

## The Chemistry of Ultrasonic Degradation of Organic Compounds

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**Abstract:** The destruction of toxic organic molecules using advanced oxidation processes (AOPs) is a potent tool for pollution control and environmental protection. Ultrasound is a convenient and effective method of generating hydroxyl radicals which is the key oxidant in AOPs. This review describes the use of ultrasound and associated chemical reactions, with and without additives, as a powerful means of remediating water contaminated with organic pollutants. After a brief introduction to ultrasound and sonochemistry, their application for the oxidation of polycyclic aromatic hydrocarbons, phenol and substituted phenols is considered. Next is the decomposition of chlorinated phenols, and other chlorinated organics, then removal of recalcitrant smaller organic molecules. A discussion follows of recent work that has investigated the effects of initial concentration of substrates; the use of different ultrasonic frequencies; the inclusion of oxidising species, inorganic particles, or salts and their contribution to enhanced degradation. Finally, brief comments are made on the status of ultrasound as an AOP treatment.

**Keywords:** Sonication, degradation, oxidation, pollutants, hydroxyl radicals, advanced oxidation process.

## 1.0 Introduction

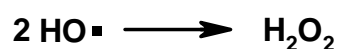
The need for clean water, which is toxin and chemical free, is an ever increasing challenge in the 21<sup>st</sup> century. Biological processes are extremely efficient and cost-effective at removing most organic compounds from wastewater but this technique has its limits when persistent organic pollutants are present. Consequently, new techniques are necessary to degrade these potentially toxic compounds and the most effective is advanced oxidative processes (AOPs) [1]. This general oxidative approach is based on the production of hydroxyl radicals (HO•) which, apart from fluorine, is the most powerful oxidant known. On reaction with HO•, organic pollutants (particularly aromatics) rapidly convert into oxidised species which then further degrade into smaller non-toxic molecules or fully mineralise to CO<sub>2</sub> and H<sub>2</sub>O. There are a number of methods for generating hydroxyl radicals using AOPs but only the use of ultrasound in degradation of organic pollutants will be discussed in this review.

Ultrasound is considered to be the region between 18 kHz up to 10 MHz and is responsible for a huge number of chemical and physical effects. Sonochemistry – the application of ultrasound in chemistry involves frequencies between 20 kHz and 2 MHz. Much of the early work in this area has been described in a number of excellent reviews but these have tended to be either rather general and/or historical [2-5] or very specific [6,7]. Reviews directly related to the topic were published in 2001 [8] and 2009 [9] and the purpose of the current work is to describe recent results obtained from studies on the use of ultrasound applied to the degradation (oxidation) of a variety of organic compounds. A brief introduction to ultrasound and its use as an advanced oxidation process is followed by descriptions of new work (since 2000)

carried out on the sono-degradation of: phenols, substituted phenols, chlorinated aromatics, and selected small organic molecules. Only ultrasonic techniques will be described in this review and consequently, multi-hyphenated processes such as sono-electrochemistry, sono-photochemistry and sono-luminescence have been excluded, as have hydrodynamic cavitation techniques.

### 1.1 Chemistry of ultrasonic degradation

When aqueous solutions are irradiated with ultrasound the H-O bond in water is homolytically cleaved to form hydroxyl radicals and hydrogen atoms (Scheme 1). This process is the result of cavitation, whereby very high temperatures and pressures are generated within an imploding bubble. The fate of both these species depends on the conditions of the reaction and the presence of other (organic) compounds. The most common reaction is dimerisation of the hydroxyl radical producing hydrogen peroxide and the amount of H<sub>2</sub>O<sub>2</sub> generated is often used as a measure of the effectiveness of the ultrasonic equipment employed [10].



#### Scheme 1

In 1983, Riesz [11] reported the direct evidence for the formation of HO• and H• in cavitation bubbles produced by 50 kHz ultrasound in argon saturated aqueous solutions. Later, Petrier et al. [10], showed that higher frequencies (514 kHz) were more effective than 20 kHz at generating HO• and, hence, hydrogen peroxide in oxygen or argon saturated water. Surprisingly, although 514 kHz was superior for

H<sub>2</sub>O<sub>2</sub> production with both gases, it was found that when the sonication is performed in the presence of oxygen rather than argon, peroxide production was greater at 514 kHz but with argon 20 kHz was better. These results allowed for the postulation as to what is happening in and around the cavitation bubble. When radicals are produced inside the bubble they can recombine or escape into the surrounding solvent. What actually transpires depends on the frequency used, the dissolved gas and the rates of the radical reactions. With higher frequency the cavitation bubble collapses with the release of less energy over a shorter timescale resulting in ejection of the HO• and the formation of H<sub>2</sub>O<sub>2</sub>. However, at a frequency of 20 kHz the hydroxyl radicals can react with organic compounds and begin a degradation process. This work was extended [12] by relating the rate of degradation of chlorobenzene and 4-chlorophenol to their vapour pressures and solubility in water. At 300 kHz, it was found that if the two compounds were present together in a sonicated solution then there was sequential degradation whereby the more volatile chlorobenzene was able to enter the cavitation bubble and be destroyed. Degradation of 4-chlorophenol only began after complete removal of the chlorobenzene. However, in oxygen-saturated water both compounds degraded simultaneously and two possible explanations were offered based on the enhanced production of HO•. Firstly, the presence of oxygen in the immediate volume surrounding the cavitation bubble enhances hydroxyl radical production in this shell of supercritical water and/or the degradation of chlorobenzene in the bubble produces chlorine atoms which increase the amount of hydroxyl radicals which then decompose the less volatile component.

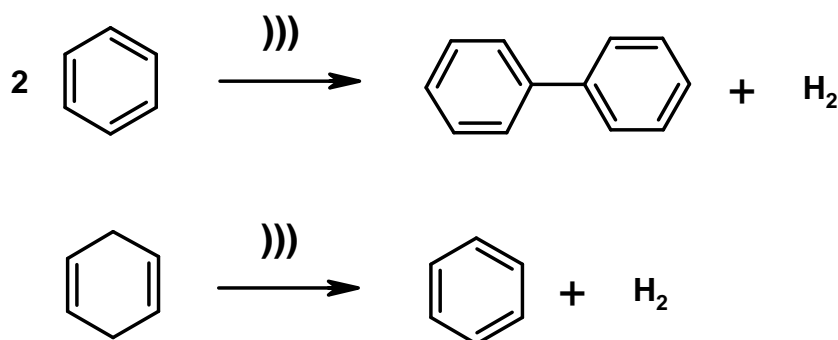
## **2. Degradation of Non-Chlorinated Aromatic Compounds**

### **2.1 Degradation of polycyclic aromatic hydrocarbons (PAHs)**

The sono-degradation of simple polycyclic aromatic hydrocarbons follows first order kinetics [13]. The rate of degradation was substantially decreased in the presence of other organics due to radical scavenging. However, the rate is enhanced when oxygen, but not nitrogen, was bubbled through the solution before sonication indicating that oxygen is involved in the degradation of PAHs. A HPLC study of the sono-degradation of phenanthrene at 30 kHz [14] showed that anthracene and naphthalene were initially formed but the main product identified was phenol, particularly in the absence of light. The effect of operating conditions and the presence of additional components on the sonochemical degradation of PAHs with 24 and 80 kHz unveiled that degradation was found to decrease with increasing initial concentration and temperature and decreasing frequency and power. When butan-1-ol, a classic hydroxyl radical scavenger was added, the amount of degradation was substantially decreased but on addition of ferrous ion enhanced degradation was observed [15].

Ondruschka et al. [16] extended the studies by investigating the cyclic hydrocarbons ( $C_6H_x$ ): benzene, 1,3-cyclohexadiene, 1,4-cyclohexadiene and cyclohexene. The sonolysis followed first-order kinetics and corresponded closely to the solubility of the substrates in water. As previously observed, the rate of degradation was inversely proportional to concentration and benzene was much more resistant to degradation than cyclohexene. Interestingly, the aquasonolysis of benzene yielded biphenyl but 1,4-cyclohexadiene gave mainly benzene (Scheme 2). Later work [17] confirmed that the order of yield of benzene formation on aquasonolysis was 1,4-cyclohexadiene > 1,3-cyclohexadiene > cyclohexene. When the reaction was studied in a variety of

organic solvents, it was found that the sonication proceeded faster in polar than in non-polar solvents. This work provides an insight into the cavitation mechanisms pertaining to aquasonolysis of aromatic compounds and the sono-reaction rates and the sonoproducts were found to be dependent on the physicochemical properties of the solvents used, as well as the volatility, the polarity and the reactivity of the reactants [18].



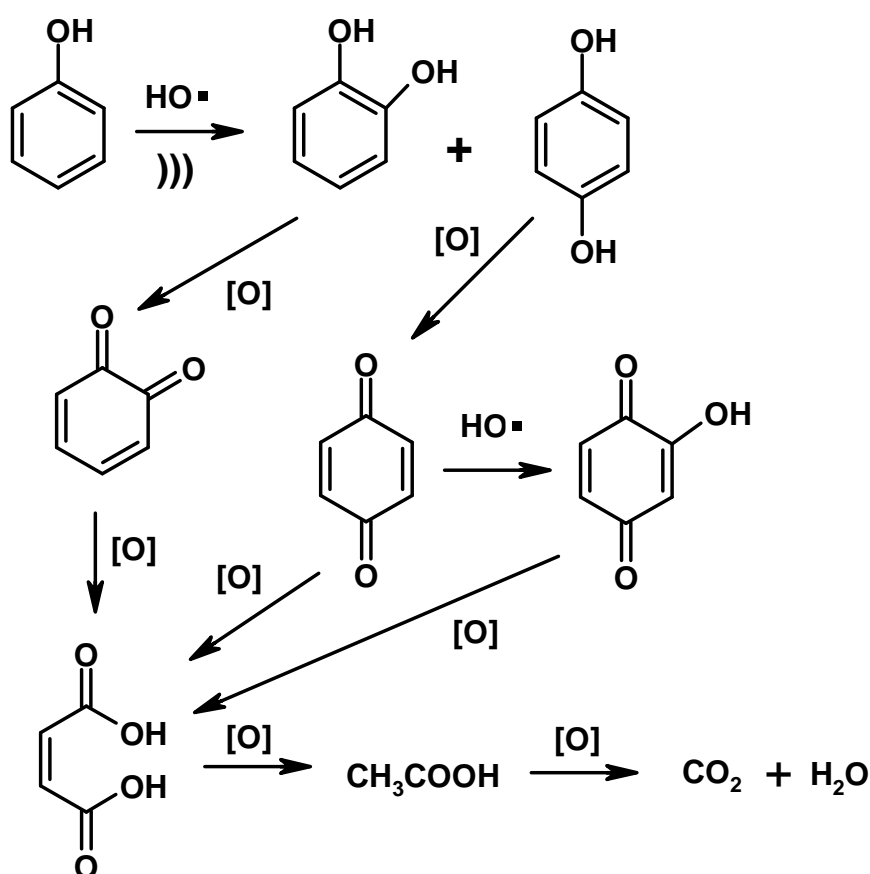
**Scheme 2**

When thiophene and substituted thiophenes are treated with ultrasound in water it is found that the rate constants correlate well with the water solubilities and Henry's Law constants. Once more, initial concentration has a major effect on the degradation rate and it appears that the transfer of organics between the cavitation bubble and the bulk liquid strongly influences the sonolysis. The production of carbon disulphide and diacetylene indicates that pyrolysis is the main pathway of degradation [19].

## 2.2 Degradation of phenol

Phenol is a pollutant in its own right but is also an excellent model compound for a number of toxic chemicals found in wastewater from a variety of industries. Much work has been carried out on the sonochemical decomposition of phenol and has been

reviewed recently [20]. The reaction begins with hydroxyl radical attack at the ortho- and para- positions of the phenol followed by further oxidation to quinones, ring opening and oxidation to diacids. The final steps produce smaller molecules including the oxidatively resistant acetic and formic acids. Under certain conditions complete mineralisation can occur (Scheme 3).



**Scheme 3**

Entezari et al. [21] have described a comparison of a cylindrical ultrasonic reactor operating at 35 kHz with the more traditional 20 kHz frequency and 500 kHz - all delivering the same power of 50 W. The rate of phenol destruction was higher at 500 kHz than at 35 or 20 kHz when water alone was used but on the addition of hydrogen peroxide and copper sulphate (Fenton-like conditions) the most efficient system was

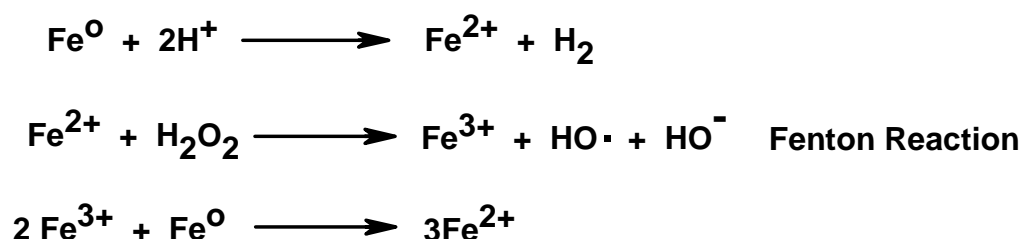
at 35 kHz as a result of different factors rather than just a frequency effect. Other additives have been used to enhance the sono-degradation of phenol. When the volatile hydrogen atom scavengers  $\text{CCl}_4$  and perfluorohexane were added to aqueous solutions of phenol, degradation rates were seen to increase probably due to amplified production of chlorine atoms rather than hydrogen atom scavenging [22]. Phenol degradation is also enhanced by the addition of NaCl and ozone. The latter hybrid technique could be used to produce intermediate acids which are much more biodegradable [23].

Catalytic wet peroxide oxidation is an alternative method for degradation of phenol and has now been investigated along with ultrasound irradiation [24]. This technique uses mixed Al-Fe pillared clay (FAZA) in a variety of physical forms and ultrasound was found to enhance the oxidation performance of the catalyst. The improvement was due to a decrease in diffusion resistance in the catalyst pores. A multivariate study by factorial design of experiments using another novel heterogeneous catalyst, Fe-SBA-15 along with hydrogen peroxide and ultrasound has been reported [25]. Ultrasound was found to increase phenol oxidation without damaging the iron catalyst. The influence of the variables  $\text{H}_2\text{O}_2$  concentration, catalyst loading, and presence or absence of ultrasound was studied. Very high mineralisation was obtained and the technique of coupling ultrasound/Fe-SBA-15/ $\text{H}_2\text{O}_2$  may be a powerful procedure for ambient temperature wastewater treatment. The work was extended to examine the effect of different frequencies on the degradation of phenol solutions. It was established that coupling 584 kHz with the Fe-SBA-15 catalyst in the presence of optimal amounts of  $\text{H}_2\text{O}_2$  was the most efficient methodology for phenol mineralisation [26]. Bremner and co-workers have investigated the uses of the, so



called, advanced Fenton process (AFP) to degrade a variety of pollutants including phenol [27] and the use of ultrasound to enhance degradation of phenol using the AFP was later studied. Total organic carbon (TOC) measurements were used to determine the effectiveness of phenol oxidation as ascertained by the Taguchi experimental design method [28]. It was found that removal of phenol from aqueous solution was similar at pH 2.0 and 2.5 but the amount of H<sub>2</sub>O<sub>2</sub> and the initial concentration of phenol used were major factors. Sonication with an ultrasonic bath produced some increased oxidation but a cup-horn sonicator showed that TOC decrease was favoured by higher intensity.

The AFP process proceeds in acid solution via the generation of ferrous ions from zero-valent iron. The former then react with hydrogen peroxide in a normal Fenton process to generate hydroxyl radicals which oxidise phenol as shown in Scheme 4. What makes the AFP unique is that the ferric ions thus produced are recycled by interaction with the zero-valent iron in a concerted oxidative-reductive step generating additional ferrous ions.



**Scheme 4**

The degradation of phenol was also investigated using 20, 300 and 520 kHz ultrasound along with hydrogen peroxide or ozone as oxidant and the zero-valent

metals iron and copper [29]. The most efficacious conditions involved iron as catalyst with hydrogen peroxide and 300 kHz ultrasound which was superior to the use of ozone along with copper metal and ultrasound. A similar result was observed when the same wavelengths were investigated with a variation in the conditions of pH and initial phenol concentration [30]. Powdered coal ash as an additive has also been investigated [31]. It was found that when phenol was sonicated (200 kHz) with and without powdered coal ash (53-106  $\mu\text{m}$ ) the latter process was faster and the optimum amount of coal ash was around 0.5 wt%. It was shown that hydroxyl radicals rather than hydrogen peroxide were the oxidising species and the roughness of surface presented by the coal increased the nucleation sites and hence reactivity.

### **2.3 Degradation of substituted phenols**

Von Sonntag [31] studied the sonolysis of 4-nitrophenol in argon-saturated water using 321 kHz and found that at pH 10, when the 4-nitrophenol was fully deprotonated, the degradation proceeded by hydroxyl radical action. However, at pH 4 the mechanism changes and oxidative-pyrolytic degradation becomes more prevalent as indicated by the production of CO, CO<sub>2</sub> and H<sub>2</sub>. A study of the degradation of 4-nitrophenol using ultrasound operating at 25 and 40 kHz and, interestingly, a combination of these two frequencies showed that the joint mode of operation improved the rate of degradation probably due to an increase in acoustic pressure experienced with the dual frequency [33]. An intriguing study on sono-degradation was carried out by simultaneously irradiating 4-nitrophenol and aniline in oxygen saturated water with 610 kHz ultrasound [34]. The pH of the solution plays an important part in the degradation with hydrophilic substances, such as 4-nitrophenol, being degraded faster at low pH due to their ability to diffuse to the

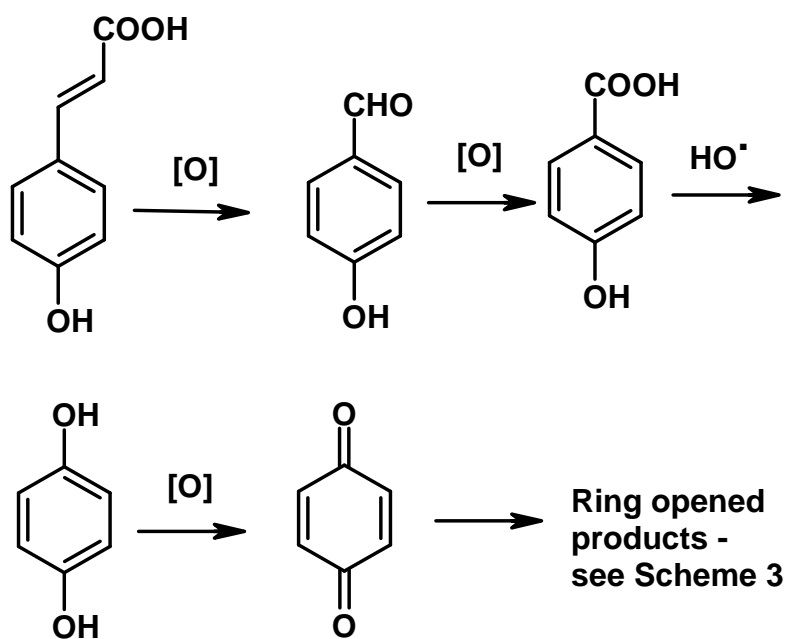
hydrophobic gas bubble-liquid interface. Not surprisingly, degradation of aniline shows the opposite effect with maximum removal at basic pH. The rate of reaction of uncharged aniline (pH ~4.6) with HO• is about one third of that at pH 9.

The degradation of 2,4-dinitrophenol has also received some attention [35,36]. Since sonication alone is not sufficiently rapid, certain additives were investigated in order to increase the rate of reaction. Enhancement in rates was observed with the addition of FeSO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>, CuO, CCl<sub>4</sub>, O<sub>3</sub>, NaCl, and KI but Na<sub>2</sub>CO<sub>3</sub> was found to inhibit the reaction when pulsed 20 kHz ultrasound was used.

Polyethoxylates of alkylphenols are used industrially as surfactants but produce the toxic, persistent pollutants, nonylphenols, which also exhibit oestrogenic activity. Thus, there is considerable interest in removing these pollutants using AOPs and sonication has been investigated. It was found that with 200 kHz ultrasound and argon, oxygen or air atmospheres the sono-degradation of alkylphenols depended on the alkyl chain length. The rate of degradation was decreased in the presence of 2-methyl-2-propanol indicating that hydroxyl radicals were the main oxidant involved. The TOC decreased by 50-70% during sonication in the presence of Fe(II) and Fe(III) under argon and oxygen [37].

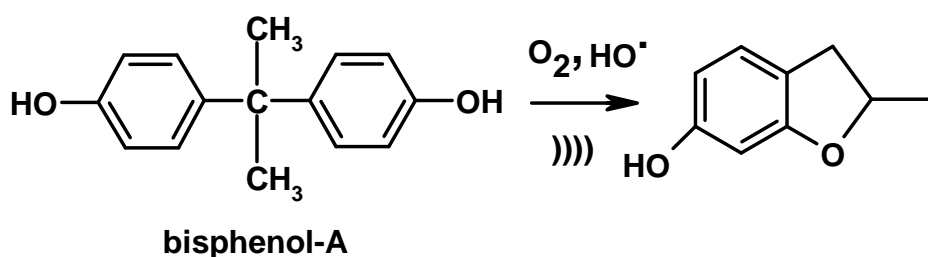
Cravotto et al. [38] have studied the integrated sonochemical and microbial treatment for removal of nonylphenols from water. Polluted water containing 1000 ppm of nonylphenol was subjected to the sono-Fenton process followed by biosorption by the fungus *Paecilomyces lilacinus*. A decrease in nonylphenol content of 90% was

achieved by first treating the sample with 300 kHz ultrasound in the presence of  $\text{FeSO}_4/\text{H}_2\text{O}_2$  for 1h and then inoculating the fungus and culturing for a further 7 days. Catalytic wet peroxide oxidation and ultrasound were also applied to the degradation of 4-hydroxybenzoic acid – a phenolic compound found in olive mill wastewater and a model for humic acids. The use of a mixed Al-Fe pillared clay and  $\text{H}_2\text{O}_2$  in conjunction with ultrasound (20 kHz) led to an increased degradation of the substrate compared to comparable silent reactions [39]. The degradation of p-coumaric acid and p-hydroxybenzaldehyde, which are also seen in olive oil mill wastewater, has been studied using an 80 kHz horn sonicator [40]. The effectiveness of removal of the substrates increased with greater power and decreasing initial concentration and temperature. Addition of free radical scavengers suppressed the degradation but radical promoters such as Fe (II) and  $\text{H}_2\text{O}_2$  had a positive effect on the oxidative process and a degradation pathway was suggested based on HPLC analyses of reaction mixtures (Scheme 5).



Scheme 5

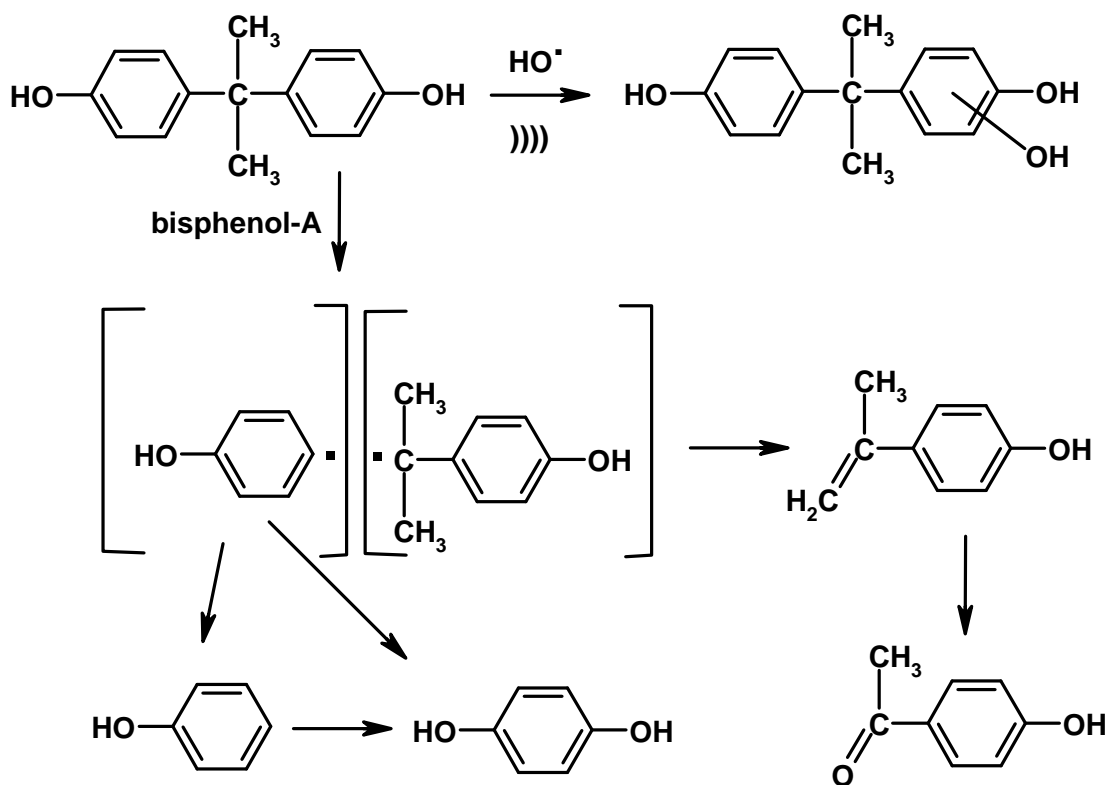
There has recently been considerable interest in the sonochemically enhanced degradation of bisphenol-A (BPA) since this compound is a major endocrine disruptor that is relatively resistant to normal biological treatment. The effects of the dissolved gases such as O<sub>2</sub>, Ar, air or N<sub>2</sub> on the sonolysis of BPA were studied using 500 kHz ultrasound [41]. The rate of decomposition of BPA was in the order of gases shown above with O<sub>2</sub> being two times more effective than Ar. GC-MS was used to identify a novel intermediate which was only formed in oxygen and was attributed to the reaction with HO• radicals (Scheme 6).



**Scheme 6**

An alternative procedure for degradation, compared the classical Fenton reaction with the sono-Fenton process [42] and reported that the rate was affected by pH and concentration of Fe(II). Both methods were found to be useful for degradation of BPA but the sono-Fenton process was superior. BPA degradation has also been investigated using 300 kHz ultrasound by varying the substrate concentrations, pH, the presence of hydroxyl radical scavengers and various gases [43]. As is usually found, high initial concentration of the phenol is detrimental to the degradation as is high pH. Degradation is fastest in air saturated aqueous solution which is surprisingly superior to oxygen saturation. Both *t*-butanol and carbonate ions greatly decreased the rate of decomposition.

Petrier and co-workers have studied the ultrasonically enhanced degradation of BPA in some depth [44,45]. Ultrasound (300 kHz) was employed alone and compared with the silent Fenton process in both deionised water and in natural water (containing a number of anions and cations). Uniquely, hydrogen peroxide for the Fenton reaction was added very slowly at a rate comparable to that at which ultrasound would have generated the oxidant in the absence of BPA. Both processes showed the same BPA removal rate in deionised water but ultrasonic treatment was slightly more efficient in natural water. HPLC/MS was used to identify intermediates which were largely formed as a result of HO• attack [44]. In an extension to this work [45] BPA degradation was investigated using ultrasound (300-800 kHz), and varying the saturating gas, BPA concentration, and ultrasonic power. The best conditions for removal of BPA were with 300 kHz ultrasound, O<sub>2</sub> and 80 W. BPA was readily eliminated completely in 90 min but TOC was still quite high due to highly ultrasonically recalcitrant small organic acids. The presence of hydroxylated aromatics indicated that the main degradation pathway involved HO•. Recently, water contaminated with low concentrations of BPA, was treated with 20 kHz ultrasound and the effects of sonic intensity and ozone were studied [46]. Additionally, since halomethanes are present in chlorinated drinking water the effect of the presence of CCl<sub>4</sub> on the degradation was also investigated and the main aromatic products identified by gc-ms are shown in Scheme 7.



**Scheme 7**

### 3.0 Degradation of Chlorinated Organics

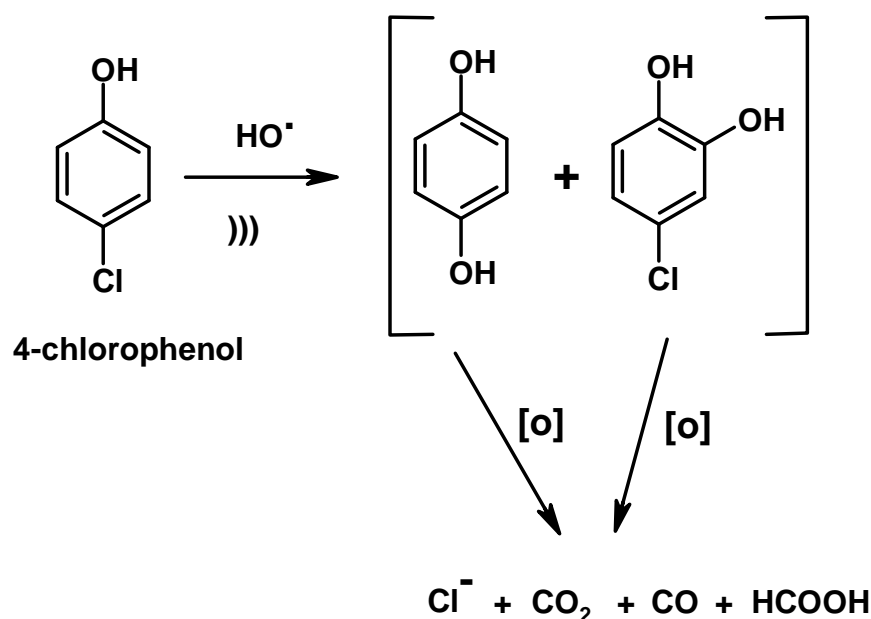
The sonochemical degradation of aromatic and chloroaromatic contaminants was reviewed by Petrier and Casadonte [47] in 2001. They summarised earlier work on sonochemical equipment, the ultrasonic treatment of water and discussed the mechanisms by which ultrasound generates reactive species that degrade aromatic pollutants. Also relevant, but not involving ultrasound is a general discussion of degradation of chlorophenols using advanced oxidation processes [48].

#### 3.1 Chlorophenols

When fertiliser or chemical effluents are treated with chlorine to remove colour, chlorophenols are often formed as toxic and recalcitrant by-products. Considerable effort has been expended in applying ultrasonic techniques for the decomposition of such pollutants. Lin and Ma [49] showed that over 99% of 2-chlorophenol was

decomposed and 86% was mineralised with the application of ultrasound (20 kHz) in the presence of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$ . The reaction was monitored by its redox potential that rose slightly with increasing amounts of  $\text{Fe}^{2+}$ . The main intermediate formed during the decomposition was identified as 2-chloro-p-benzoquinone and this readily decomposed further during the treatment. Teo [50] observed similar results when three different types of ultrasonic device were used and hydrogen peroxide or gas saturation (air or argon) were applied during the degradation. Nagata et al. [51] studied the degradation of a variety of chlorophenols using 200 kHz ultrasound under an air or argon atmosphere. The generation of hydroxyl radicals accounted for the main degradation process, as indicated by partial inhibition with t-butanol, though some oxidation occurred via pyrolysis. The addition of  $\text{Fe}^{2+}$  accelerated the degradation, probably due to Fenton-type reactions with generated  $\text{H}_2\text{O}_2$ . The effects of substrate concentration, temperature and ultrasonic frequency on the sonolysis of 4-chlorophenol (4-CP) in oxygen-saturated water led to further insight into the mechanism of degradation [52]. The main intermediates were identified as hydroquinone and 4-chlorocatechol which were further degraded to  $\text{Cl}^-$ ,  $\text{CO}_2$ , CO and HCOOH on extended treatment (Scheme 8). The rate of degradation of 4-CP depended on its concentration indicating that degradation proceeds in the bulk solution at low values but at higher concentration oxidation reactions are favoured at the gas-liquid interface. A lower temperature is advantageous for the degradation when using 20 kHz ultrasound but at 500 kHz there was little effect. The maximum rate of degradation was found to occur at 200 kHz.





**Scheme 8**

The degradation of 4-chlorophenol has also been studied using very high frequency (1.7 MHz) ultrasound with a reported low energy consumption [53]. Surprisingly, compared to all other reports, a higher concentration of substrate showed a faster rate probably due to the fact that the mechanism is high temperature pyrolysis rather than HO• oxidation and no intermediate products were detected.

The use of additives in conjunction with ultrasound for degradation of 2-CP has been shown to be more effective than just sonication [54]. On sonolysis alone, 2-CP was degraded in a radical reaction but in the presence of TiO<sub>2</sub> the reaction was more rapid probably due to continuous cleaning and activation of the catalyst. The optimised degradation, uncovered by varying intensity, temperature and amount of catalyst used led to a removal rate of around 10 times of that seen in the absence of ultrasound.

The benefit of using ultrasound, along with copper catalysed Fenton reactions, has also been described for degradation of 4-CP [55]. The synergistic effect of ultrasound and H<sub>2</sub>O<sub>2</sub> was only observed with the supported catalysts Cu/Al and Cu/Zn possibly

due to enhanced dispersion on sonication. Heterogeneous Cu/Al catalysis gave best 4-CP and TOC decrease but, interestingly, this was not mirrored with a homogeneous copper catalyst. Junk and co-workers [56] have described the sonolytic degradation (920 kHz) of a variety of aromatic organic pollutants including chlorophenols (and 4-fluorophenol) and found that the rate of mineralisation was dependent on substrate structure and concentration, bulk temperature, pH and the presence of other solutes such as detergents and humic acids. Virtually complete mineralisation was observed with no evidence of organic by-products and a chloride release corresponding to around 80% of the stoichiometric amounts. Temperature had little influence on the process but the presence of detergents had a small but statistically significant effect. Cravotto et al. have also used ultrasound to degrade a variety of persistent organic pollutants (POPs) in the presence of Fenton's reagent [57]. With 20.2 kHz ultrasound POP's were partially degraded at neutral pH; acidification with acetic acid to pH 2.0-2.3 did not affect the process but use of sulphuric acid (pH 1.7-2.0) ensured complete degradation. Interestingly, the authors report that similar results were obtained by use of microwave radiation for 15 min at 200W.

Polychlorinated phenols may also show enhanced rates of removal on sonication. Degradation of 2,4-dichlorophenol using 489 kHz ultrasound was studied in the presence of oxygen, air, argon and nitrogen [58]. The rate of substrate removal increases markedly when argon or oxygen is present but is low with nitrogen saturation. When the effect of pH was studied it was found that the best results were obtained at pH = 6.3 with O<sub>2</sub> present which was 2-4 times higher than at acidic or basic pH. Degradation of 2,4,6-trichlorophenol has also been investigated [59] at 20 kHz with different power input of ultrasound in the presence of TiO<sub>2</sub>. Remarkably,

rates of degradation were found to be best at highest intensities in the absence of catalyst but the opposite was seen in the presence of TiO<sub>2</sub>.

Pentachlorophenol (PCP) has been used as components of biocides, pesticides, insecticides and wood preservatives but is now classed as a priority pollutant in many countries. Consequently, the degradation of aqueous solutions of PCP is very important and has been studied using 20 and 500 kHz ultrasound as well as in the presence of ozone [60]. It appears that both pyrolysis and hydroxyl radical processes both occur. Addition of ozone did not affect the first-order degradation constant for PCP as it was similar to the rate constant combination for separate treatments.

Although definitely not ultrasound, a very interesting report on the degradation of PCP with audible frequency sound in the presence of ozone has been described [61]. The audible sound was produced with a large steel bar which was driven by three electromagnets and vibrated at 430 Hz. Ozone dissolution and PCP degradation were considerably increased by audible sonication compared to merely stirring and ozone bubbling. The authors suggest that the effect is probably due to induction of strong turbulence but that no hydrogen peroxide was produced and no decomposition was observed by sonolysis in the absence of ozone.

The cresol, 2-chloro-5-methylphenol (2C5MP), is used in the manufacture of resins, herbicides, pharmaceuticals and surfactants. Degradation of an aqueous solution of 2C5MP in the presence of TiO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> in conjunction with ultrasound (33 kHz) has recently been reported [62]. The best degradation rates were obtained with a combination of ultrasound, hydrogen peroxide and titanium dioxide. The order of the effect of inorganic ions on degradation rate of 2C5MP was Cl<sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > HPO<sub>4</sub><sup>2-</sup> >

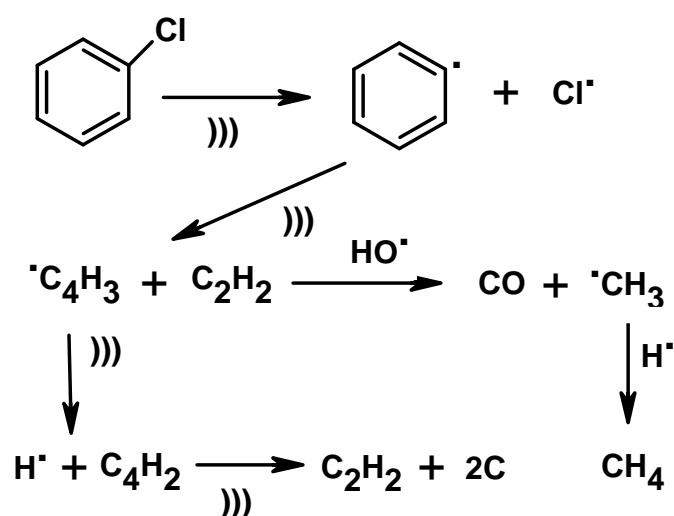
$\text{HCO}_3^-$ . Further addition of  $\text{CCl}_4$  and  $\text{CH}_3\text{OH}$  indicated that the main degradation route was via hydroxyl radicals.

The advanced Fenton process (zero valent iron and hydrogen peroxide in acid conditions) when allied to ultrasonic treatment has been shown to be a powerful combination for the mineralisation of organic species [63]. When 2,4-dichlorophenoxyacetic acid (2,4-D) is stirred and irradiated in the absence of any additives for 60 min there is an 11% decrease in TOC which rises to 18% when iron powder is applied. However, when the substrate is stirred with iron powder, hydrogen peroxide and subjected to 20 kHz ultrasound there is a rapid drop in residual TOC which levels out after 20 min at around 60% removal. The reaction proceeds via Fenton-like chemistry augmented by ultrasonic physical effects.

### **3.2 Other chlorinated organics**

The effect of ultrasound on various chlorinated aromatics has also been investigated. Aqueous solutions of chlorobenzene and polychlorinated biphenyls have been subjected to 200 kHz sonication [64] under an atmosphere of argon. After 30 min sonication, over 80% of the initial amounts of substrates had been degraded and it was found that degradation rates increased in line with their vapour pressure. In a follow up study the effect of ultrasound on chlorobenzene (CB) in water containing iron and palladium sulphates was reported [65]. The authors postulate that the CB degradation begins with pyrolysis inside the cavitation bubble giving, initially, benzene radicals which migrate outside the bubble where they are converted into benzene. Polyphenols were also identified and possible mechanisms discussed. The degradation of chlorinated aromatics has also been studied with 500 kHz ultrasound

[66]. The carbon-chlorine bonds are rapidly cleaved resulting in formation of CO, C<sub>2</sub>H<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub> and brown carbonaceous particles suggesting high temperature pyrolysis. Ultrasonic degradation of CB (Scheme 9) occurs in both the cavitation bubbles and the gas-liquid interface where mostly high temperature combustion occurs rather than hydroxyl radical attack (although this latter mechanism may apply at lower initial substrate concentrations).



**Scheme 9**

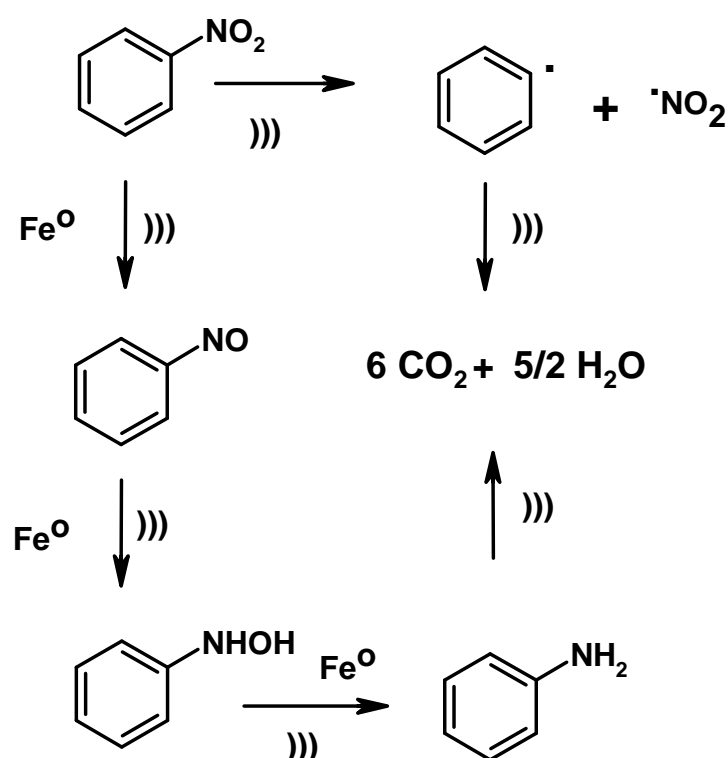
The hydroxyl radical probe compound 4-chlorobenzoic acid (4-CBA) has been studied with a view to imparting some mechanistic information on hydroxyl radical generation and reaction with ultrasound in the presence of FeOOH-H<sub>2</sub>O<sub>2</sub> [67]. The degradation rate of 4-CBA was determined at various concentrations of H<sub>2</sub>O<sub>2</sub> and goethite (FeOOH) and at different pHs. The rates of degradation were enhanced by ultrasound and were fastest at a pH below 4 with added FeOOH-H<sub>2</sub>O<sub>2</sub>. The positive effect of sonication was ascribed mainly to the cleaning and activation of the FeOOH surfaces and the greater mass transport of the reactants.

The herbicide (4-chloro-2-methylphenoxy) acetic acid (MCPA) is commonly used in rice fields in Japan and consequently wastewater may be contaminated by toxic compounds [68]. Consequently, ultrasonic degradation of aqueous solutions was investigated with 500 kHz under an argon atmosphere by monitoring chloride ion liberation, TOC and by-product production. After 180 min sonication with a power of 21 W, MCPA was fully decomposed although 60 % of the TOC remained in solution even after 6 h. GC-MS was used to identify the by-products which included 4-chloro-2-methylphenol, 4-chlorocatechol, methylhydroquinone, cresol, acetic acid and formic acid. Further insight into this degradation was obtained when the sonication was performed in the presence of nitrogen, air, oxygen, argon, and argon/air (60/40% v/v) [69]. The rate of decomposition was found to be greater in oxygen-enriched atmospheres due to enhanced radical production although dechlorination and TOC removal rates were higher with argon alone. However, the most effective conditions for overall removal of MCPA were sonication in Ar/O<sub>2</sub> (60/40% v/v).

Peters has described model studies related to remediation of ground water contaminated with simpler, more volatile chlorinated alkanes and alkenes [70]. Using pure and natural water contaminated with 1,2-dichloroethane along with ultrasound at frequencies of 20, 206, 361, 620 and 1086 kHz it was concluded that the chlorinated hydrocarbons were completely destroyed in 60-120 min via pseudo-first order kinetics. The destruction rate in deionised water and in ground water depended only on the dose rate but not the frequency although the energy efficiency decreases with higher frequency.

#### 4.0 Degradation of non-chlorinated simple organics

Nitro-aromatics often arise as explosives or rocket fuels or as by-products from the pharmaceutical or dye industries and their stability to conventional treatment render them particularly recalcitrant. However, TNT and its environmental transformation products can be degraded during sonication at 20 kHz [56]. The release of nitrate ion was monitored during the oxidation over 32 h and accounted for 74, 68 and 63% of the total nitrogen content of the nitro-substrates examined. Virtually, all the degradations discussed in this review thus far have involved ultrasound under oxidising conditions but the process can be equally effective in the presence of zero valent metals. Thus, a combination of sonication along with  $\text{Fe}^0$  is successful for nitrobenzene reduction but not for aniline [71]. The rate enhancements are most likely due to continuous cleaning and activation of the  $\text{Fe}^0$  surface and to increased mass transport. The relative amounts of nitrosobenzene and aniline are altered on ultrasonic treatment (Scheme 10).



## Scheme 10

The explosives RDX and ADN are also rapidly degraded with ultrasound when used in conjunction with zero valent aluminium at high pH [72]. Both explosives decompose in 20 min on sonication with 20 kHz ultrasound but no reaction is observed in the absence of  $\text{Al}^0$  and NaOH and a similar result is found when the additives are zeolites, alumina or titanium dioxide. Results indicate that the mechanism probably involves generation of fine aluminium powder and/or aluminium hydride which forces reductive denitration of the explosives.

The ultrasound enhanced degradation of aniline has also been studied in the presence of ozone [73]. It was found that little decomposition was observed with ultrasound alone although ozone on its own did give complete removal after 25 min. However, the combination technique was not only effective in rapidly oxidising aniline but gave a much better TOC decrease. As is common with these oxidations, only 50 % TOC removal was observed with the combined effect of US/ $\text{O}_3$ . The observed by-products included nitrobenzene, p-benzoquinone, p-aminophenol and low molecular weight carboxylic acids.

Generally, small organic acids are the end point of sonochemical oxidation of aromatic species and are thought to be very resistant to mineralisation. However, ultrasonic degradation of acetic acid has been reported using relatively low power (0.1–0.4W) with a frequency range of 30–100 kHz. The best frequency for degradation was found to be 60 kHz and, interestingly, the degradation rate increased up to a power input of 0.2 W and then decreased [74]. Further work at 40 kHz



indicated that the amount of degradation was enhanced with lower power input and lower initial concentration of acetic acid and on addition of NaCl [75]. The same group also used a similar acoustic set-up to study the degradation of oxalic acid [76] and found that the amount of degradation increased with higher ultrasonic power and the inclusion of NaCl but decreased on addition of hydrogen peroxide or when saturated with air or nitrogen gas. Formic acid has been used as a model compound for degradation studies with four different types of sonochemical reactor [77]. The extent of degradation was studied by varying such factors as time, initial concentration, intensity and frequency of irradiation, introduction of air, and liquid level in the case of the ultrasonic bath. When efficiency of degradation was taken into account the most expedient unit was a triple frequency (20, 30 and 50 kHz) hexagonal flow cell. Formic acid degradation was also studied [78] using a high frequency (590 kHz) stirred cup-horn reactor and the optimum conditions were found to be an initial concentration of 500mg/L, 200 rpm stirrer speed and the presence of dissolved oxygen. Additionally, process intensification was studied by the addition of NaCl, with 4% giving the best results.

1,4-Dioxane is known to be a by-product of surfactant production and it has similar physical properties to that of water and thus has the potential of contaminating potable water resources. Consequently, a number of groups have studied its decomposition using sonochemical enhancement. Ultrasound at 205, 358, 618, and 1071 kHz was deployed along with Fe (II) to degrade 1,4-dioxane and the fastest rate of mineralisation was seen at 358 kHz where 95% of the substrate was removed (TOC measurements) in 50 min. The addition of the hydroxyl radical scavenger, sodium bicarbonate, reduced the rate of decomposition but did not stop the degradation

completely [79]. Zoh et al. have studied the effect of adding  $\text{Fe}^0$ ,  $\text{Fe(II)}$  and  $\text{S}_2\text{O}_8^{2-}$  during the sonication of aqueous 1,4-dioxane [80]. They found that 80% of the organic was removed in 200 min on sonication alone but this was increased by about 20% when the oxidants were added individually to the sonicated solution. The effects of both  $\text{TiO}_2$  and  $\text{SiO}_2$  on the sonochemical oxidation of 1,4-dioxane, in an fascinating development, have been reported [81].  $\text{TiO}_2$  proved more effective than  $\text{SiO}_2$  but the photocatalytic destruction through sonoluminescence was not the main mechanism but rather the fact that sonication produced "thermally excited holes" in the  $\text{TiO}_2$ . Also, "oxygen vacancies" in the  $\text{TiO}_2$  surface aid the decomposition by enhancing cavitation. Further reports of this technique are awaited to see if this is a general phenomenon but see reference [62] for related work.

The widespread use of the gasoline additive methyl t-butyl ether (MTBE) has resulted in its frequent detection in groundwater and surface water. As a consequence, work on the sonolytic (20 kHz) degradation of MTBE has been described [82]. An increase in the rate of degradation was seen with higher power input and rise in temperature but the addition of potassium persulphate and, separately  $\text{Fe(II)/H}_2\text{O}_2$ , had a dramatic positive effect on the decomposition, with *tert*-butyl formate and acetone identified as the major products. Taste and odour problems present a challenge to water companies and 2-methylisoborneol (MIB) and geosmin (GSM) (produced by cyanobacteria) are often present and impart a musty odour to water. It has been found that irradiation of aqueous solutions of MIB and GSM with 640 kHz ultrasound produces rapid degradation via mainly radical processes. However, pyrolysis also occurs and by-products have been identified and the mechanism of the oxidation proposed [83].

Ibuprofen (IBP) is widely used as a pain reliever but it is a persistent organic pollutant as it is not biodegraded in the normal sewage treatment process. The use of 300 kHz ultrasound increased the extent of degradation from 30% to 98% in 30 min when the initial concentration was low. The rate of degradation increased under air or oxygen and was best carried out at acidic pH. Although, complete removal of IBP was achieved, the presence of intractable degradation products meant that there was still residual TOC but this could be dealt with in a subsequent biological step [84].

#### **4.0 Conclusions**

It is generally accepted that ultrasound generates three zones of reactivity: the centre of the cavitating bubble, the bubble-liquid interface, and the bulk solution. Different oxidising species may exist in each zone and reactants and products must diffuse into and then out of the various zones for effective oxidation to occur. Much of the early work utilizing ultrasound prior to 2000 has been extensively reviewed by Adewuyi [85] but more recently, there have been many additional studies into the precise mechanism of ultrasonic degradation of pollutants and of further ways to enhance the effect. There is no doubt that ultrasound is a powerful tool in the area of advanced oxidation processes. With the inclusion of additives, whether they are oxidising species, inorganic particles, or salts, and the use of different frequencies of ultrasound, the efficacy of the process of ultrasonic degradation has been significantly improved over the period of this review and many groups are contributing to further enhancing the effectiveness of this technique crucial to environmental remediation.

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