Chapter 2
Theory and Fundamentals of Ultrasound

Abstract The application of ultrasonic technology has been receiving wide attention by the world in wastewater treatment and environmental remediation areas. The use of ultrasound technology is shown to be very promising for the degradation of persistent organic compounds in wastewater as it is proven to be an effective method for degrading organic effluent into less toxic compounds. The advantages of this technology include potential chemical-free and simultaneous oxidation, thermolysis, shear degradation, enhanced mass-transfer processes together etc. Overall, sonochemical oxidation uses ultrasound to produce cavitation phenomena, which is defined as the phenomena of the formation, growth and subsequent collapse of microbubbles, releasing large magnitude of energy, and induces localized extreme conditions. The sonochemical destruction of pollutants in aqueous phase generally involves several reaction pathways such as pyrolysis inside the bubble and hydroxyl radical-mediated reactions at the bubble–liquid interface and/or in the liquid bulk. This chapter mainly reviews the fundamental of ultrasound technology.

Keywords Bulk region · Cavitation · Hot-spot theory · Interfacial region · Sonolysis · Ultrasonic waves

2.1 Theoretical Aspects of Ultrasound

During the past several years, ultrasound has been effectively applied as an emerging advanced oxidation process (AOP) for a wide variety of pollutants in wastewater treatment. It is proven to be an effective method for degrading organic effluents into less toxic compounds and able to mineralize the compounds completely in certain cases (Guo et al. 2010). The ultrasound process does not require addition of oxidants or catalyst, and does not generate additional waste streams as compared to adsorption or ozonation processes. Ultrasound process is also not affected by the toxicity and low biodegradability of compounds (Fu et al. 2007).

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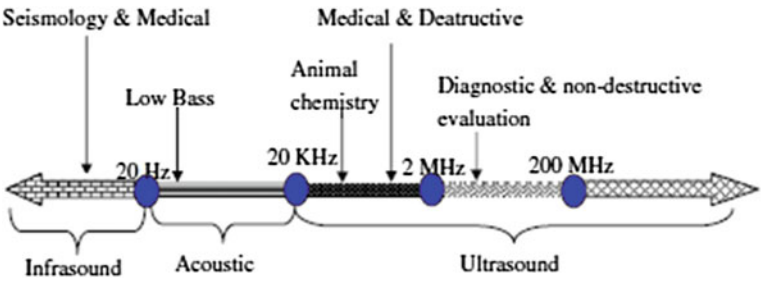

Fig. 2.1 Diagram of ultrasound range. Reprinted with permission from Pilli et al. (2011). Copyright (2011), Elsevier

Besides, ultrasonic degradation is claimed to be a non-random process, with cleavage taking place roughly at the center of the molecule and with degrading rate faster with larger molecule (Grönroos et al. 2008).

Ultrasonic waves (occurs at frequencies above 20 kHz) are a branch of sound waves and it exhibits all the characteristics properties of sound waves. Basically, they are classified into four different categories (namely, longitudinal/compressional waves, transverse/shear waves, surface/Rayleight waves, and plate/Lamb waves) based on the mode of vibration of the particle in the medium, with respect to the direction of the propagation of the initial waves (Raj et al. 2004). Depending on the frequency, ultrasound is divided into three categories, namely power ultrasound (20–100 kHz), high frequency ultrasound (100 kHz–1 MHz), and diagnostic ultrasound (1–500 MHz). Ultrasound ranging from 20 to 100 kHz is used in chemically important systems, in which chemical and physical changes are desired as it has the ability to cause cavitations of bubbles (Pilli et al. 2011; Rastogi 2011). Ultrasound ranging from 1 to 10 MHz is used for animal navigation and communication, detection of cracks or flaws in solids, and under water echo location, as well as diagnostic purposes (as shown in Fig. 2.1) (Pilli et al. 2011).

When applied on liquid, ultrasound waves consist of a cyclic succession of expansion (rarefaction) and compression phases imparted by mechanical vibration (Tang 2003). Compression cycles exert a positive pressure and push the liquid molecules together, while expansion cycles exert a negative pressure and pull the molecules apart (Vajnhandl and Marechal 2005). When pressure amplitude exceeds the tensile strength of liquid in the rarefaction regions, small vapor-filled voids called cavitation bubbles are formed (Chen 2012). Generally, pure liquids possess great tensile strengths and thus, available ultrasonic generators are unable to produce high enough negative pressures to cause cavitation. However, most of the liquids are usually impure and its tensile strength is reduced due to the presence of numerous small particles, pre-existing dissolved solids, and other contaminants. The impurities in liquid represent weak points in a liquid where nucleation of cavitation bubbles will occur (Vajnhandl and Marechal 2005). For instance, when pure water is used, more than 1,000 atm of negative pressure would

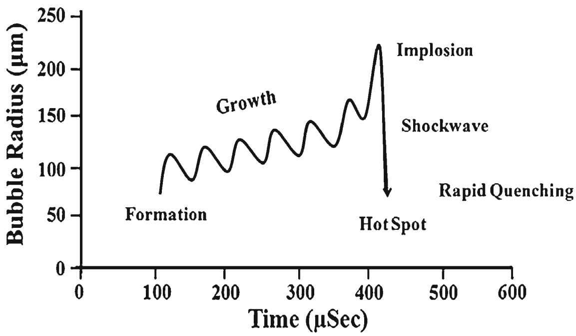

Fig. 2.2 Growth and implosion of cavitation bubbles in aqueous solution under ultrasonic irradiation. Reprinted with permission from Pang et al. (2011). Copyright (2011), Elsevier

be required for cavitation whereas for tap water, only a few atmosphere of pressure would be sufficient to form bubbles (Chowdhury and Viraraghavan 2009).

Once a bubble is created, two different cavitation phenomena which could take place in the liquid are: stable or transient cavitation. In stable cavitation, bubble wall couples with the acoustical field and oscillates about the equilibrium radius for several cycles. This occurs at low acoustic intensities, where the size of the bubble oscillates in phase with expansion and compression cycles and the bubbles grow slowly over many acoustical cycles (Thangavadivel et al. 2012). Due to its small variation in bubble size changes, this process is of little significance in terms of chemical effects (Destaillats et al. 2003). The process is also called rectified diffusion as during expansion, water vapor, dissolved gases and organic vapor will enter the bubble and will leave during contraction because of the effect of bubble surface area (Thangavadivel et al. 2012). When high intensity acoustic field is introduced, transient cavitation usually occurs. This causes growing cavitation bubble to eventually become unstable after a number of cycle and collapse during the compression cycle of ultrasonic wave. In this cavitation phenomena, the size of a bubble drastically increase from tens to hundreds of times the equilibrium radius before it collapses violently in less than a microsecond (Destaillats et al. 2003; Vajnhandl and Marechal 2005). Nevertheless, the classification of cavitation is vague as stable cavitation could lead to transient cavitation or transient cavitation could produce very small bubbles that undergo stable cavitation (Vajnhandl and Marechal 2005). In summary, phenomenon of cavitation consists of the repetition of three distinct steps: formation (nucleation), rapid growth (expansion) during the cycles until it reaches a critical size, and violent collapse in the liquid as shown in Fig. 2.2 (Pang et al. 2011).

The produced cavitation serves as a mean to concentrate the diffused sound energy. Either in low or high intensity acoustic field, once a cavity bubble experienced rapid growth and could no longer absorb the energy efficiently, the liquid will rush in and the cavity will eventually implode (Suslick 1989, 1990). Upon collapsing, each of the bubble would act as a hotspot, generating energy to increase the temperature and pressure up to 5,000 K and 500 atm, respectively, and cooling rate as fast as 10^9 K/s (Suslick 1990). The formation and growth of the cavitation bubbles is shown in Fig. 2.3. These collapsing bubbles create an unusual

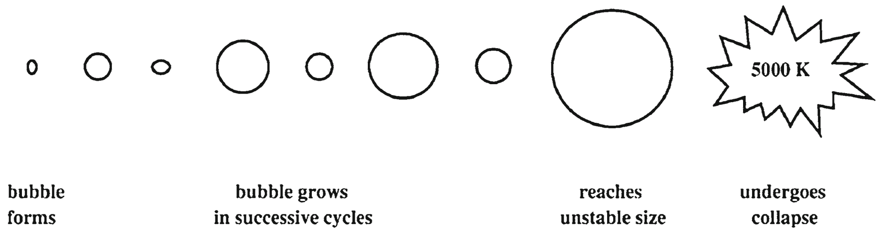

Fig. 2.3 Cavitation bubble formation, growth and collapse. Reprinted with permission from Chowdhury and Viraraghavan (2009). Copyright (2009), Elsevier

mechanism for high-energy chemical reactions due to enormous local temperatures and pressure (Suslick 1990).

There are many parameters which affect the cavitation and bubble collapse process and are listed as follows.

(a) Sound wave frequency: High frequency will reduce cavitational effect because (1) the negative pressure produced by rarefaction cycle is insufficient in duration and/or intensity to initiate cavitation or (2) compression cycle occurs faster than the time for microbubbles to collapse (Adewuyi 2001). At lower frequency, more violent cavitations will be produced, resulting in higher localized temperatures and pressure (Vajnhandl and Marechal 2005).
(b) Intensity of sound wave: Increasing intensity will increase the acoustic amplitude, resulting in a more violent cavitation bubble collapse (Adewuyi 2001).
(c) Solvent characteristics: Cavities are more readily formed in solvents with high vapor pressure, low viscosity, and low surface tension (Adewuyi 2001). However, the higher the vapor pressure, the less violent the bubbles collapse would be due to more vapor entering the bubbles (Peters 1996).
(d) Gas properties: Presence of soluble gases will result in the formation of larger number of cavitation nuclei. However, higher gas solubility would cause more gas molecules to diffuse into cavitational bubble, causing its collapse to be less violent (Vajnhandl and Marechal 2005). Heat capacity ratio (C_p/C_v) or polytropic ratio (γ) and thermal conductivity of the gas will also affect the amount of heat release during the collapse (Peters 1996; Adewuyi 2001).
(e) External pressure: Higher external pressure will reduce the vapor pressure of liquid and increases the intensity needed to induce cavitation (Vajnhandl and Marechal 2005).
(f) Temperature: For non-volatile substrates (that react through radical reaction in solution), reducing the reaction temperature will result in an increase in sonochemical reaction rates. The increase in cavitation intensity is caused by the lowering of vapor pressure and thus, reducing the amount of vapor diffusing into the bubbles to cushion the cavitational collapse (Destaillats et al. 2003; Adewuyi 2001).

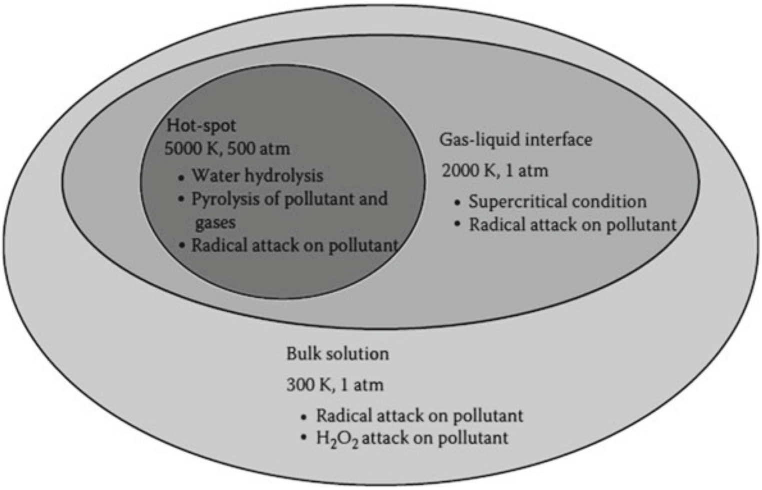

Fig. 2.4 Reaction zone in cavitation process. Reprinted with permission from Chowdhury and Viraraghavan (2009). Copyright (2009), Elsevier

There are four theories to explain sonochemical effects: (1) hot-spot theory; (2) "electrical" theory; (3) "plasma discharge" theory,and (4) supercritical theory. These theories lead to various mode of reactivity: pyrolytic decomposition, OH· oxidation, plasma chemistry, and supercritical water oxidation. Among these theories, hot-spot theory is widely accepted in explaining sonochemical reactions in the environmental field (Adewuyi 2001). According to hot-spot theory, each microbubble acts as a small microreacter which produces different reactive species and heat during its collapse (Vajnhandl and Marechal 2005). The temperature profile shows that there are three zones associated with a cavitational bubble (Chen 2012), as depicted in Fig. 2.4:

(a) Thermolytic center (hot spot), the core of the bubbles with localized hot temperature (~5,000 K) and high pressure (~500 atm) during final collapse of cavitation. Inside this region, bubble water molecules are pyrolyzed forming OH· and H· in the gas phase. The substrate either reacts with the OH· or undergoes pyrolysis.
(b) Interfacial region between the cavitational bubble and bulk liquid, similar reaction as hot spot occurs, but in aqueous phase. However, additional reaction occurs in this region, in which OH· recombine to form H_2O_2. In this region, hydrophobic compounds are more concentrated than the bulk solution.
(c) The bulk region, the temperature remains at a level similar to room temperature because cavitation is an adiabatic process. In bulk phase, the reactions occurred are basically between the substrate and the OH· or H_2O_2

There is a clear distinction between the effects of ultrasound in homogeneous and heterogeneous media. For homogeneous media, sonochemical reactions are related to new chemical species produced during cavitation, whereas for the latter, enhancement of the reactions could also be related to mechanical effects induced in liquid system by sonication (Destaillats et al. 2003). Sonochemistry usually deals with reactions in liquid component. When ultrasound is applied, it will induce the sonolysis of water molecules and thermal dissociation of oxygen molecule, if present, to produce different kinds of reactive species such as OH·, H·, O· and hydroperoxyl radicals (OOH·). Reactive species production follows the following reactions, with ‘)))’ denotes the ultrasonic irradiation (Eqs. 2.1–2.13) (Pang et al. 2011). Sonolysis of water also produces H_2O_2 and H_2 gas via OH· and H·. Even though oxygen improves sonochemical activities, its presence is not essential for water sonolysis as sonochemical oxidation and reduction process can proceed in the presence of any gas. However, presence of oxygen could scavenge the H· (and thus suppressing the recombination of OH· and H·), forming OOH·, which acts as oxidizing agents (Adewuyi 2001).

$$H_2O +))) \rightarrow OH\cdot + H\cdot \quad (2.1)$$

$$O_2 +))) \rightarrow 2O\cdot \quad (2.2)$$

$$OH\cdot + O\cdot \rightarrow OOH\cdot \quad (2.3)$$

$$O\cdot + H_2O\cdot \rightarrow 2OH\cdot \quad (2.4)$$

$$H\cdot + O_2 \rightarrow OOH\cdot \quad (2.5)$$

$$OH\cdot + H\cdot \rightarrow H_2O\cdot \quad (2.6)$$

$$2OH\cdot \rightarrow H_2O + O\cdot \quad (2.7)$$

$$OOH\cdot + OH\cdot \rightarrow O_2 + H_2O \quad (2.8)$$

$$2OH\cdot \rightarrow H_2O_2 \quad (2.9)$$

$$2OOH\cdot \rightarrow H_2O_2 + O_2 \quad (2.10)$$

$$H\cdot + H_2O_2 \rightarrow OH\cdot + H_2O \quad (2.11)$$

$$OH\cdot + H_2O_2 \rightarrow OOH\cdot + H_2O \quad (2.12)$$

$$2H\cdot \rightarrow H_2 \quad (2.13)$$

Besides chemical effects, ultrasound can also produce significant physical effects (sonophysical). When ultrasound is introduced, liquid medium will absorb the acoustic energy from sound waves and flow along the wave’s propagation direction. Physical effects such as microstreaming, microstreamers, microjets, and shock waves can also be produced by cavitation bubbles, resulting turbulent fluid movement and a microscale velocity gradient in the vicinity of cavitational bubbles (Chen 2012).

(a) Microstreaming is the propagation of ultrasound waves through a liquid medium which creates small amplitude oscillatory motion of fluid elements around a mean position (Kuppa and Moholkar 2010). This phenomenon constitutes to an unusual type of fluid flow associated with velocity, temperature and pressure gradient (Tang 2003).
(b) Microstreamers are formed by cavitation bubbles travelling within the liquid to nodes or antinodes driven by *Bjerknes forces*. These bubbles travel in ribbon like structures along tortuous pathways (Chen 2012).
(c) Microjets are formed by the asymmetric collapse of cavitational bubbles near a micro-particle surface, with speed in the order of 100 m/s. The microjets will subsequently produce an asymmetric shock wave upon implosion of the bubble, resulting in direct erosion on particle's surface and de-aggregation of particles (Pang et al. 2011; Chen 2012).
(d) Shockwaves are produced by adiabatic compression of cavitational bubbles during the compression phase of radial motion. At the point of maximum compression, bubble wall comes to a sudden halt and rebounces at high velocity. The converging fluid elements are reflected back from bubble interface, creating a high pressure shock wave that propagates through the medium (Kuppa and Moholkar 2010).

The fluid movement produced by ultrasound could enhance the physical mass-transfer processes between solid-bulk and gas-bulk interfaces. Hence, these sonophysical effects described above can facilitate various mixing, breaking down of particles and macromolecules, polymer degradation, desorption, extraction, and cleaning processes (Chen 2012; Yasuda and Koda 2012).

2.2 Conclusion

Ultrasonic cavitation, which is an AOP, has been proposed as an attractive alternative method for the treatment of contaminants due to its advantages of being non-selective and without generating secondary pollutants. Four different theories are usually used to explain sonochemical effect but hot-spot theory is usually used to explain the process, in which microbubbles are produced to generate heat and different reactive species. Ultrasonic cavitation is known to generate reactive species such as OH·, H·, O· and OOH·, which are able to oxidize almost all toxic contaminants present in the environments. The mechanisms of ultrasound make it unique when compared with other AOPs. However, it is found that the degradation rate is rather slow by merely using ultrasonic treatment alone. Therefore, some efforts have been devoted to increase the degradation efficiency by applying hybrid techniques.

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