to these results, both cavitation techniques, in combination with H<sub>2</sub>O<sub>2</sub>, can effectively be used in the degradation of organic contaminants in a wider pH range.

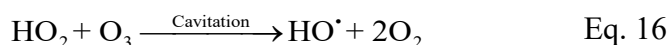
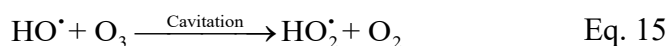
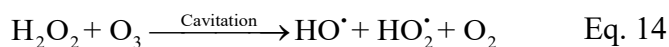
Decomposition of diclofenac sodium using hybrid processes based on hydrodynamic cavitation and hydrogen peroxide has been reported by Bagal and Gogate (2014b). It was combined with the addition of catalyst (TiO<sub>2</sub>). Effect of inlet fluid pressure (2-4 bar), initial pH of the solution (2-7.5) as well as TiO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> loadings were studied to optimize the operating conditions. The maximum extent of degradation of diclofenac sodium achieved by sole hydrodynamic cavitation was 26.85 at an optimized inlet pressure of 3 bar and pH of 4. Hybrid processes of hydrodynamic cavitation with UV, UV/TiO<sub>2</sub> and UV/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> resulted in enhanced degradation as compared to individual processes. 95% degradation and 76% TOC removal have been observed when hydrodynamic cavitation was coupled with UV/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> at optimal conditions. In this case, the synergy index was estimated to be 2.5.

Studies on the degradation of 2,4-dinitrophenol revealed higher removal efficiency for a homogeneous Fenton process coupled with HC rather than Fenton-like processes coupled with HC. Thus, underestimated optimal conditions, conventional Fenton process ([H<sub>2</sub>O<sub>2</sub>] = 0.3 g/L, [FeSO<sub>4</sub>] = 0.6 g/L) in combination with hydrodynamic cavitation gave complete degradation of 2,4-dinitrophenol in 60 min, whereas Fenton ([H<sub>2</sub>O<sub>2</sub>] = 0.4 g/L, [Fe] = 0.6 g/L) resulted in 54.1%

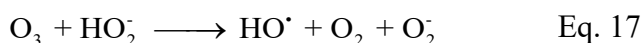
of degradation in 120 min. The Fenton-like process, with a loading ratio of H<sub>2</sub>O<sub>2</sub>: CuO (1:6), achieved 29.8% in 120 min (Bagal and Gogate, 2013). These processes have demonstrated greater efficiency than the sum of individual efficiencies that could be achieved with a separate treatment – which proved the synergism of the combined processes.

#### 4.2.3 Hybrid processes based on peroxone and cavitation phenomenon

The combination of H<sub>2</sub>O<sub>2</sub> with O<sub>3</sub> is a type of AOP with a high oxidation capacity and is named as peroxone. The reaction of H<sub>2</sub>O<sub>2</sub> with O<sub>3</sub> gives rise to a large number of HO•, responsible species for the degradation of organic contaminants present in wastewaters. The superior activity of the peroxone process over ozonation was demonstrated for the degradation of refractory organic compounds. An increase in HO• concentration in the reaction system was suggested as the main factor of the improvement, which was induced by accelerated decomposition of O<sub>3</sub> in the presence of H<sub>2</sub>O<sub>2</sub> (Gagol et al., 2018b). The mechanism of reactive radicals (HO• and HO<sub>2</sub>•) formation during the peroxone process involves decomposition of O<sub>3</sub> via electron transfer with H<sub>2</sub>O<sub>2</sub> or activation of H<sub>2</sub>O<sub>2</sub> at alkaline conditions. The resulted HO• and HO<sub>2</sub>• are capable of oxidizing practically every contaminant present in the treated medium. The reactions generating reactive radicals during peroxone process can be summarized as follows (Boczka et al., 2018):



It was reported that H<sub>2</sub>O<sub>2</sub> transforms into ionized form (HO<sub>2</sub><sup>-</sup>, pK<sub>a</sub> = 11.6), which rapidly reacts with ozone yielding HO• according to the following reaction (Paillard et al., 1988):



This reaction is significantly intensified at high pH values and increases HO• concentration, thereby increasing the efficacy of the process. Favorable contribution of basic pH on the removal of various pollutants by cavitation/peroxone system has been widely reported. For instance, carbon disulfide (CS<sub>2</sub>), dimethyl sulfide (C<sub>2</sub>H<sub>6</sub>S), and di-*tert*-butyl-disulfide (t-Bu<sub>2</sub>S<sub>2</sub>) were effectively removed from the effluent of bitumen production by HC and AC combined with peroxone process at strongly alkaline pH (Gagol et al., 2019). Complete degradation of CS<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>S, t-Bu<sub>2</sub>S<sub>2</sub> by the combined operation of hydrodynamic cavitation (C<sub>v</sub> = 0.14) with peroxone



was achieved in 30 min, while the sole use of HC took 120 min to reach the same degradation rate. Similar trends in the degradation of the target organosulfur compounds were observed during acoustic cavitation (173 W/L, 25 kHz) with peroxone. Based on oxidation rates, the system of AC + peroxone was found faster than HC + peroxone in the degradation of t-Bu<sub>2</sub>S<sub>2</sub>, as the sonic energy is effective in breaking down and oxidation of this contaminant. Both techniques demonstrated the rapid removal of sulfide ions and organosulfur contaminants from the caustic industrial effluent without pH adjustment. COD reduction results of the post-oxidative effluent showed no significant difference between hydrodynamic and acoustic cavitation in combination with peroxone. Thus, 51 and 59% of COD removal were obtained for acoustic (172.9 W/L, 25 kHz) and hydrodynamic cavitation (220 W/L) aided by peroxone in 360 min, respectively. Slightly higher effectiveness of the HC + peroxone system was attributed to the increase of ozone solubility in the bulk of the effluent as the stream of O<sub>3</sub> is injected into the overpressure zone of the Venturi tube.

Further investigations revealed that both methods are highly effective in the degradation of aromatic compounds, alcohols, aldehydes, and ketones (Gagol et al., 2018c). Similarly, the positive impact of the combination of HC ( $C_v = 0.11$ , pH 7.8) and peroxone was demonstrated in the elimination of natural organic matter from drinking water. In this case, studies on the efficiency of DOC removal showed a decrease of the initial concentration (up to 3 mg/L) by 40% after 60 min (Čehovin et al., 2017).

The application of hybrid processes based on cavitation and peroxone proved to have significant advantages. It follows from Gagol et al. (2018a):

- increased formation of hydroxyl radicals in cavitation conditions,
- increased mass transfer of ozone to the aqueous phase (it must be absorbed by water from injected gas phase) and
- the higher rate constant values of organic pollutant degradation.

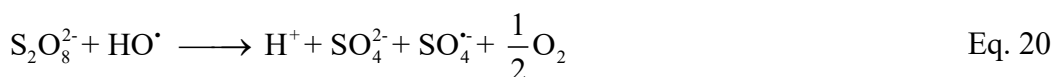
#### 4.2.4 Hybrid processes based on persulfate and cavitation phenomenon

In recent years, sulfate radical based AOPs (S-AOPs) has been identified as an alternative to classical AOPs (i.e., hydroxyl radical based AOPs) and received a growing interest of researchers. S-AOPs generate and use sulfate radicals (SO<sub>4</sub><sup>•-</sup>), which possess a strong oxidation potential (2.6 V). Sulfate radicals have a longer half-life than OH<sup>•</sup> (SO<sub>4</sub><sup>•-</sup> = 30 - 40 μs and OH<sup>•</sup> =





< 1 μs) (Oh et al., 2016). Therefore,  $\text{SO}_4^{\bullet-}$  could diffuse efficiently into the reaction mixture with high mass transfer and larger contact time for the reaction with target contaminants (Oh et al., 2016).  $\text{SO}_4^{\bullet-}$  prefer electron-transfer reactions, whereas  $\text{OH}^{\bullet}$  reacts through a series of reactions involving electron transfer, electrophilic addition, and hydrogen abstraction (Oh et al., 2016). The combination of the high oxidation potential of  $\text{SO}_4^{\bullet-}$  and slow consumption rate of precursor oxidant (stability), makes S-AOPs very effective for the degradation of recalcitrant organic compounds. Two types of  $\text{SO}_4^{\bullet-}$  precursors are commonly used in S-AOPs: persulfate (PS) and peroxymonosulfate (PMS). Persulfate ( $\text{S}_2\text{O}_8^{2-}$ ) can be activated by heat, UV-irradiation, and transition metal ions to produce  $\text{SO}_4^{\bullet-}$ . Cavitation bubbles induced by ultrasound irradiation or generated by hydrodynamic cavitation were reported to initiate the activation of PS in aqueous solution at ambient conditions. The mechanism of PS activation in a cavitating bubble system was proposed to occur by two possible mechanisms. First, the  $\text{SO}_4^{\bullet-}$  can be formed as a result of the thermal dissociation of PS due to localized high temperature and high pressure in the “hot spots” of collapsing bubbles. Second, extreme conditions in the “hot spots” lead to homolytic cleavage of water molecules yielding  $\text{HO}^{\bullet}$  and  $\text{H}^{\bullet}$ . Interaction of the produced radicals with PS results in the formation of  $\text{SO}_4^{\bullet-}$  (Fernandes et al., 2018; Wei et al., 2017):



Thermal dissociation of water takes place in the gaseous phase of the cavitation bubble, inside of which the temperature can reach 2000-5000 K. The released temperature heats the liquid sheath surrounding the bubble core resulting in a higher temperature, pressure and possible supercritical water zone in the interfacial region. It is assumed that the formation of  $\text{SO}_4^{\bullet-}$  takes place in the interfacial region between the gaseous and liquid phase, inside the supercritical water layer, where the diffusivity and reactivity of PS are enhanced. Formed adducts are released from the interfacial region to bulk aqueous solution, where the activation of PS is negligible due to ambient temperature (Wei et al., 2017). In addition, the energy emitted during the cavitation bubble collapse increases the production of  $\text{HO}^{\bullet}$  by the reaction of  $\text{SO}_4^{\bullet-}$  with water and  $\text{HO}^-$ .



HO<sup>•</sup> can destroy oxidizable contaminants or convert SO<sub>4</sub><sup>2-</sup> to SO<sub>4</sub><sup>•-</sup> by electron transfer mechanism (Wei et al., 2017):



PS activated by cavitation exhibited a considerable potential in water treatment due to low operating cost and simple design of the equipment. PS activation achieved by HC was found effective in the degradation of persistent organic pollutants, endocrine-disrupting chemicals, bio-refractory dyes, etc. The degradation of bisphenol A was investigated under a cost effective HC-PS system using varying operating conditions (Choi et al., 2018). To achieve optimal degradation efficiency, the operating parameters such as HC inlet pressure, PS loading, pH, temperature, and water matrix have been studied. In this study, an orifice plate with a concentric hole of 2 mm diameter was used as a cavitating device. Application of the PS-HC process at the optimum pressure of 0.5 MPa and cavitation number ( $C_v$ ) of 1.02 showed that the degradation rate constant of bisphenol A was  $12.7 \times 10^{-3} \text{ min}^{-1}$ .

On the other hand, degradation rate constants of  $1 \times 10^{-3}$  and  $4.7 \times 10^{-3} \text{ min}^{-1}$  were calculated for sole HC and sole PS treatments, respectively. The synergy index was 2.23. Although the main degradation mechanism of bisphenol A using the PS-HC system corresponded to SO<sub>4</sub><sup>•-</sup>, a minor contribution from HO<sup>•</sup> (10.32%) was also observed.

Combined treatment strategy based on cavitation and PS was examined to decolorize model wastewaters containing widely used bio refractory dyes, i.e., Orange Acid-II and Brilliant Green (Gogate and Bhosale, 2013). Comparison of cavitating conditions generated by HC and AC indicated maximum decolorization for HC combined with PS for both dye effluents. At the optimum conditions, HC combined with PS ( $C = 535.72 \text{ mg/L}$ ) completely decolorized Orange Acid-II after 60 min of the treatment. In the case of the AC-PS system, at an oxidant loading of 1.61 g/L, 70% of decolorization was obtained after 120 min. Enhancement in dye decolorization was related to the active zone, over which cavitation events occur. Thus, HC provides more active sites in the pipe line to form SO<sub>4</sub><sup>•-</sup>, whereas cavitation events in AC occur near the tip of the horn generating US irradiation. Significant enhancement in the degradation of naphthol blue-black dye was achieved by PS activated by AC at low US frequency and power (Ferkos et al.,



2017). Sonochemical degradation of naphthol blue-black in the presence of PS investigated at 20 kHz showed enhancement in degradation efficiency of 36% compared to the sole AC process.

On the other hand, the enhancement was only 10% in the US system, with a very high frequency of 585 kHz. These observations coincide with the study on operating acoustic power, where the enhancement of the degradation rate increased significantly at the lower acoustic power. Such a trend of reactions was attributed to the intensification of radical-radical recombination reaction due to excess of radicals production. Generation of  $\text{SO}_4^{\cdot-}$  was elevated at higher acoustic power as more heat from cavitation bubbles was dissipated. The maximum internal bubble temperature was reported to be 4140 K at 80 W and 1147 K at 10 W.

#### 4.2.5 Hybrid processes based on peroxymonosulfate and cavitation phenomenon

$\text{SO}_4^{\cdot-}$  can also be produced by breaking the two oxygen bonds from peroxymonosulfate (PMS). Activation technologies of PMS are similar to PS and include different methods such as thermal activation (Patil et al., 2014; Oh et al., 2009), UV irradiation (Mahdi-Ahmed and Chiron, 2014), transition metal ions ( $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ) (Ji et al., 2015; Oh et al., 2016; Guo et al., 2015), carbonaceous materials (Duan et al., 2015), etc. Extreme conditions generated by the implosive collapse of cavitation bubbles have also been tried as an activation approach of PMS (Oh et al., 2016; Yin et al., 2018). Activation of PMS, along with the degradation reactions of target compounds, are all assumed to occur near the interfacial region during the cavitation process. In general, activation of PMS has resulted in the formation of  $\text{SO}_4^{\cdot-}$  and  $\text{HO}^{\cdot}$  (Fernandes et al., 2019):



Application of cavitation was reported to be highly efficient in PMS activation towards the degradation of contaminants present in water (Yin et al., 2018; Fernandes et al., 2019; Fernandes et al., 2018). Degradation of Cresol Red dye was drastically intensified by the addition of oxone (PMS) under the US with a working frequency of 300 kHz. 99% of decolorization degree was attained in the presence of PMS in 75 min, while sonolysis alone gave 90% in 120 min (Soumia and Petrier, 2016). The increase in PMS concentration from  $10^{-4}$  to  $10^{-1}$  M substantially increased the apparent rate constant of the bleaching process from 0.042 to 0.083  $\text{min}^{-1}$ , respectively. Simultaneous formation of  $\text{SO}_4^{\cdot-}$  and  $\text{HO}^{\cdot}$  was proposed favorable to the rapid degradation of Cresol Red molecule as both radicals have a unique mechanism of the

reaction. Synergistic effect of  $\text{SO}_4^{\cdot-}$  and  $\text{HO}^{\cdot}$  produced by PMS/acoustic cavitation system (20 kHz, 500 W) resulted in 95% removal of Cresol Red in 60 min, while 83% and 46% of decolorization degree were obtained by using PS/acoustic cavitation and  $\text{H}_2\text{O}_2$ /acoustic cavitation systems, respectively (Kurukutla et al., 2015). Simultaneous generation of  $\text{SO}_4^{\cdot-}$  and  $\text{HO}^{\cdot}$  during the PMS/US process (20 kHz, 600 W) was demonstrated by quenching experiments and electron paramagnetic resonance spectrometry. The contribution of both radicals increased the efficiency of sulfamethazine antibiotic degradation. Kinetic studies revealed that the degradation rate of sulfamethazine by PMS/US was 6.4 and 86 times higher than that of sole PS and US processes (Yin et al., 2018). Reduction of the reaction energy barrier required for the oxidation of amoxicillin was observed during its degradation under  $\text{Co}^{2+}$ /Oxone/US process (20 kHz, 200 W). Studies on mineralization of amoxicillin showed that COD removal efficiencies were in the order of Oxone < Oxone/ $\text{Co}^{2+}$  < Oxone/US <  $\text{Co}^{2+}$ /Oxone/US (Su et al., 2012; Guo et al., 2013). The accelerated formation of free radicals ( $\text{SO}_4^{\cdot-}$  and  $\text{HO}^{\cdot}$ ) provided by an increased number of active cavitation bubbles and fast activation of PMS is considered as the main enhancement routes of PMS/US process assisted by the US irradiation (Soumia and Petrier, 2016; Ghanbari and Moradi, 2017).

### 4.3 Sonocatalytic advanced oxidation process

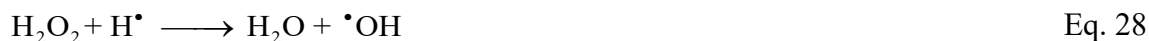
Recently, the utilization of ultrasound in the presence of an appropriate catalyst is named sonocatalysis and is considered as one of the promising and efficient treatment techniques for the degradation of refractory organic pollutants in aquatic environments. Ultrasound alone cannot directly interact with organic compounds because the ultrasound energy is not sufficient to even change their vibrational energy levels. Moreover, the ultrasound waves are larger than the dimension of the target molecules (Gholami et al., 2019a). Utilization of ultrasound alone leads to the formation of  $\cdot\text{OH}$  in the bulk solution to degrade organic pollutants due to the cavitation phenomenon; however, the amount of  $\cdot\text{OH}$  generated via ultrasonication is not enough to effectively destruct and mineralize the organic pollutants. Therefore, the treatment of polluted streams by ultrasounds alone needs higher reaction time and, consequently, higher energy to overcome this issue. To solve this limitation, catalytically enhanced ultrasonic degradation, i.e., sonocatalysis, was developed as an AOP for the decomposition of refractory organic pollutants based on the implementation of an appropriate catalyst with sonocatalytic properties (Soltani et



al., 2019a; Soltani et al., 2019b). In this regard, nanostructured catalysts such as ZnO (Karaca et al., 2016; Khataee et al., 2015a; Khataee et al., 2016) and TiO<sub>2</sub> (Khataee et al., 2017; Nuengmatcha et al., 2016) are widely applied for the sonocatalytic processes. An aquatic phase with a sufficient amount of heterogeneous catalyst produces many more interfaces for the enhanced creation of cavitation bubbles (Gholami et al., 2019b). The best results have been obtained when nanostructured sonocatalysts are used for the sonocatalysis due to their higher surface area and remarkable active sites. Therefore, nanostructured sonocatalysts produce more free radical species under ultrasonication. The presence of a suitable sonocatalyst results in the fast decomposition of organic pollutant owing to the formation of extra nuclei for the creation of cavitation bubbles. High pressure (> 1800 atm) along with high temperature (> 5000 K) are produced via violent collapse of cavitation bubbles named as “hot spot” phenomenon, promoting the pyrolysis of water molecules to  $\cdot\text{OH}$  and  $\text{H}^{\cdot}$  as presented in the following equations (Khataee et al., 2015c; Soltani et al., 2019b):

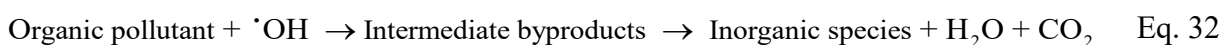
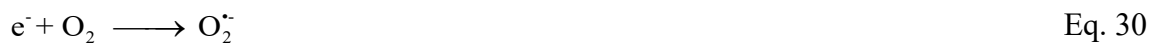


Therefore, hydrogen peroxide can be produced as a result of the interaction of the generated  $\cdot\text{OH}$  in the bulk solution as well as the liquid-bubble interface (Eq. 27). Hydrogen peroxide molecules further reacted with hydrogen radicals, producing  $\cdot\text{OH}$  in the solution (Eq. 28):



When an appropriate heterogeneous sonocatalyst (both undoped and doped sonocatalyst) is used, as-generated hydrogen peroxides react with the sonocatalyst surface, thereby generating a number of free radicals for the improved degradation of organic pollutants. In addition, extra nuclei are provided when heterogeneous sonocatalyst is used, which intensifies the formation rate of cavitation bubbles, promoting the pyrolysis rate of water molecules (Khataee et al., 2015b; Khataee et al., 2015c; Soltani et al., 2016a). The cavitation phenomenon is unsymmetrical close to the solid-liquid interface because the sonocatalyst fine particles act as a wall for the transmission of cavitation bubbles. The inrush of liquid from one side of the cavitation bubbles initiates forceful micro-jets, resulting in the surface cleaning, the boundary layers extermination, and enhanced mass and heat transfer in the bulk solution (Gholami et al., 2019a). From another point of view, heterogeneous sonocatalyst can act as a photocatalyst that can utilize the energy

emitted during the bubble collapse (named as “sonoluminescence” phenomenon). In this regard, the ultrasound leads to the formation of a wide-wavelength light during cavitation phenomenon, which stimulates the sonocatalyst to play photocatalytic role generating electron-hole ( $e^-/h^+$ ) pairs and subsequently,  $\cdot\text{OH}$  in the sono-reactor as shown in the following reactions ((Khataee et al., 2015c; Soltani et al., 2016a):



According to the above reactions, the as-generated  $e^-$  interact with dissolved oxygen molecules producing superoxide radical anion ( $\text{O}_2^{\cdot-}$ ) as well as the reaction of  $h^+$  with water results in the formation of  $\cdot\text{OH}$  in the solution. At the same time,  $h^+$  or  $e^-$  can react directly with adsorbed pollutants. According to the published reports (Abdullah & Ling, 2010; Soltani et al., 2019b; Soltani et al., 2016b; Wang et al., 2007a; Wang et al., 2009), sonocatalytic degradation of various organic compounds by different sonocatalysts (ZnO,  $\text{TiO}_2$ , MgO, etc.) followed pseudo-first-order kinetic model, described as Eq. 33:

$$\ln C = \ln C_0 - k_{\text{app}} t \quad \text{Eq. 33}$$

where  $C_0$  and  $C$  are the initial and remaining concentration of the target compound at the specified reaction time of zero and  $t$  min, respectively.  $k_{\text{app}}$  refers to the apparent reaction rate constant of the kinetic model ( $\text{min}^{-1}$ ). The application of doped sonocatalysts has also been considered to hinder the recombination of sono-generated  $e^-h^+$  pairs in order to enhance the production rate of  $\cdot\text{OH}$ . For this purpose, heavy and rare-earth metals have been incorporated into pure sonocatalyst lattice that has successfully improved catalytic activity of the sonocatalyst under ultrasonication (Khataee et al., 2015b; Khataee et al., 2015c; Khataee et al., 2016; Wang et al., 2009). Regarding the economic aspects of the sonocatalytic treatment techniques, immobilization of particulate sonocatalysts on suitable support including clay (Karaca et al., 2016; Soltani et al., 2016a; Soltani et al., 2016b) and carbon (Khataee et al., 2017; Nuengmatcha et al., 2016; Zhang et al., 2011) based substances is considered to avoid the washout of precious catalyst from the sono-reactor. Also, it has been confirmed that the immobilization of particulate sonocatalysts may lead to the enhanced sonocatalytic decomposition of organic contaminants.

This enhancement is associated with the creation of additional nuclei for the formation of more cavitation bubbles, thereby generating more  $\cdot\text{OH}$  in the liquid phase (Karaca et al., 2016). Besides, the immobilization prevents the aggregation of fine sonocatalyst particles in the solution (Soltani et al., 2016b; Soltani et al., 2019b). In the case of carbon-based substances supported sonocatalysts, the lower recombination rate of sono-generated  $e^-$ - $h^+$  pairs is reported (Gholami et al., 2019b). Overall, the sonocatalysis is an efficient purification method for the decomposition of organic compounds in comparison with the ultrasound alone. However, this process needs to be further examined to verify its ability under real conditions to treat real industrial wastewaters containing both organic and inorganic compounds. Moreover, the release of sonocatalyst particles into various ecosystems must also be considered. It is required to assess the bio-toxicity of the treated effluent before being discharged into the environment.

#### 4.3.1 Applications of Sonocatalysis

Sonocatalysis is considered as a powerful and promising treatment technique for the effective degradation of various persistent pollutants in aquatic environments. In this regard, sonocatalysis has been successfully utilized for the treatment of colored wastewaters containing organic dyes. There are many research results in which the sonocatalysis has been effectively applied for the decolorization of synthetic and real textile wastewaters using various forms of sonocatalysts (Khataee et al., 2018; Nuengmatcha et al., 2016; Sheydaei and Khataee, 2015; Pang and Abdullah, 2013; Soltani and Safari, 2016). The efficiency of the sonocatalysis for the treatment of real textile wastewaters is specified in terms of chemical oxygen demand (COD) and total organic carbon (TOC) reduction. However, longer reaction time is required to attain effective decolorization and mineralization in real wastewaters in comparison with synthetic wastewaters. In the case of sonocatalysis for real wastewaters, the issue of the presence of scavenging compounds is of great concern. The hydroxyl radicals formed during sonocatalysis are prone to be deactivated by various inorganic ( $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ , etc.) and organic (alcoholic compounds, phenols, organic acids, etc.) radical scavengers which are abundant in real textile wastewaters (Asghar et al., 2015). Overall, the sonocatalysis is an economically feasible treatment process with high usability for the reclamation of real textile wastewaters if the careful selection of the sonocatalyst, along with the optimization of operational parameters, is conducted.





The sonocatalytic process is also used as an effective alternative to the photocatalytic process (ultraviolet irradiation together with a suitable photocatalyst) for the treatment of wastewater generated through the pulping process. The turbidity of the pulping process wastewater decreases the efficiency of photocatalytic processes. Overall, the sonocatalysis has been utilized for the degradation of lignin as well as for the pretreatment of the biomass of lignocellulose for the enhanced saccharification via an enzymatic process (Ninomiya et al., 2013).

In recent years, the sonocatalytic processes are widely utilized for the effective degradation of emerging contaminants such as antibiotics, endocrine disrupting compounds, personal care products, pesticides, herbicides, veterinary medications, chromate, perchlorate, nitrosamines, fuel oxygenates, etc. (Chu et al., 2017; Peña-Guzmán et al., 2019; Robles-Molina et al., 2014) from polluted water and wastewater. Sulfa drugs as widely used pharmaceutical compounds were effectively degraded by the sonocatalysis over neodymium-doped lead selenide. The removal efficiency of 86% was obtained within the reaction time of 90 min in the presence of 0.5 mmol/L peroxydisulfate as an effective radical enhancer (Khataee et al., 2015a). There are many successful reports regarding the sonocatalytic degradation of various antibiotic compounds such as gemifloxacin (Gholami et al., 2019a), tetracycline (Subramani et al., 2019; Soltani et al., 2019a), ampicillin (Mirzaei et al., 2019a), and ciprofloxacin (Hassani et al., 2017). Catalytically enhanced ultrasounds have been utilized for the decomposition of hormones such as 17 $\alpha$ -ethinylestradiol (EE2), Estrone (E1), and 17 $\beta$ -Estradiol (E2) (Chu et al., 2017). Among them, 17 $\alpha$ -ethinylestradiol and endocrine-disrupting compound, bisphenol A, are efficiently decomposed through sonocatalysis over TiO<sub>2</sub>-wire mesh. This type of sonocatalyst can be continuously reused for the catalytic production of hydrogen peroxide and subsequent degradation of such emerging contaminants (Her et al., 2011).

Because of its high potential to be reused in repeated experimental runs, magnetically separable TiO<sub>2</sub> is also used for the degradation of ibuprofen as a nonsteroidal anti-inflammatory drug (NSAID). According to the reported results, an average rate constant value of  $17 \pm 0.3 \times 10^{-3} \text{ min}^{-1}$  has been obtained within five repetitive experimental tests (Kang et al., 2015). A cost-effective mineral catalyst named sepiolite has also been used for the sonocatalytic degradation of methylparaben. This emerging compound is extensively used in a variety of personal-care products and cosmetics. Based on the obtained results, the high frequency of ultrasounds favored



the sonocatalysis of methylparaben (Savun-Hekimoğlu and Ince, 2019). Overall, sonocatalysis could be considered as an efficient treatment process for the degradation of emerging contaminants, but attempts have been focused on the treatment of emerging contaminants in laboratory scales experiments. Although the effect of the presence of various radical scavenging compounds on the efficiency of sonocatalytic processes is evaluated. However, the effectiveness of this type of catalytic process for the treatment of real wastewaters containing emerging contaminants should be assessed.

## 5. Factors influencing the efficiencies of treatment processes

### 5.1 Effect of pH

The efficiencies of the treatment processes depend on the pH of the solution medium. The initial pH of the solution plays an essential role in the formation of pollutant speciation, active intermediates, and the reactivity for their decomposition (Wang et al., 2017). The influence of pH on the oxidation potential of intermediate compounds and  $\cdot\text{OH}$  produced at the cavitation process is considered for the degradation studies. Many studies reveal that acidic conditions are generally preferable for dye degradation when compared with alkaline conditions. The use of lower pH enhances  $\cdot\text{OH}$  formation and reduces the recombination rate. Furthermore, the pollutant in a molecular or ionic state depends on its acid dissociation constant value ( $\text{pK}_a$ ) (Rajoriya et al., 2017). For different contaminants, the optimum pH value for higher degradation efficiency is different.

In hydrodynamic cavitation processes combined with oxidants or Fenton's reagent, the oxidation potential of the oxidants or Fe concentration in the solution was strongly influenced by the initial solution pH. Fenton's reagent is more efficient at acidic conditions in the range of pH 3-4. At pH lower than 3, the generation of  $(\text{Fe(II)(H}_2\text{O)})^+$  enhances, which reacts slowly with hydrogen peroxide, thereby reducing the production of reactive hydroxyl radicals (Fischbacher et al., 2017). Furthermore, at a very low pH, the scavenging effect of  $\text{H}^+$  comes into effect, which could restrict the rate of degradation by consuming hydroxyl radicals. Furthermore, hydrogen peroxide reacts with a proton to give an hydroperoxonium ion ( $\text{H}_3\text{O}_2^+$ ) and makes hydrogen peroxide electrophilic. Thus, the stability of hydrogen peroxide increases, and their reactivity with ferrous ion decreases, which results in a reduction of degradation kinetics of Fenton's process at very low pH (Sreeja and Sosamony, 2016).



Wang et al. (2017) reported that the hydrodynamic cavitation process combined with TiO<sub>2</sub> photocatalysis gave a high rate constant for degradation of tetracycline at pH 10. As solution pH increases, hydroxide anions increases, which favors the generation of hydroxyl radicals through holes oxidation in the photocatalytic system. This can be the main cause for higher degradation effect at alkaline pH for the combined hydrodynamic cavitation and photocatalysis process.

## 5.2 Effect of temperature

Temperature is considered one of the most influential parameters on the ultrasound cavitation leading to changes in the reaction rate and degree of degradation. Higher temperature causes a rise in the vapor pressure of the solution leading to the formation of vaporous cavities in the system. At higher temperatures, the solution boils, leading to negative acoustic wave pressure. In the meantime, the cavitation bubble fills with water vapor instantly, which decreases degradation efficiency. Choi et al. (2018) investigated the effect of temperature in changing the activation energy and behavior of the bisphenol A. It was reported that the increase in temperature from 10 to 50° C results in the increase of reaction rate constant by 12 folds. Son et al. (2011) reported that an increase in bulk temperature reduced the cavitation effect. When the temperature was increased beyond the optimum temperature of 30° C, the degradation efficiency of 1,4-dioxane decreased. This is because, at higher temperatures, the collision of cavities occurs, which lower the implosion effect; thus, a steady decline in the generation of hydroxyl radicals occurs. Therefore, lower operating temperature ranges from 25 to 40° C is generally preferred. In some cases, it could be raised to 50° C, where the radical formation from the pollutant also plays an essential role in the degradation mechanism (Wang et al., 2011).

## 5.3 Effect of the initial concentration of pollutant

Another essential parameter influencing the effectiveness of treatment processes is the initial pollutant concentration. Generally, the increase in the initial concentration of pollutants leads to a reduced degradation efficiency of a cavitation process. This negative effect in cavitation treatment may be due to the insufficient amount of hydroxyl radicals generated for the available pollutant molecules. The amount of  $\cdot\text{OH}$  which attacks the pollutant molecules would be constant while the increase in pollutant concentration gives rise to a greater number of available pollutant molecules. As a result, the level of pollutant degradation percentage would be lowered. In the hydrodynamic cavitation process combined with photocatalytic treatment



(Caliskan et al., 2017), it has been shown that the degradation of RR 180 dye at an operating pressure of 5 bar was reduced from 67 to 41% (in terms of TOC) as the dye concentration increased from 50 to 150 mg/L.

#### **5.4 Effect of inorganic ions**

The domestic and industrial wastewater contains inorganic salts in higher proportions. Therefore, many researchers studied the influence of inorganic ions on hydrodynamic cavitation-based wastewater treatment processes. Some studies revealed that the presence of chloride and sulfate salts exert no significant effect on the treatment process (Wang et al., 2017). Khodami and Nezamzadeh-Ejhi (2015) postulated that the increase in chloride ion reduces the degradation efficiency as chloride acts as an electron donor. Thus, the increase in chloride ions reduced the generation of  $\cdot\text{OH}$ . Also, the chloride radicals have much lower oxidation potential than  $\cdot\text{OH}$ . The inhibition effect of sulfate salts is due to their ability to act as electron scavenger.

The effect of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  as hydroxyl radical scavengers was investigated by several researchers. Interestingly it has been found that the carbonate radicals, resulted from the reaction of carbonate ions with  $\cdot\text{OH}$ , react very fast with electron-rich organic compounds such as aromatics and anilines. Besides, the recombination rate of these radicals is very slow, and the presence of these compounds increases the pH value, which also contributes to the lower degradation (Wang et al., 2017; Thi et al., 2013; Merouani et al., 2010).

### **6. Applications of cavitation processes in environmental protection**

#### **6.1 Application of cavitation for wastewater treatment containing volatile organic compounds**

Volatile organic compounds (VOCs) are organic compounds that can evaporate under normal atmospheric conditions of temperature and pressure. More strictly, according to European Union regulations, it is any organic compound having an initial boiling point less than or equal to 250°C measured at a standard pressure of 101.3 kPa (European Parliament and Council, Directive 2004/42/CE). Industrial discharges (pharmaceutical, petroleum refinery, paper, dye, and textile industry effluents) are the main sources contributing to the presence of VOCs in municipal wastewater (Costa et al., 2012; Cheng, and Hsieh, 2013; Xie et al., 2016; Cai et al., 2019; Yakout et al., 2019; Soltani et al., 2019c). Among other classifications of VOCs, there are three important

groups of VOCs, i.e., nitrogen-containing VOCs (N-VOC), sulfur-containing VOCs (S-VOC) and oxygen-containing VOCs (O-VOC). Hydroxyl radicals are very reactive species that effectively degrade pollutant molecules, and a combination of AOPs with cavitation technologies generates more hydroxyl radicals, which will enhance VOC removal from wastewater (Roy and Moholkar, 2019).

High concentrations of VOCs are found in wastewater originated from the refinery industry, i.e., petroleum bitumen effluents containing a high amount of VOCs (Boczkaj et al., 2017). These effluents are produced during oxidation of the vacuum distillation of crude oil to produce oxidized bitumen. During vacuum distillation as well as bitumen production (bitumen blowing process), a partial thermal cracking takes place on the heating elements of the installations. Under such conditions, several groups of VOCs are formed – primary aromatic and other unsaturated compounds that undergo further conversion via oxidation reactions. A considerable amount of organosulfur compounds, ketones, aldehydes, pyridine, and its derivatives, as well as polycyclic aromatic hydrocarbons (PAHs), are present in post oxidative effluents which contributes to its odorous character and high toxicity in the environment (Boczkaj et al., 2010; 2014). Except for biodegradation and adsorption, the AOPs and their combination with cavitation are seen as a good approach in the treatment of refinery effluents. Treatment of bitumen effluents was performed by AOPs, sole and in combination with hydrodynamic cavitation. A combination of hydrodynamic cavitation and ozone was found to be the most effective process compared with other approaches of HC and AOPs in the treatment of effluents from the production of bitumen with 40% COD and 50% BOD<sub>5</sub> reduction (Boczkaj et al., 2018). In another study where wastewater from bitumen effluents was performed by sole AOPs, the authors claimed that the most effective AOP was the peroxone process (a combination of O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>) with 43 and 34% reduction of COD and BOD<sub>5</sub> respectively (Boczkaj et al., 2017). The BOD<sub>5</sub> reduction was 10% higher when ozone was coupled with hydrodynamic cavitation, compared to the peroxone(O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>) process.

The effectiveness of cavitation in the degradation of VOCs was also proved by Gągol et al., 2019. They studied the degradation of sulfide ions and organic sulfides with combined processes of hydrodynamic cavitation and AOPs. They concluded that in 30 min of reaction, 60% of organosulfur compounds were oxidized by the sole cavitation process; meanwhile, complete oxidation was obtained for the coupled process of cavitation and oxidants O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>.



Complete degradation was obtained in 15 minutes for the coupled process of hydrodynamic cavitation and peroxone.

The combination of AOPs and cavitation have shown promising results in degrading the organic pollutants in terms of both treatment time and cost-effectiveness. Goel et al. (2004) performed the treatment of several volatile and non-volatile organic compounds (Benzene, Toluene, Styrene, Ethylbenzene, Trichloroethylene, Eosin B) in two types of sonication reactors, a probe, and ultrasonic bath. Effect of oxidant ( $H_2O_2$ ) and electrolyte (NaCl solution) coupled with sonocavitation, was also investigated. They found that sonochemical degradation was a suitable alternative, and the reaction rates were higher for ultrasonication with probe compared to ultrasonic bath for both volatile and non-volatile compounds. Operating conditions are important factors in the decomposition of VOCs. Jiang et al. (2002) studied the degradation of volatile chlorinated aromatics (chlorobenzene, 1,4-dichlorobenzene, and 1-chloronaphthalene) using an ultrasonic transducer and found that initial substrate concentration and ultrasonic intensity were important features in the sonochemical decomposition of volatiles.

Hydrodynamic cavitation is a large-scale technique, which generates free reactive radicals and high temperature that easily degrade pollutant molecules, being, therefore, an AOP (Gogate and Pandit, 2001). Chakinala et al. (2008) investigated the mineralization of phenol with hydrodynamic cavitation and heterogeneous advanced Fenton process (AFP). They concluded that AFP, in combination with hydrodynamic cavitation, effectively degraded phenol from wastewater. Moreover, zero-valent iron was considered as a promising catalyst for the treatment of phenolic aqueous solutions by the combination of HC/AFP.

## **6.2 Removal of pesticides from wastewater by cavitation technologies**

Pesticides are substances used to prevent or destroy certain insects and various types of parasites (Kumar et al., 2012). Pesticides can be classified into two major groups based on target organisms (insecticide, herbicides, fungicides, rodenticides, wood preservatives, garden chemicals, and household disinfectants) and based on chemical structure (organochlorine, organophosphate, carbamates, and pyrethroids) (Yadav and Devi., 2017). Pesticides are discharged in aqueous systems by agricultural wastewater and non-agricultural wastewater (industrial facilities, public health, forestry activity) (Köck-Schulmeyer et al., 2013). Pesticides acquire a detrimental effect on human health, and they can enter into the body through different



routes such as food chain, inhalation, dermal and ocular exposure (Kumar et al., 2012). Therefore, it was highly important to develop advanced technologies that prevent or destroy pesticides.

Atrazine (1-chloro-3-ethylamino-5-isopropylamine-2,4,6-triazine) is a herbicide widely used in agriculture. Degradation of atrazine was investigated using hydrodynamic cavitation combined with chemical oxidants  $H_2O_2$ , UV, SPS (activated sodium persulfate) (Jawale et al., 2018). Jawale et al. (2018) found that the combination of HC +  $H_2O_2$  + SPS resulted in complete degradation and 87% COD reduction. Their results demonstrated that the hybrid treatment approach based on cavitation could be effectively used for the degradation of ATZ. Dicofol, an organochlorine pesticide, was degraded by hydrodynamic cavitation under optimized conditions (inlet pressure 7 bar,  $C_v = 0.17$ ) with 85% total organic carbon (TOC) removal in 60 min treatment time (Panda and Manickam, 2019).

In another case, the degradation of methyl parathion using hydrodynamic cavitation with different additives ( $H_2O_2$ ,  $CCl_4$ , Fenton's reagent) resulted in 56.4% TOC reduction in 30 min for the process of HC +  $H_2O_2$  (Patil and Gogate, 2012). Similarly, Joshi et al. (2012) studied the degradation of dichlorvos by hydrodynamic cavitation under optimized parameters and a maximum extent of degradation of 91.5% in 60 min treatment time was obtained for the coupled process of hydrodynamic cavitation and Fenton's process. The same contaminant was degraded in the sonochemical reactor combined with additives ( $H_2O_2$ ,  $CCl_4$ , Fenton's reagent), and the highest degradation was obtained for the combined process of sonocavitation and Fenton's reagent named as a sono-Fenton process (Golash and Gogate, 2012). Therefore, it can be understood that in the studies as mentioned above, optimized treatment schemes, based on a combination of sonochemistry or hydrodynamic cavitation with Fenton's chemistry, were effective approaches in the removal of dichlorvos from aqueous systems.

Randhavane (2019) studied the effect of geometric parameters in the treatment of chlorpyrifos using hydrodynamic cavitation, and the obtained results confirmed that the highest COD removal (60%) and 98% chlorpyrifos degradation was obtained for orifice plate with a configuration of 17 holes having a 1.5 mm diameter and the cavitation number of 1.54 in 120 min treatment time.

Ultrasonic cavitation, in combination with  $H_2O_2$ , Fenton's, and photo-Fenton's process, was used to degrade methomyl, a carbamate group pesticide that is used against many insects and

pests. It was proved that the most effective process with maximum mineralization of 78.8% was ultrasound and photo-Fenton's process in only 9 min time of treatment (Raut-Jadhav et al., 2016).

### **6.3 Removal of pharmaceuticals from wastewaters induced by cavitation technologies**

Emerging Compounds (EC) have become a major concern in the pollution of the aquatic environment; therefore, increased attention towards this problem resulted in the development of new technologies for wastewater treatment (Musmarra et al., 2016). Pharmaceuticals and their by-products have been in the scope of researchers as pollutants of emerging concern that need to be kept under control. The pharmaceuticals are discharged into the aquatic environment via healthcare facilities, hospital discharges, agriculture wastewater, and veterinary activities (Ghoshdastidar et al., 2015). The concentration of pharmaceuticals in wastewater is found to be in the range of ng/L to ug/L (Zupanc et al., 2013). The resistance of these compounds to treatment is favored by their physicochemical properties and biodegradability. Low removal of organic compounds, high cost of treatment, and low efficiency are some of the drawbacks related to conventional methods that can be easily overcome by the use of AOPs (Musmarra et al., 2016; Renita et al., 2017). AOPs include photocatalysis, sonocatalysis, Fenton, electro-Fenton, ozone-based hybrid processes, and cavitation processes (Mirzaee et al., 2019; Igwegbe et al., 2019). Sonocavitation is already proved to be an effective method in the removal of ubiquitous compounds from wastewater (Capocelli et al., 2012; Serna-Galvis et al., 2019). Hydrodynamic cavitation (HC) is considered as a good opportunity to fade away the disadvantages of ultrasound, such as high energy consumption, and it is seen as a more viable and worthwhile method (Musmarra et al., 2016).

Antibiotics from the representative group of fluoroquinolone and  $\beta$ -lactam antibiotics (cephalosporin and penicillin) are the most consumed pharmaceuticals. They are found in municipal waste treatment plants [MWTP] from hospital wastewater discharges [HWW] (Zupanc et al., 2013; Verlicchi et al., 2012; VanBoeckel et al., 2014). Serna-Galvis et al. (2019) studied the sonochemical degradation of six antibiotics from three different classes such as fluoroquinolones (ciprofloxacin and norfloxacin), penicillins (oxacillin and cloxacillin) and cephalosporins (cephalexin and cefadroxil). They concluded that the application of ultrasonic waves leads to a satisfactory result in the degradation of antibiotics. Hydroxyl radicals that are



generated from ultrasound attacked the penicillin and cephalosporin cores from the  $\beta$ -lactam antibiotics, whereas the fluoroquinolone was decarboxylated. Other researchers (Serna-Galvis et al., 2016) evaluated the effect of high-frequency ultrasound to degrade the penicillin antibiotic (oxacillin). They concluded that under the effect of ultrasound treatment, by-products of antibiotics were converted into biodegradable compounds. Furthermore, it was proved that the combination of the sonochemical process with biological systems could be a practical alternative for the treatment of water containing oxacillin and other pharmaceutical additives.

Dicloxacillin (DXC) is another  $\beta$ -lactam antibiotic of the penicillin family. Villegas-Guzman et al. (2015) studied the inhibition effect of dissolved salts present in water for the degradation of DXC assisted by ultrasound. They found that antimicrobial activity was eliminated after 360 min under ultrasonic treatment with 30% of COD removal.

Ciprofloxacin (CIP), a fluoroquinolone class pharmaceutical, has an irreversible effect in the ecosystem, resulting in toxicity to microorganisms (Capocelli et al., 2012). CIP removal from aqueous systems by sonochemical, sono-nano-chemical, and sono-nano-chemical/persulfate processes was studied by Igwegbe et al. (2019). They found 99, 70 and 36% removal efficiency of CIP by sono-nano-ZnO/PS process (US/ZnO/PS), sono-nano-chemical (US/ZnO) process and sonochemical (US) process, respectively, at a frequency of 60 kHz, 10 min treatment time and neutral pH. The effect of ultrasonic cavitation in the degradation of CIP and ibuprofen in the presence of different organic compositions was investigated by Xiao et al. (2014), and a high rate of degradation was reported. Sonochemical degradation of levofloxacin under the effect of rate enhancers ( $\text{CCl}_4$ ) and rate inhibitor (t-butanol) was investigated by Guo et al. (2010) and concluded that sonochemical oxidation could be used for pretreatment of effluent containing levofloxacin before biological treatment processes.

Ibuprofen (IBP), a NSAID, is a widely used medicament that helps to reduce fever, headache, toothache, or pains caused by other injuries. It is used for humans and domestic animal healthcare, farming, etc. (Wang et al., 2019). Degradation of IBP by sonocavitation treatment was studied by Mendez-Arriaga et al. (2008), and they inferred that degradation of IBP under ultrasound treatment was increased from 30 to 98% in 30 min; meanwhile, the same analgesic solution was treated by hydrodynamic cavitation, and over 60% of ibuprofen was degraded in 60 min (Musmarra et al., 2016).





Except for uses of ultrasonic cavitation in the degradation of different groups of pharmaceuticals, hydrodynamic cavitation is also considered as a reliable technology to degrade pharmaceutical contaminants. Degradation of six pharmaceuticals such as clofibrac acid, ibuprofen, naproxen, ketoprofen, carbamazepine and diclofenac under the effect of hydrodynamic cavitation (HC), biological processes and UV was studied by Renita et al. (2017). The studies revealed that under optimal conditions for hydrodynamic cavitation, removal efficiencies were ranging from 72 to 86% in the case of naproxen, carbamazepine, and diclofenac, and from 45 to 52% for clofibrac acid, ibuprofen, and ketoprofen. Ibuprofen, naproxen, and ketoprofen were degraded to concentrations below the LOD of the analytical method used for its determination, while the efficiency of > 98%, was observed for carbamazepine and diclofenac.

Degradation of diclofenac in the aqueous system based on hydrodynamic cavitation and heterogenous photocatalysis has revealed that combined processes of hydrodynamic cavitation with photocatalysts or AOPs resulted in higher degradation of contaminants than in individual processes (Bagal and Gogate, 2014b). They found that the combination of hydrodynamic cavitation with UV, UV/TiO<sub>2</sub>, and UV/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> enhances the degradation of target pollutants. The highest degradation was observed for the hydrodynamic cavitation process combined with UV/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> with 95% degradation and a 76% reduction in TOC. Another use of the combined process of hydrodynamic cavitation and AOPs was investigated by Thanekar et al. (2018). They found that the degradation of carbamazepine by hydrodynamic cavitation as a sole process reached only 38.7% degradation, while for combined processes of HC + O<sub>3</sub>, HC + H<sub>2</sub>O<sub>2</sub>, HC + UV, HC + O<sub>3</sub> + H<sub>2</sub>O<sub>2</sub> obtained degradation rates were respectively 91.4%, 58.3%, 52.9%, and 100%. It can be understood the effectiveness of the combined process of HC and AOPs. Degradation of carbamazepine was also studied under the effect of sonoelectrochemical oxidation, sono-photodegradation, and combined hydrodynamic and acoustic cavitation (HAC) (Tran et al., 2017; Expósito et al., 2017; Braeutigam et al., 2012).

Villaroel et al. (2014) studied the degradation of acetaminophen (ACE) in water by ultrasound. They found that ultrasound has a great potential in the degradation of ACE because it transforms to biodegradable by-product. The effect of ultrasonic degradation was also studied by other researchers (Jagannathan et al., 2013; Im et al., 2014). Mirzaee et al. (2019) studied the degradation of paracetamol under ultrasonic irradiation combined with air-dispersion cathode with a sacrificial iron anode, which generates Fe<sub>3</sub>O<sub>4</sub> nanostructures that help in the degradation of

paracetamol. The hybrid method of US coupled with NADC-ECP (nano-composite air dispersion cathode) in the presence of  $\text{Fe}_3\text{O}_4$  nanostructures was proved to be a very effective method with a synergism of 39.8%. The sonocatalysis of ACE over catalysts of nano-sized ZnO incorporated into PSW (powdered stone waste) (ZnO/PSW) was studied by Soltani et al. (2019b). They concluded that the highest degradation efficiency of 98.1% was achieved for ZnO/PSW-sonocatalytic process assisted by UVC light.

#### **6.4 Domestic effluents**

The rapid growth of urban communities, along with the development of industrial and agricultural water consumption, raises an increasing demand for water sanitation and protection. The use of water for industrial, agriculture, and domestic purposes is commonly associated with the deterioration of water quality due to the constant accumulation of contaminants. Characterization of wastewater is a part of research activities undertaken to optimize the design of the unit of wastewater treatment plants (WWTPs). Domestic wastewater in municipal WWTPs consists of waste produced by households with various contributions from rainwater, industrial, and agriculture wastewaters. Domestic effluents are produced by individual users and have been less described at habitat scale due to the broad variability of the behavior, lifestyle, and standard of living among different users. Domestic effluent is the water that has been used by a community. It is composed of human body waste, together with the water used for flushing toilets, personal washing, laundry, food preparation, and cleaning of kitchen utensils (Mara et al., 2013). Domestic effluents are historically classified into two main categories: blackwater and greywater. Blackwater is collected from toilets and consists of fecal matter, toilet paper, flush water, urine, and spillage. This fraction of domestic effluents contains pathogenic bacteria, which may cause diseases. Greywater includes various emission sources, such as kitchen sink, dishwasher, washing machine, shower, and other personal care activities (Mara et al., 2013; Boutin et al., 2016).

The contaminants present in domestic effluents are divided into three categories: suspended solids, organic matter (chemical oxygen demand and biological oxygen demand), and nutrients (nitrogen and phosphorus-containing compounds). Conventional water treatment processes are used to remove the contaminants for reuse of the treated water (Wang et al., 2007b). Many studies have been conducted to improve the quality of the treated water by



upgrading the existing conventional treatment processes. Thus, suspended and dissolved solids amenable to biological treatment are suggested to be removed by assisting the preliminary treatment with a chemical coagulant (Semerjian and Ayoub, 2003). Introduction of AOPs, as well as other physicochemical processes into conventional water treatment practices, is the recent trend in the development of rational use of water resources.

## **6.5 Treatment of industrial wastewater by cavitation**

Industrial activity is a topic of concern in environmental pollution due to the large quantity of wastewater discharge in the aquatic environment, contaminated with pharmaceuticals, dyes, pesticides (Thanekar et al., 2018). Researchers have studied the treatment of industrial wastewater with cavitation, AOPs, and the combination of both (Boczka et al., 2017; Gagol et al., 2018c).

The combined process of HC/O<sub>3</sub> was reported to be a very effective method in the treatment of bitumen effluent with a maximum reduction of 40% in COD and 60% in BOD (Gagol et al., 2018c). Chakinala et al. (2008) studied the treatment of industrial wastewater containing phenolic compounds using hydrodynamic cavitation induced by a liquid whistle reactor coupled with the AFP. The combined process of HC/AFP resulted in (60-80%) removal of TOC in 150 min time of treatment.

The treatment of the textile dyeing industry (TDI) effluent was studied using a hybrid combination of HC with air, ozone, oxygen, and Fenton's reagent (Rajoriya et al., 2018). The combined process of HC and Fenton's reagent (FeSO<sub>4</sub>·7H<sub>2</sub>O: H<sub>2</sub>O<sub>2</sub> as 1:5) was the most effective process with 48% TOC and 38% COD reduction in 15 and 120 min, respectively, with almost complete decolorization 98% of the TDI effluent. Raut Jadhav et al. (2016) studied the efficiency of the combination of hydrodynamic cavitation with additives (H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>) for the treatment of pesticide industry effluent. They found that the combined process of HC + H<sub>2</sub>O<sub>2</sub> was the most cost-effective due to its higher cavitation yield and lower power consumption.

Gore et al. (2014) studied the degradation of orange 4 dye using hydrodynamic cavitation based hybrid techniques. They revealed that the mineralization rate was higher for the combined process of hydrodynamic cavitation and ozone (76.25%), followed by HC + H<sub>2</sub>O<sub>2</sub> (31.90%) and (14.67%) for HC alone. The synergetic coefficient of greater than one for the hybrid processes of



HC + H<sub>2</sub>O<sub>2</sub> and HC + Ozone showed that the combination of HC with other oxidizing agents is better than the individual processes for the degradation of dye effluent containing orange 4 dye.

Ayare et al. (2019) investigated the treatment of phosphonate containing industrial wastewater by sonocatalysis combined with oxidation processes. They found that maximum COD reduction was obtained for the combined operation of sonocatalysis (TiO<sub>2</sub>) with ozone and H<sub>2</sub>O<sub>2</sub> (US+O<sub>3</sub>+H<sub>2</sub>O<sub>2</sub>+TiO<sub>2</sub>) with 95.8% COD reduction, while the use of sole ultrasound resulted in 37.2% COD reduction. A study regarding the removal of dinitrotoluene and trinitrotoluene from industrial wastewater by sonocavitation combined with titanium dioxide was carried out by Chen et al. (2011). They concluded that ultrasonic irradiation, coupled with TiO<sub>2</sub>, is a potential method for the treatment of nitrotoluenes in wastewater, and the mineralization of nitrotoluenes leads to carbon dioxide, nitrate ions, and water.

### **6.6 Miscellaneous application of cavitation technologies.**

In addition to the wide use of cavitation in wastewater treatment, such as removal and degradation of different types of pollutants (pharmaceuticals, pesticides, volatile and non-volatile organic compounds, heavy metals, dyes, etc), it also has miscellaneous applications like biotechnology (Gogate and Kabadi, 2009), food and water processing (Gogate, 2011), mineral processing (Ladola et al., 2014), biodiesel production (Chipurici et al., 2019), upgrading of heavy oil (Sawarkar, 2019), desulfurization/denitrogenation of fuels (Baradaran and Sadeghi, 2019).

Hydrodynamic cavitation was found to be an effective application technique in yeast cell breakage and is considered as the most energy-efficient method compared to blade blender and acoustic cavitation techniques (Save et al., 1994). In the food processing industry, hydrodynamic cavitation is used for food sterilization to prolong the shelf life of easily-spoiled products (Gogate, 2011; Milly et al., 2007; Arrojo et al., 2008).

Hilares et al. (2018) studied bioethanol production from sugarcane bagasse using hydrodynamic cavitation assisted-pretreatment and column reactors. They found that HC-assisted alkaline-hydrogen peroxide (NaOH-H<sub>2</sub>O<sub>2</sub>) pretreatment strategy might offer an option for sugarcane bagasse based biorefineries. Askarian et al. (2017) investigated the role of hydrodynamic cavitation in upgrading the heavy oil in the presence of an appropriate hydrogen donor. They revealed that adding 2 vol% gasoline as hydrogen donor into the heavy oil cavitation upgrading process reduced the viscosity of heavy oil by about 33%. It was observed



that diesel cuts and API gravity increased by 6.5 vol% and 2.9 %; meanwhile, extra heavy cuts and viscosity decreased 20 vol% and 84%, respectively. Ramos et al. (2018) studied oxidative desulfurization of model diesel with the ultrasound-assisted synthesis in the presence of mesostructured catalysts (FeOx/SBA-15 and FeOx/Zr-SBA-15). SBA-15 is mesoporous silica which was impregnated with Zr and desired amount of an aqueous solution of  $\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$  to obtain FeOx/SBA-15 and FeOx/Zr-SBA-15. They reported that dibenzothiophene (DBT) (30% Fe/Zr-SBA-15, 300 ppm DBT in 100 ml n-hexadecane) was completely removed from model fuel within 30 min of treatment time.

In addition to hydrodynamic cavitation, ultrasound is also an applicable technology in the food industry, mineral processing, nanotechnology, industrial welding, surface cleaning, and environmental protection (Madhu et al., 2019; Nithila et al., 2014; Seymour et al., 2002; Chemat and Khan, 2012; Yusaf and Al-Juboori, 2014).

The literature published so far indicate that cavitation is useful for the major research fields and for economy driving industries such as wastewater treatment plants, food industry, and fuel processing. Currently, ongoing research strongly focuses on improvements of cavitation-based technology concerning environmental protection applications as well as to make it more beneficial from the economic point of view.

## **Conclusions and future perspectives**

Cavitation based AOPs already proved its usefulness for several applications. In many cases, the sole use of cavitation allows us to effectively degrade the pollutants present in aqueous phases such as dyes, pharmaceuticals, and VOCs. An important advantageous aspect of hybrid processes based on cavitation is the synergy between this phenomenon and external oxidants, which are effectively converted to reactive radical species.

Future research on this topic should include two essential aspects – first related to the scientific value of published results and second to the applicational character of developed processes.

In the first case, to assure usefulness of obtained results on fundamentals of cavitation phenomena in relation to AOPs, scientists must provide as many details as possible on their system configuration and process conditions. The most important data are often missing, and their importance is explained below.

1. A lack of a clear description (or a scheme) of geometry and dimensions of elements present in the hydrodynamic cavitation system, as well as used flow rates and pressure in the system, makes the published results less useful for other researchers. This information is essential to calculate the cavitation number. All necessary data, along with the calculated cavitation number, should always be provided in the article or supplementary material linked to the article. Cavitation number should be calculated based on equation 1 instead of other concepts of defining this parameter.
2. In the case of sonocavitation systems, geometry and type of ultrasonic device must be characterized, including power and frequency of the instrument, as well as all details of ultrasonic transducers or sonotrodes used in the studies. It should also include the placement of the transducers in the system.
3. The aqueous medium treated in the studies must be characterized in terms of all physicochemical parameters that can affect the obtained results. These parameters include pH, color, clarity, the occurrence of emulsions, the presence of inorganic ions, and details of present dissolved organic compounds. In the case of real wastewater, the matrix effects often have a significant influence on the obtained effectiveness. Lack of deep analysis of factors affecting the obtained effectiveness lowers the value of obtained results as well as make them highly uncertain.
4. Studies on model effluents must include all these aspects mentioned in point 3 during process optimization.
5. Catalytic processes must be characterized in terms of catalyst used and its recycling ability concerning comparable performance over several cycles of treatment. The high energy of cavitation can cause leaching of several elements, including metal ions from catalyst into the aqueous phase. This aspect must be controlled during the process. Examples of such discussion can be found in paper of Fedorov et al., 2020.
6. Processes aided by UV light must be characterized concerning power and type of UV lamp. The wavelength at which photooxidation is expected in the spectrum of the lamp should be provided. This allows evaluating what the real power is needed for a specific wavelength to obtain effective degradation of target pollutants is.
7. Turbidity values of the aqueous phase and their changes dependent on heterogenous catalyst concentration must be measured for sonocatalytic and photocatalytic processes. This aspect

is very important in the discussion of the effect of catalyst dose since the turbidity of the high load of catalyst solutions often is a limiting factor of the sonocatalytic and photocatalytic processes effectiveness.

8. Evaluation of the changes of a total load of pollutants (controlled by COD or TOC and BOD) and its mineralization should be studied along with monitoring of target pollutants. If total degradation is not obtained, the COD should be used to measure the degradation of organic pollutants rather than the TOC. In the case of TOC, the effect will be underestimated (transformation of one organic compound to another one is not changing the organic carbon content in the effluent).
9. Optimization of the process conditions should include the minimization of the addition of external oxidants coupled with the analysis of energy costs of the cavitation process.
10. The monitoring of by-products formation should be included in the studies. Especially oxygen-containing compounds should be monitored as one of the most possible by-products formed during AOPs (Makoś et al. 2019).
11. Compounds present in the matrix of real wastewater should be characterized along with the defined purpose of the treatment. In several cases, the treatment process is focused on the removal of some target compounds, which should be degraded due to its specific toxicity. Often, the final treatment stage is performed via biological treatment using a dedicated type of wastewater activated sludge. Overall load of pollutants (and its change at the pre-treatment stage by chemical oxidation) is not so important; however, the presence of “critical” pollutants - highly toxic for such a type of microorganisms is the main aspect causing the need of implementation of pre-treatment by AOPs. Thus, the context of the research must be pointed out, and the advantages of cavitation based AOPs highlighted.

The second aspect of future research relates to the applicational value of obtained results. The studies should focus on the evaluation of the effectiveness of cavitation based AOPs in pilot-scale units. Moreover, the development of protocols allowing to scale up the processes to industrial scale is one of the important niches in this field. Studies on improvements of process economics in the laboratory as well as pilot-scale systems should focus on the energy-efficient generation of cavitation as well as coupling with solar cell units to make the cavitation processes a fully “green chemistry” approach.



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