

The ultrasonic reaction schemes biology essay

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An unusual environment with enormous temperatures and pressures is created as an effect of cavitation collapse thereby initiating chemical reactions aiding degradation of recalcitrant compounds. The ultrasonic energy induces huge heat energy (pyrolysis) or the production of reactive free radicals which impacts on the chemical reactions occurring. The mass transfer rate in an aqueous solution during ultrasonic irradiation is thus accelerated via turbulence. The three potential zones where chemical and physical reactions occur in sonochemistry are inside the micro-bubbles, interfacial liquid region between the bubbles and the bulk solution and, in the bulk solution (Adewuyi, 2001). In the gaseous phase cavity where temperatures are in the order of 5000 K, pyrolysis of water molecules occurs, producing $\bullet\text{OH}$ and $\bullet\text{H}$. The degradation pathway inside the bubbles is either pyrolysis or radical attack, depending on the substrate chemical nature. In the interfacial region, supercritical conditions resulting from very high temperatures and pressures, lead to ionisation of water molecules and further degradation of the pollutants. It is estimated that the concentration of $\bullet\text{OH}$ that could be achieved in the interfacial zone upon cavitation collapse is as high as 4 mM (Lu and Weavers, 2002; Okitsu et al., 2005). In the bulk phase, decomposition of pollutants basically occurs by attack by $\bullet\text{OH}$ radicals or H_2O_2 produced diffusing into the bulk solution. Since cavitation is an adiabatic process, temperature in the bulk phase is similar to room temperature (Thompson and Doraiswamy, 1999). High-speed micro-jets of liquids in the order of 100 m/s are generated near the micro-particle surface as a result of cavitation bubbles collapsing (Pang et al., 2011), thus, generating ultrasonic asymmetric shock wave. Based on their volatility,

hydrophobic and hydrophilic compounds behave differently when subjected to ultrasonic irradiation; highly volatile hydrophobic compounds are easily destroyed inside cavitation bubbles whilst less or non-volatile hydrophilic compounds impede oxidation by ultrasound inside bubbles (Chowdhury and Viraraghavan, 2009). Figure 2.: Sonochemical reaction zones (Source: Chowdhury and Viraraghavan, 2009)

Sonochemical kinetic mechanism of water molecules

The splitting of water molecules induced by ultrasonic irradiation is caused by a series of reactions (Ince and Tezcanli-Güyer, 2004; Inoue et al., 2006):

Table 2.: Sonolysis mechanism of water

molecules	Mechanism	Equations	Description	Thermal dissociation	Note: '))'
	denotes ultrasonic irradiation	(1)(2)(3)	The thermal dissociation of water molecules in the cavities results in the formation of reactive species such as, •OH, •H and •OOH. The local concentration of •OH is highest at the point of collapse, such that a large amount of the hydroxyl radicals is recombined at the gas-liquid interface and then released into the bulk solution (Eren, 2012).		
	Recombination of free radicals	(4)(5)	The reactions induce the formation of H ₂ O ₂ which normally occur either outside the hot cavitation bubbles or at the cooler interface (Pang et al., 2011).		

Factors influencing sonochemical reactions

The diffusion of •OH radicals, which is the basis of sonolysis, is governed by several parameters such as frequency, ultrasonic power, geometry of sonicator, the presence of dissolved gas, and additional oxidants (Eren, 2012) as given in Table 2. 5. Table 2.: Factors affecting sonochemical

degradation Factors Effects on sonochemical degradation Ultrasonic frequency As per Tezcanli-Guyer (2003), sonochemical effects are energetically more effective at medium frequency (300-600 Hz) than at short frequencies (20-100 Hz) due to easy mass transfer from liquid to vapour phase and enhances the formation of $\bullet\text{OH}$. Hydrophilic and non-volatile organics such as dyes are more easily degraded at higher frequencies whilst low frequencies favor effective degradation of volatile and hydrophobic compounds. Bubble lifetime is shorter at higher frequencies which brings about quick collapse and makes possible the ejection of radicals and, hence prevents recombination reactions from occurring inside the bubble or its interface (Vajnhandl and Le Marechal, 2007). Acoustic power An increase in acoustic power results in an increase in the rate of reaction to a maximum until it decreased with further increase in power. An optimum acoustic power exists above which a great number of bubbles are generated, forming a dense cloud near the probe tip, hindering the transmission of energy through the liquid (Vajnhandl and Le Marechal, 2007). pH Dye degradation is substantially reinforced at acidic conditions mainly due to protonation of negatively charged SO_3^- sites which provide hydrophobic enrichment of the molecules (Behnajady et al., 2008). Thus, additional oxidation reactions at the gas-liquid interface occur as a result of more dye molecules approaching to the negatively charged cavity bubbles where $\bullet\text{OH}$ radicals are in abundance. Conversely, under alkaline conditions, degradation is hindered due to presence of ions such as HCO_3^- and CO_3^{2-} which acts as $\bullet\text{OH}$ scavengers. Initial dye concentration Increasing initial dye concentrations lead to a reduction in the ultrasonic degradation of dye as excess dye

molecules at the interfacial zone act as physical barriers preventing mass transfer at the bubble-liquid interface (Goel et al., 2004). Besides, the generation of dye metabolites and OH scavengers (CO₃²⁻ and SO₄²⁻) is enriched which further decreased dye degradation (He et al., 2008; Eren, 2012). Temperature An increase in temperature results in an overall decreased in the reaction effect. Bubbles formed during cavitation contain more vapors although the temperature rise effects in an increase in the equilibrium vapor pressure of the system which facilitate bubble formation. This increase in vapor mitigates the ultrasonic energy produced upon cavitation. Thus, the largest sonochemical effects, contrary to chemical reactions, are obtained at lower temperatures whereby there is sufficient gas nuclei required for cavitation formation (Thompson and Doraiswamy, 1999).

Presence of dissolved gases Dissolved gases act as nucleation sites for cavitation (Thompson and Doraiswamy, 1999). As a result of cavitation bubble implosions, the gases are expelled from the liquid such that cavitation events become difficult to initiate. Hence, continuous gas flow should be supplied which facilitate generation of cavitation bubbles. A gas having a high specific heat ratio provides greater cavitation effects than one with a low specific heat ratio (Thompson and Doraiswamy, 1999). Dye degradation by sonolysis is significantly enhanced with gas flow of monatomic gases such as argon and helium as more energy is converted upon cavitation, as compared to diatomic gases such as nitrogen and oxygen. Extremely soluble gases impact negatively on cavitation effects due to the formed bubbles re-dissolving before collapse occurs. Table 2.: Some recent studies which used ultrasound as a basic tool for dyestuff degradation

in homogeneous reactions
No. Dye/ Initial concentration
Sonochemical
conditions
Experimental conditions
Results