

## Phenol degradation using 20, 300 and 520 kHz ultrasonic reactors with hydrogen peroxide or ozone and zero valent metals

Rashmi Chand<sup>a</sup>, Nilsun H. Ince<sup>b</sup>, David H. Bremner<sup>a,\*</sup>

<sup>a</sup>Applied Environmental Sciences, School of Contemporary Sciences, University of Abertay Dundee, Dundee DD1 1HG, Scotland, UK

<sup>b</sup>Institute of Environmental Sciences, Bogazici Univeristy, 34342 Bebek, Istanbul, Turkey

### Abstract

The extent of phenol degradation by the advanced oxidation process in the presence of zero valent iron (ZVI) and zero valent copper (ZVC) was studied using 20, 300 and 520 kHz ultrasonic (US) reactors. The results support the hypothesis that phenols are converted by ZVI and ZVC to products that are oxidised more rapidly by Fenton's reagent. Experimental data shows that with ZVI, when the reaction was subjected to 300 kHz, complete phenol removal and 37% TOC mineralization was achieved within 25 min, whereas, in the case of 20 kHz US treatment no phenol was detected after 45 min and 39% TOC mineralization was observed. This novel study also investigated the use of zero valent copper (ZVC) and results showed that with 20, 300 and 520 kHz ultrasonic reactors, phenol removal was 10–98%, however, the maximum TOC mineralization achieved was only 26%. A comparative study between hydrogen peroxide and ozone as a suitable oxidant for Fenton-like reactions in conjunction with zero valent catalysts showed that an integrated approach of US/Air/ZVC/H<sub>2</sub>O<sub>2</sub> system works better than US/ZVC/O<sub>3</sub> (the ZOO process).

**Keywords:** Ultrasound, Zero valent catalyst, Cavitation, Phenol, Fenton Reaction.

\*Corresponding author: Tel.: +44 1382 308667; Fax: +44 1382 308663  
E-mail: [d.bremner@abertay.ac.uk](mailto:d.bremner@abertay.ac.uk) (David H. Bremner)

## 1. Introduction

Access to fresh, clean, uncontaminated water is recognised as a universal need for all societies. This, combined with the global requirement to protect our environment, continues to motivate a legislative drive toward more stringent limits on the amount of pollutants present in industrial wastewater discharge. This new legislation, is forcing de-pollution measures and in order to meet this challenge, industrial demand has grown for innovative and improved water treatment methodologies for both disinfection and pollutant removal.

Phenol is a common and important pollutant as it is found in variety of effluent streams from chemical industries (resins, plastics, textiles, pulp and paper, coal conversion, etc.) [1] and is often used as a model pollutant in wastewater remediation studies [2–4]. Wastewater containing phenol, even in low concentration, is considered to be toxic and thus, cannot be discharged directly into open water or to the normal sewage system. Therefore, removal of such hazardous effluents needs prior treatment before discharge. Conventional chemical, physical and biological treatments, such as advanced oxidation, adsorption using activated carbon particles and fibres or air stripping, have been used for ‘de-phenolisation’ of industrial wastewater [5]. Generation of hazardous by-products in all such processes further demands highly effective and improved ‘green’ technology which at the same time should involve low energy consumption and be highly cost effective. Several studies since 1990’s have focussed on the use of ultrasound in the degradation of phenols and by-products [6].

The action of ultrasound in aqueous solution produces radicals such as  $H\cdot$ ,  $HO\cdot$  and  $HOO\cdot$  via cavitation, and can be termed as an Advanced Oxidation Process (AOP) and, recently, acoustic ultrasound which produces cavitation has been introduced as a “green technology” due to its phenomenal *in situ* generation of oxidising radical species, which in turn react with the hazardous pollutants and mineralise them to non-toxic moieties that can easily be discharged into the sewage system [7]. Ince et al. (2001) reviewed and discussed ultrasound as a methodology for degrading harmful organic

compounds [8]. A number of ultrasonic frequencies have been utilised to study degradation of several organic compounds and the rate of degradation often depends on optimum operating conditions, reactor geometry and the components in the wastewater stream. Such parameters are very important for maximum yield and efficiency [9–12]. Ultrasound alone does not produce sufficient oxidising species from water to carry out degradation so often it is utilised along with Fenton reactions (Sono-Fenton and Photo-Fenton) [13].

Recently, the use of zero valent metals (ZVMs) such as iron, copper, nickel and zinc, have played a significant role in mineralising organic pollutants in wastewater [14–23]. Tratnyek et al. (1995) and Nurmi et al. (2005) have discussed the properties, electrochemistry, kinetics and interfacial phenomenon affecting contaminant remediation with zero valent iron metals [24,25].

The present work describes phenol degradation studies using zero valent iron (powder) and zero valent copper (metal pieces) as pseudo-catalysts in conjunction with a Fenton-like reaction and three frequencies of ultrasound. Degradation effectiveness of zero valent copper (high surface area copper flitters and fine rod-shaped solid copper particles) was compared with zero valent iron powder. Also, efficiencies of a range of ultrasonic reactors (20, 300 and 520 kHz) to produce hydroxyl radicals were gauged by measuring hydrogen peroxide production. The efficacy of ozone as an oxidant in Fenton-like reactions was also assessed in these US reactors.

## **2. Experimental**

### **2.1 Chemicals and equipment**

Phenol (99.8%) was obtained from Fluka; zero valent iron powder (325 mesh, 97%) from Sigma-Aldrich and hydrogen peroxide (Analytical reagent 30%) from Fisher Scientific. Two different kinds of copper catalyst were used: (i) zero valent copper metal flitters from BDH Ltd. and (ii) copper turnings (270 mesh) was obtained from May and Baker Ltd. Deionised water (MilliQ) was used throughout the study. Three ultrasonic reactors of different frequencies

were used: 20 kHz (Bandelin SonoPlus, tip diameter = 12 mm) and 300 kHz and 520 kHz ultrasonic reactors (UNDATIM Ultrasoncs). The overhead stirrer (Heidolph RZR 2020) used for control experiments and for use with the 520 kHz ultrasonic reactor was operated at 200 rpm. H<sub>2</sub>O<sub>2</sub> production was measured spectrophotometrically (Unicam, Enotek Ltd.); total organic carbon was determined by a TOC Analyser TOC-V<sub>CSH</sub> (Shimadzu) and phenol removal was measured on a calibrated GC (Agilent Technologies, Model 6890N). Ozone was generated using an OzoneLab 100 generator (Yanco Industries Ltd).

### **2.2 US/Air/H<sub>2</sub>O<sub>2</sub> system**

The sono-Fenton experiments were carried out in three different frequency ultrasonic reactors, 20, 300 and 520 kHz, having different capacities of 80, 100 and 300 mL, respectively, using appropriate volumes of aqueous phenol solution (2.5 mM) as a model pollutant. The pH was adjusted to 3 with appropriate amounts of H<sub>2</sub>SO<sub>4</sub> (0.1 M). The temperature (20 ± 5 °C) was maintained with the help of a cooling glass jacket around the US reactors. The desired amounts of hydrogen peroxide (2.38 g/L) and catalysts (0.6 g/L ZVI and 1 g (5g/L) ZVC) were added to the reactors just before switching the ultrasound on (reaction time zero). Aliquots of 1–3 mL were withdrawn at set intervals during 60 min of total irradiation time and filtered through 0.45 µm nylon membranes before being analysed. Silent reactions were carried out in an identical experimental set-up but using an overhead stirrer (200 rpm) instead of ultrasound at a temperature of 20 ± 5 °C.

### **2.3 US/O<sub>3</sub> system**

Experiments were performed using ozone, at pH 3 and pH 9, under identical phenol and catalyst concentrations as described above, Ozone gas (2 ppm) was sparged into the reaction solution with the help of fine one-point bubbler at a flow rate of 0.75 LPM. Samples were removed from the reaction at appropriate times and analysed for phenol removal and TOC mineralization.

## 2.4 Phenol

Phenol removal in the reactions was estimated using GC (Aligent Technologies, Model 6890 N) with an FID detector and a TOC analyser (Shimadzu). A standard calibration line (100 mM–4.5 mM) was first constructed and TOC samples were diluted 5 times before analysis.

## 2.5 H<sub>2</sub>O<sub>2</sub> Measurement

Hydrogen peroxide measurements were made spectrophotometrically at 351 nm using the I<sub>3</sub><sup>-</sup> method [26]. Solution A: KI (33 g), NaOH (1 g) and ammonium molybdate tetrahydrate (0.1 g) were dissolved together in water and made up to 500 mL in a volumetric flask. Solution B: Potassium hydrogen phthalate (10 g) dissolved in water in a 500 mL volumetric flask. For analysis, equal volumes (e.g., 2.5 mL each) of A and B were taken and mixed with an appropriate volume of reaction solution in a volumetric flask and made up to mark with deionised water. This mixture was then analysed spectrophotometrically at 351 nm and the concentration of hydrogen peroxide was obtained from the calibration curve. Hydrogen peroxide concentration was measured in both deionised water (pH 7) and also in 2.5 mM phenol solution (pH 3). During the study, air was sparged continuously for 60 min through the solutions at 1.5 LPM and every 20 min samples (1 mL) were withdrawn for spectrophotometric analysis.

## 3 Results and Discussion

### 3.1 Hydrogen peroxide formation

Figs. 1a and b show the results for the hydrogen peroxide generation in water and in aqueous phenol (2.5 mM) at different frequencies (20, 300 and 520 kHz). Hydrogen peroxide arises [27] from the reactions of HO<sup>•</sup> and HOO<sup>•</sup> radicals in the liquid phase around the cavitation bubble.

Hydrogen peroxide concentrations were measured spectrophotometrically during 60 min of ultrasonic irradiation and were found to increase linearly with time. It is noteworthy that in the presence of phenol (pH 3 and air 1.5 LPM), the hydrogen peroxide values are much lower compared to those in pure water (pH neutral and air 1.5 LPM) due to the fact that in the former case

many of the hydroxyl radicals produced by sonication react with the phenol before they could combine to form hydrogen peroxide. In water, due to the absence of organic substrates, the  $\text{H}_2\text{O}_2$  remains as formed. The rate of formation of hydrogen peroxide changes with frequency and the highest rate was obtained at 300 kHz. In case of 2.5 mM phenol (Fig. 1b), hydrogen peroxide production at 300 kHz started to level off after 40 min and the concentration only increased from 2.62 to 3.09  $\text{mg L}^{-1}$  over the next 20 min, whereas, in the case of water the concentration increased linearly from 5.64 to 8.32  $\text{mg L}^{-1}$  between 40 and 60 min, respectively (Fig. 1a).

The rate of hydrogen peroxide production in water using 20 kHz ( $0.060 \text{ mg L}^{-1} \text{ min}^{-1}$ ) and 520 kHz ( $0.764 \text{ mg L}^{-1} \text{ min}^{-1}$ ) US is much lower than 300 kHz ( $5.737 \text{ mg L}^{-1} \text{ min}^{-1}$ ). Hydrogen peroxide production in 2.5 mM phenol solution under acidic condition (pH 3) is five time higher in the 300 kHz US reactor when compared to 20 and 520 kHz and this agrees with the work of Petrier and Francony [27] where the degradation of phenol as well as  $\text{H}_2\text{O}_2$  production was found to be highest in a 200 kHz US reactor when compared to 20, 200, 500 and 800 kHz US reactors. This could be one of the possible reasons why a relatively high degradation efficiency has been observed in 300 kHz, shown later in the study.

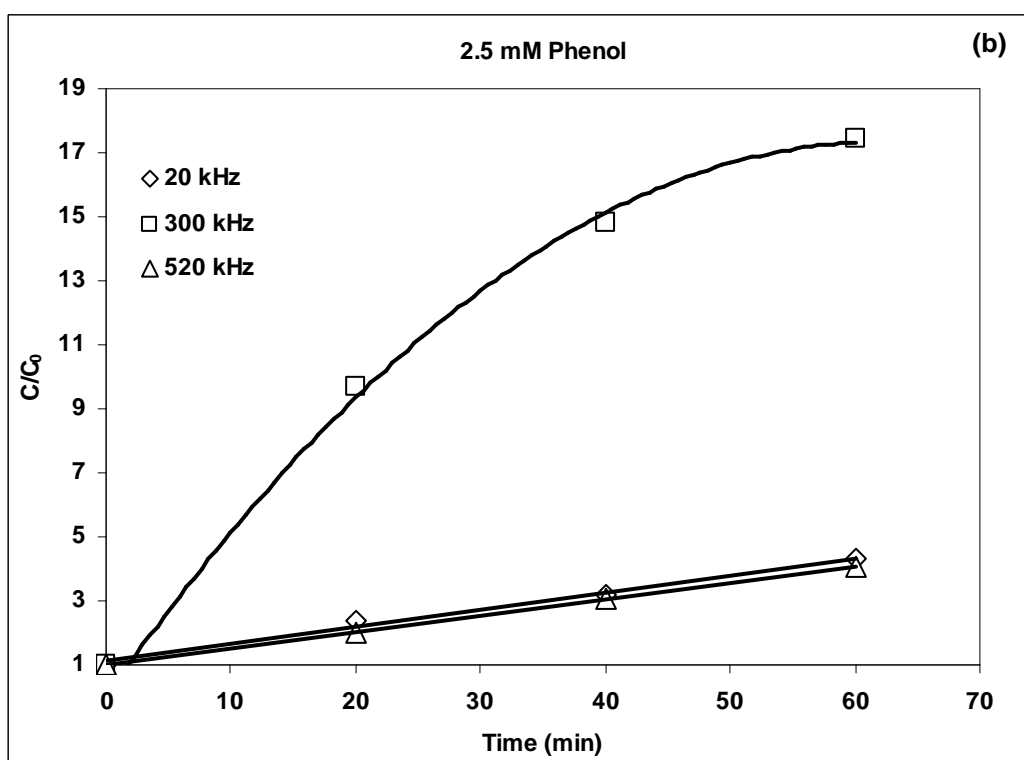
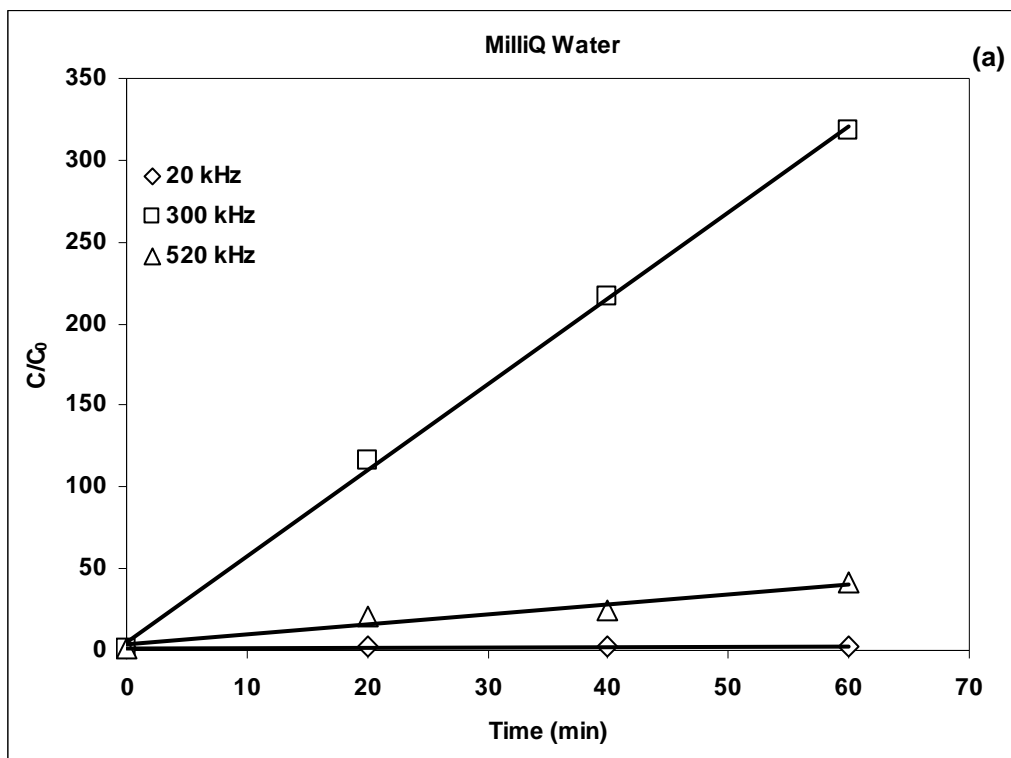


Figure 1: Hydrogen peroxide production. (a) in deionised (MilliQ) water and (b) in 2.5 mM phenol. Experimental conditions: phenol, 2.5 mM; US, 20 kHz (80 mL), 300 kHz (100 mL), 520 kHz (300 mL); reaction time, 60 min; sampling time, 20 min; air, 1.5 LPM; temperature  $20 \pm 5$  °C.

### 3.2 Preliminary experiments

The efficacy of various frequencies of US reactors utilised in phenol degradation has already been well reported in the literature [28, 29]. Preliminary experiments were performed to determine the benefits of various operational parameters, such as air, hydrogen peroxide, zero valent iron and US, on phenol removal. All preliminary tests were carried out in the 300 kHz US reactor and the results are shown in Fig. 2.

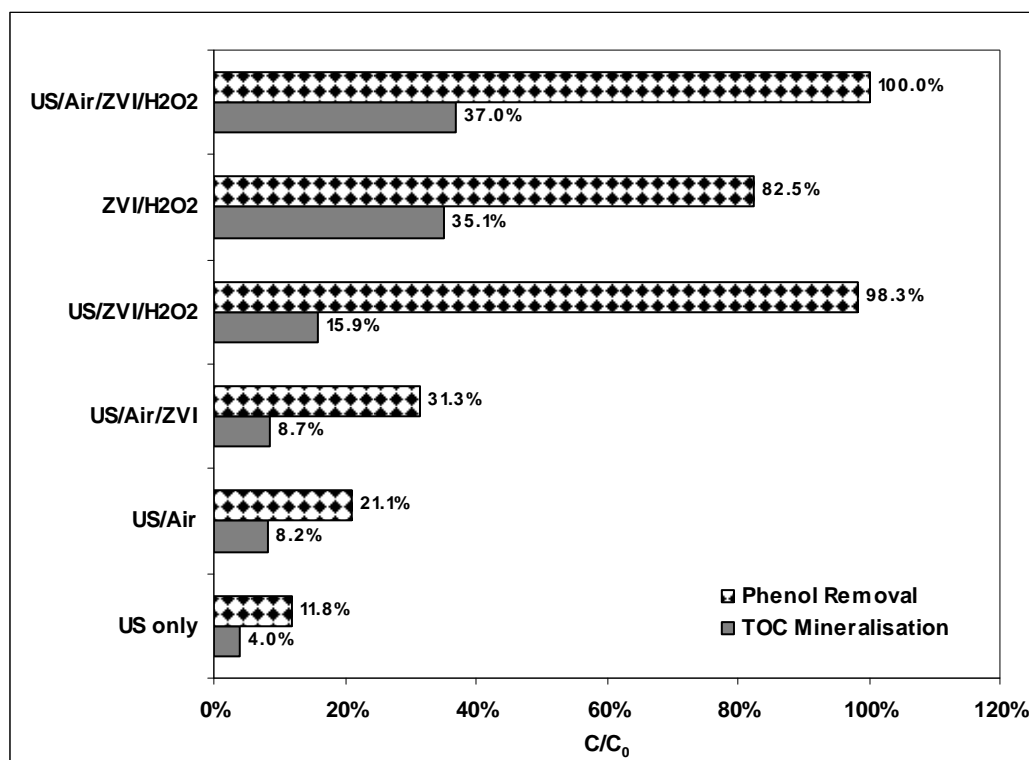
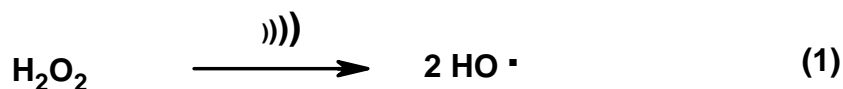


Figure 2: Effect of operational parameters on phenol degradation over 60 min, (except US/Air/ZVI/H<sub>2</sub>O<sub>2</sub>, which is the 20 min data set). Experimental conditions: phenol, 2.5 mM; US, 300 kHz; ZVM, zero valent iron (0.6 g/L); reaction time, 60 min; air, 1.5 LPM; H<sub>2</sub>O<sub>2</sub>, 2.38 g/L, temperature 20 ± 5 °C.

Results with both US and air show that the presence of air as a sparge gas has a 4–10% enhanced oxidation capacity possibly due to reaction between nitrogen and molecular oxygen to yield radical species, like, HO<sup>•</sup>, NO<sub>2</sub>, NO<sub>3</sub>, and HNO<sub>3</sub> [28]. It can also be suggested that the produced nitric acid may favour the decomposition process, leading to formation of excess HO<sup>•</sup> ( $k_{\text{HO}^{\bullet}}$ , 10<sup>12</sup> L mol<sup>-1</sup> s<sup>-1</sup>) which, may in turn, form strong oxidants like NO<sub>x</sub> ( $k_{\text{NO}_x}$ , 10<sup>7</sup> L mol<sup>-1</sup> s<sup>-1</sup>) and increase the process of oxidation of organic pollutants in wastewater [28, 30].



In Fenton-like reactions, the role of oxidant can be seen from the results, where phenol removal was only 31% in the absence of H<sub>2</sub>O<sub>2</sub> and ~98% in the presence of optimum catalysts/oxidant concentration. Possible sono-Fenton-like reactions in the presence of iron species bound to the surface of the catalysts (Fe<sup>2+</sup>/Fe<sup>3+</sup>) and H<sub>2</sub>O<sub>2</sub> are described below:



Ultrasonic irradiation of organics in water leads to generation of hydroxyl radicals responsible for pollutant removal and this efficiency is greatly enhanced by the addition of hydrogen peroxide. Thus, it was observed that the mineralization rate goes from 9 to 15% and the phenol removal ratio was remarkably high going from 31 to 98% when H<sub>2</sub>O<sub>2</sub> was added to the sonicated solutions. Molina et al. have discussed in detail the reaction pathways that occur due to addition of hydrogen peroxide in an aqueous system containing iron species [4] and explain that complex redox reactions take place leading to the formation of hydroperoxyl radicals and reduced Fe<sup>2+</sup> ions (Eq. 4). The iron species, Fe<sup>2+</sup> and Fe<sup>3+</sup>, further react with the available hydrogen peroxide and other radical species (Eq. 5 and 6) ultimately contributing to increased phenol and TOC removal.

In case of ZVI/H<sub>2</sub>O<sub>2</sub>, the fairly high TOC mineralization (35%) and lower phenol removal (83%), respectively, as compared to US/ZVI/H<sub>2</sub>O<sub>2</sub>, is attributed to the fact that in the absence of ultrasound there is still some

phenol removal (Fenton reaction) but the TOC mineralization is greatly accelerated. The phenomenon in action here could be the undissociated  $\text{H}_2\text{O}_2$  reacts strongly with phenol and its by-products and enhances the mineralization rate by 15% but a 10% decrease in the phenol removal ratio in the absence of ultrasound can be attributed to the presence of lower amount s of radical species and oxidising agents. However, in US/Air/ZVI/ $\text{H}_2\text{O}_2$ , a variety of additional strong oxidising radical species, such as  $\text{NO}_x$ ,  $\text{HO}^\bullet$ ,  $\text{HO}_2^\bullet$  formed due to the sparge gas, hydrogen peroxide and cavitation activity in the presence of iron species leads to 100% phenol removal and 37% TOC mineralization in just 20 min. Also, the active radicals produced due to interaction among the  $\text{Fe}^{2+}/\text{Fe}^{3+}/\text{H}_2\text{O}_2$  and ultrasound in acidic conditions enhances mineralization rates and by-product removal. In the Fenton process, simultaneous organic pollutant degradation is often attributed to the reaction of the  $\text{Fe}^{3+}$  with the hydroperoxy radicals to produce more  $\text{Fe}^{2+}$  which carries the reaction pathway in the cyclic fashion contributing to simultaneous and increased hydroxyl radicals to the reaction system, thereby, enhancing degradation rates.

### **3.3 Phenol degradation using US/ $\text{H}_2\text{O}_2$ system**

#### **3.3.1 Effect of US/Air/ZVI/ $\text{H}_2\text{O}_2$ system**

Initial phenol removal studies were carried out using the US/Air/ $\text{H}_2\text{O}_2$  system in conjunction with zero valent iron (0.6 g/L; ZVI) catalyst at different chosen US frequencies (20, 300 and 520 kHz). Results shown in Fig. 3 reveal that, high phenol removal efficiency was observed with the 20 and 300 kHz US reactor as phenol was undetectable after 45 and 25 min (Fig. 3a and b), respectively. However, in the 520 kHz US reactor, only 70% phenol removal was observed at the end of 60 min reaction time (Fig. 3c). It is interesting to note that the TOC mineralization at all the chosen frequencies in the US/Air/ZVI/ $\text{H}_2\text{O}_2$  system was between 37% and 40%.

The reaction rates were much faster during the initial 15 min of reaction time leading to 60–90% phenol removal and 25–30% TOC mineralization at all the

US frequencies. As evident from the results discussed above the rate of HO•/Fe<sup>2+</sup> ion production and increased availability of H<sub>2</sub>O<sub>2</sub> in the bulk solution leads to high degradation rates during the start of the reaction. Upon cavitation activity in the bulk solution, dissociation of the hydrogen peroxide is initiated and, therefore, the reaction between Fe<sup>2+</sup>/Fe<sup>3+</sup> and H<sub>2</sub>O<sub>2</sub> becomes less prevalent thereby reducing the concentration of HO•/HOO• radicals required for effective Fenton-like reactions.

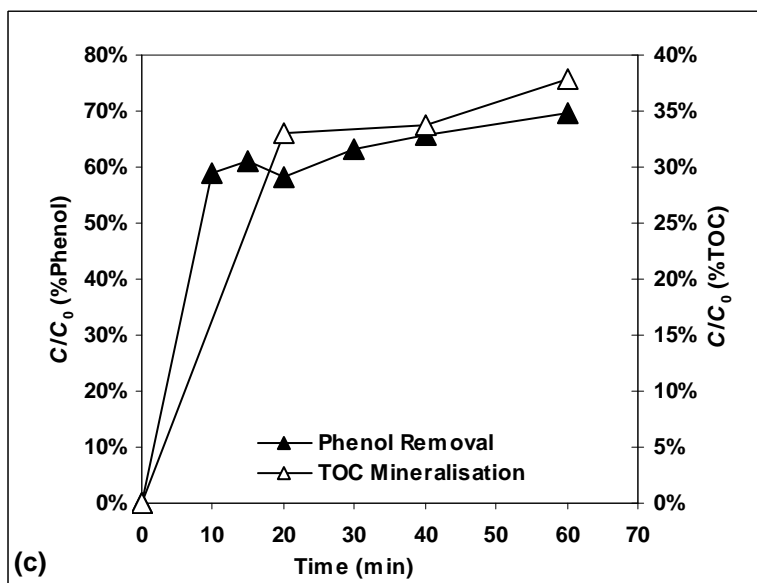
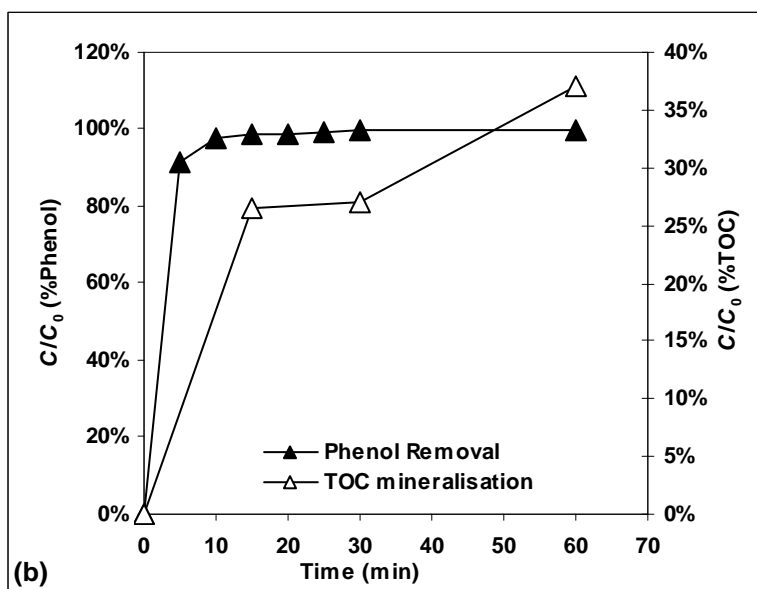
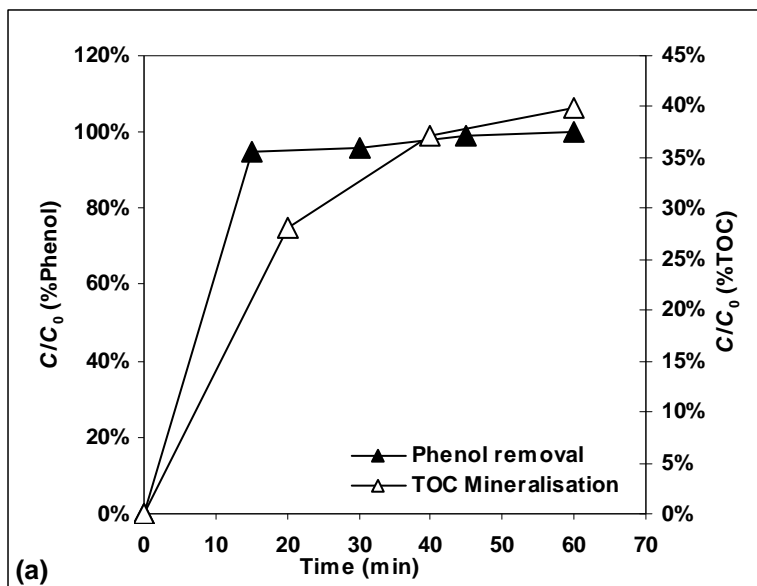


Figure 3: Effect of US/Air/ZVI/H<sub>2</sub>O<sub>2</sub> system on phenol degradation over 60 min. Experimental conditions: phenol, 2.5 mM; US frequencies, (a) 20, (b) 300 and (c) 520 kHz; ZVI, zero valent iron (0.6 g/L); reaction time, 60 min; air, 1.5 LPM; H<sub>2</sub>O<sub>2</sub>, 2.38 g/L, temperature 20 ± 5 °C.

### **3.3.2 Effect of different US frequencies and Zero-valent metal catalysts**

#### 20 kHz (80mL)

Phenol degradation studies were carried out in the 20 kHz US reactor with 80 mL capacity and tip diameter = 12 mm. Fig. 4 shows a comparative study between the ZVI and ZVCs. During the reaction with ZVC1, it was observed that, due to the small volume of the reactor and high ultrasonic intensity for 20 kHz, the fine papery-copper flitters were crushed to micro scale particles by the end of the reaction, providing a very high surface area but from the results it can be seen that only 11–30% of phenol removal was achieved with ZVCs in 60 min of reaction time, whereas with ZVI, no phenol was detected in GC analysis after 45 min. The high US intensity also leads to a decrease in particle size of the iron particles and increases the rate of reaction; therefore nearly 40% of TOC mineralization was observed after 60 min reaction time. The TOC removal was found to be negligible in case of ZVC1 and ZVC2 which relates to the low radical production with 20 kHz US and copper.

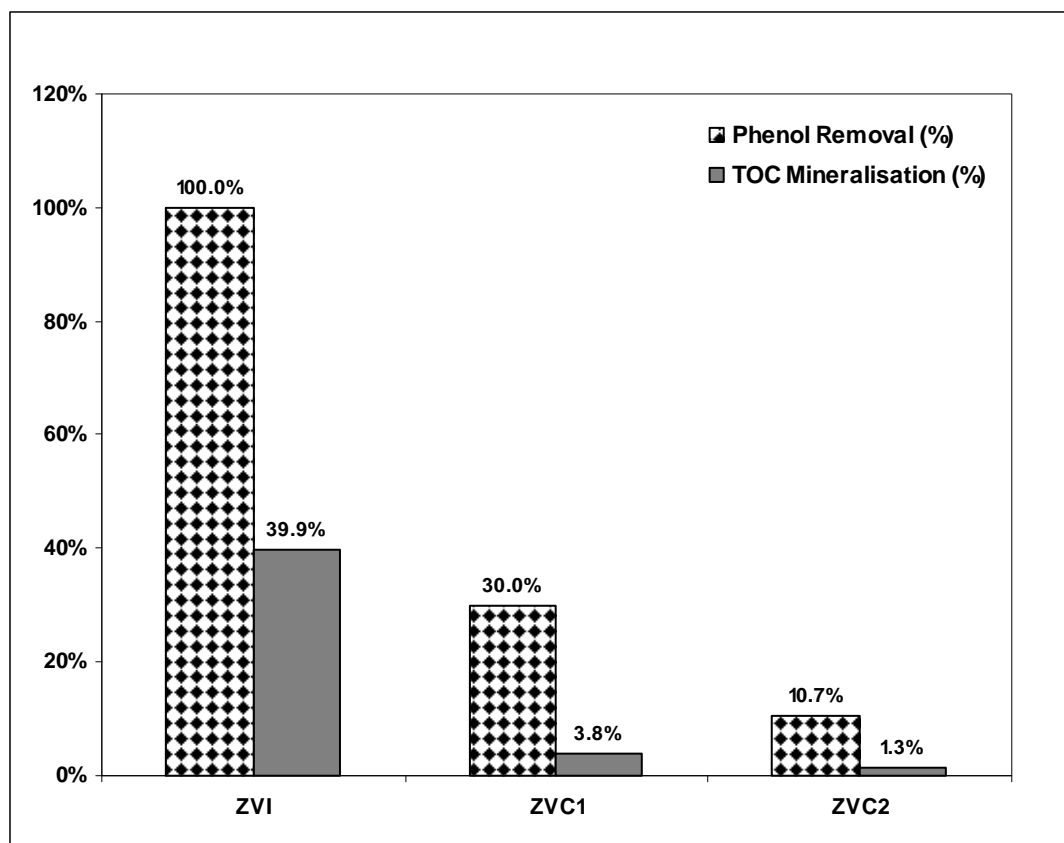


Figure 4: Comparison of ZVI and ZVCs in the 20 kHz US reactor for phenol degradation. Experimental conditions: phenol, 2.5 mM; US, 20 kHz; ZVI, 0.6 g/L; ZVC1 and ZVC2, 5 g/L; air, 1.5 LPM; H<sub>2</sub>O<sub>2</sub>, 2.38 g/L, temperature 20 ± 5 °C; reaction time, 60 min.

### 300 kHz (100 mL)

In the 300 kHz US reactor complete phenol removal was observed with ZVI and 56-98% with ZVC1 and ZVC2 (Fig. 5). In case of ZVI after 25 min of reaction time, no phenol remained and 37% TOC was removed. The fact that the 300 kHz reactor gives complete phenol removal in a shorter time compared to the 20 kHz reactor can be explained by certain reaction mechanisms where increased amount of hydrogen peroxide is produced in the reactor. Firstly, sonolysis of water occurs in the cavity leading to formation of H• and HO• radicals and secondly, HO• and HOO• formed near the bubble interface react with the phenol/organic substrate and helps in enhanced degradation. Also, this activity is greatly improved in the presence of ZVI because the iron ions produced react with hydrogen peroxide in a Fenton-like process leading to destruction of pollutants (Eq. 3–6).

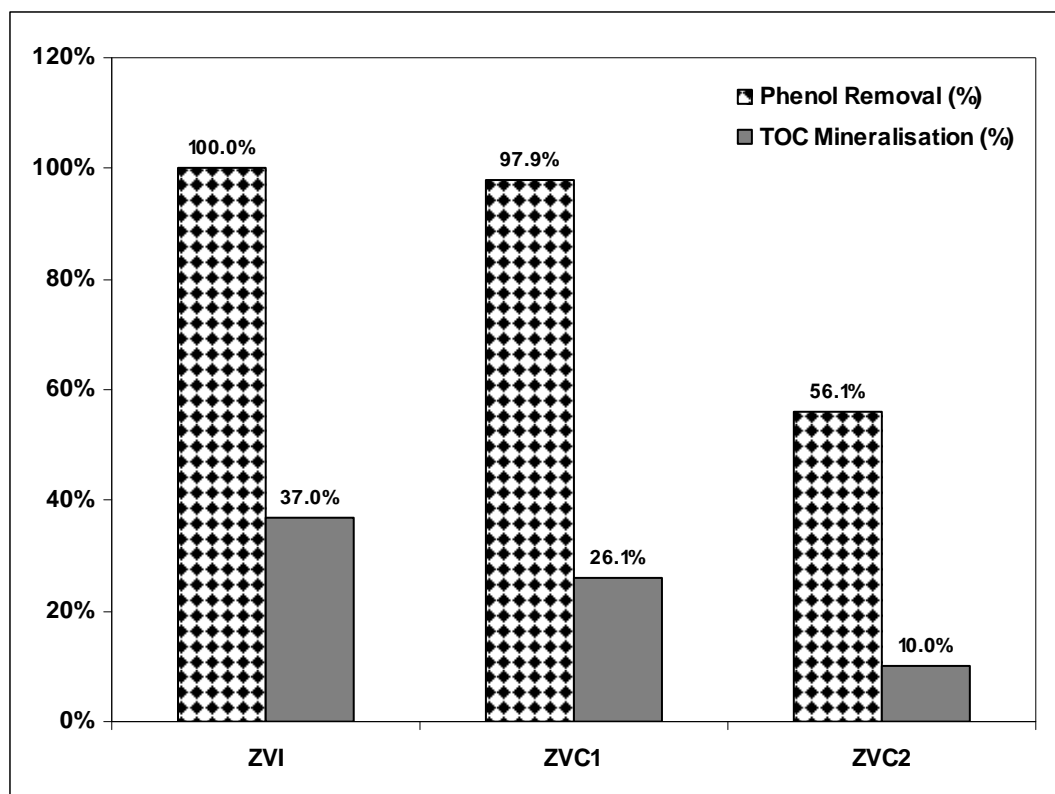


Figure 5: Comparison of ZVI and ZVCs in a 300 kHz US reactor for phenol degradation. Experimental conditions: phenol, 2.5 mM; US, 300 kHz; ZVI, 0.6 g/L; ZVC1 and ZVC2, 5 g/L; air, 1.5 LPM; H<sub>2</sub>O<sub>2</sub>, 2.38 g/L, temperature 20 ± 5 °C; reaction time, 60 min.

Guo et al. carried out a comparative study with Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/US and Cu<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/US reactions on 2,4-dinitrophenol removal and speculated that ultrasonic irradiation could possibly hinder the catalysis of Cu<sup>2+</sup> for H<sub>2</sub>O<sub>2</sub> decomposition to generate hydroxyl radicals [31]. Therefore, it can be stated that the initial reactions occurring in the system due to ultrasonic irradiation and available H<sub>2</sub>O<sub>2</sub> helps in the phenol removal at a much faster rate but since the other radicals (HO• and HOO•) required for degradation of by-products formed during phenol removal, are not available, the overall mineralization rate is reduced by 10–15% when compared to ZVI. Kim et al. studied homogeneous US/H<sub>2</sub>O<sub>2</sub>/Cu<sup>2+</sup> for 4-chlorophenol (4-CP) removal and found that despite considerable 4-CP removal, relatively low TOC mineralization was observed even at increased copper catalyst concentration [32].

### 520 kHz (300 mL)

A variety of research in 1980's discussed in detail that hydrodynamic conditions in a reactor system play a large role in coalescence. Also, if the contact time between the bubble and coalescence time is large, the bubble coalesces and this depends on organic concentration, type of reactor and aerator used [33]. The 520 kHz US reactor employed in this study has a capacity of 300 mL of solution and the transducer is located at the bottom of the reactor. This geometry does not support a high degree of coalescence among the bubbles since the contact time between the bubble and coalescence is too large. Therefore, reduced cavitation activity results in low radical production, which eventually hampers the overall degradation rate. A comparative study with and without overhead stirring was carried out in the highly optimised US/Air/ZVI/H<sub>2</sub>O<sub>2</sub> system (Fig. 6).

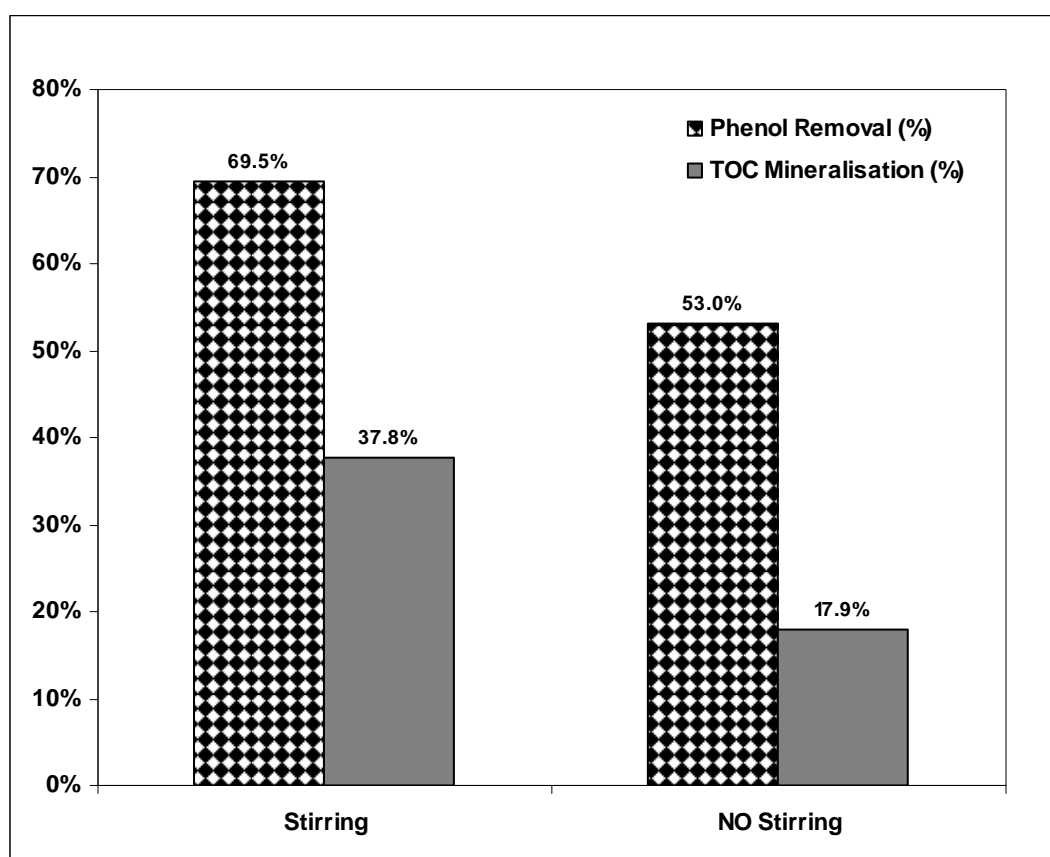


Figure 6: Performance of 520 kHz US reactor with and without stirring in the presence of US/Air/ZVI/H<sub>2</sub>O<sub>2</sub>. Experimental conditions: phenol, 2.5 mM; US, 520 kHz; ZVI, 0.6 g/L; air, 1.5 LPM; H<sub>2</sub>O<sub>2</sub>, 2.38 g/L, temperature 20 ± 5 °C; reaction time, 60 min.



Irregular radical production and non-ubiquitous bubble coalescence could also lead to fluctuations in phenol removal, which was noticed in the study and it was fairly difficult to assess the phenol removal trend with zero valent copper catalysts, therefore, the results reported in the study take into account the overall TOC mineralization in the presence of ZVI and ZVCs (Fig. 7).

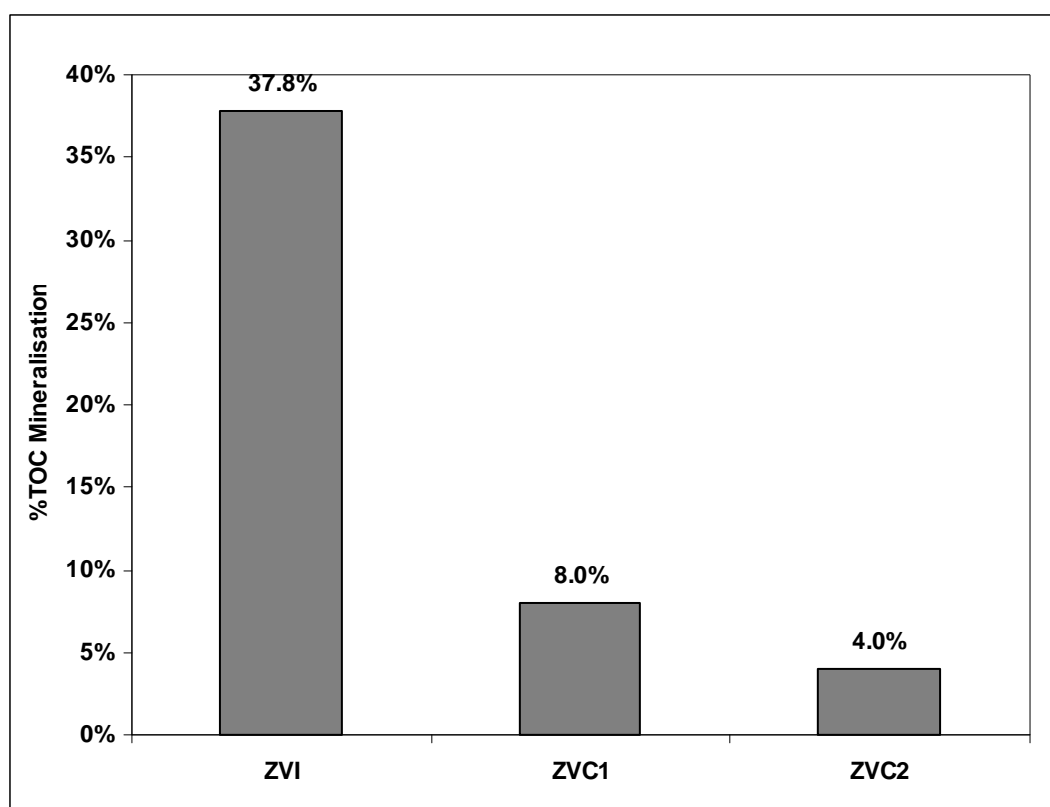


Figure 7: Comparison of ZVI and ZVCs in the 520 kHz US reactor with overhead stirrer (200 rpm) on overall TOC mineralisation. Experimental conditions: phenol, 2.5 mM; US, 520 kHz; ZVI, 0.6 g/L; ZVC1 and ZVC2, 5 g/L; air, 1.5 LPM; H<sub>2</sub>O<sub>2</sub>, 2.38 g/L, temperature 20 ± 5 °C; reaction time, 60 min.

### 3.3.3 Comparative study (20, 300 and 520 kHz)

When the three frequencies along with the three different catalysts used in this study were compared for phenol degradation, it was observed that ZVI was by far the best pseudo-catalyst and the frequency appeared to make little difference to the overall efficiency (Fig. 8). The fact that ZVI is the most effective is probably related to iron being involved in a much more Fenton-like process than copper and this has been described in a number of reports [2–

4]. A much more interesting observation can be made when the use of copper is considered - with both copper catalysts the most effective frequency is 300 kHz with 520 kHz being next and then 20 kHz. ZVC1 is zero valent copper metal which, as mentioned above, disintegrates on ultrasonic treatment and forms very small particles which could account for the enhanced activity of this catalyst over ZVC2 which is copper turnings (270 mesh) which have a much smaller surface area. Gogate (2002) studied the effect of different frequencies of irradiation on the rates of degradation and found that there exists an optimum frequency at which degradation is maximum and this was also influenced by the type of reactant and system geometry [30].

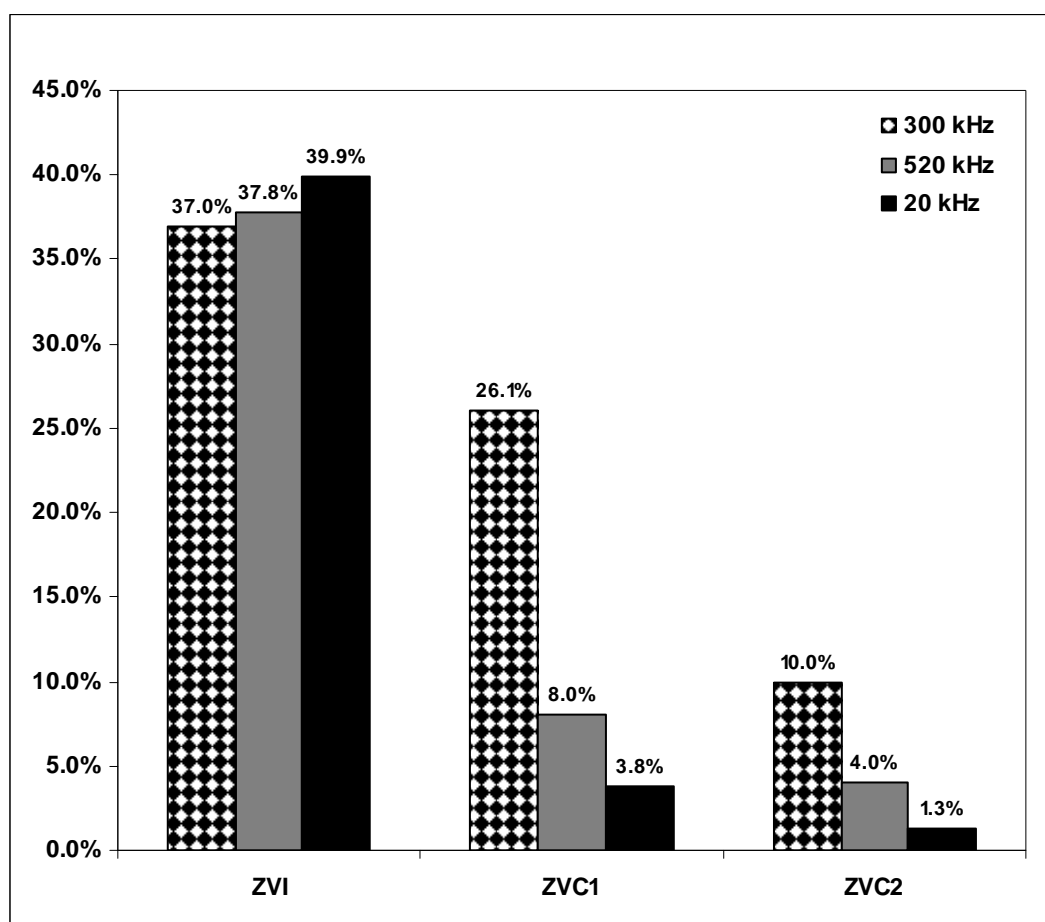
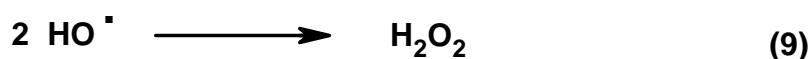
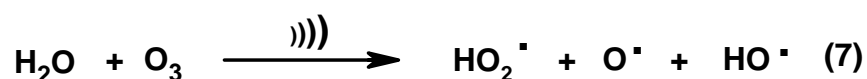


Figure 8: Phenol degradation studies with overall TOC mineralization (%) in the presence of ZVI and ZVCs in 20, 300 and 520 kHz US reactors.

### 3.4 Phenol degradation using US/O<sub>3</sub> system

#### 3.4.1 The ZOO Process

As discussed above in the US/H<sub>2</sub>O<sub>2</sub> system, the presence of iron species augmented with ultrasound is very efficient for generating hydroxyl radicals. However, hydrogen peroxide plays a dual role during oxidation since at low concentrations it acts as a source of HO<sup>•</sup> but at high concentrations it can be a radical scavenger [34]. Thus, the use of ozone as oxidant was investigated as a potential source of hydroxyl radicals particularly in the presence of ultrasound and zero-valent metals and was also of interest as the operating pH is much higher than that normally favoured by Fenton-like reactions. In the presence of ozone and ultrasound a variety of radical formation reactions can occur [29]:



The only mechanism that explains all the results of the present work with US/O<sub>3</sub> and zero valent catalysts integrated system, termed the ZOO process (zero valent catalysts assisted ozone oxidation), requires the presence of hydroxyl and perhydroxyl free radicals as intermediates in these oxidation reactions. Moreover, the mechanism for the oxidation of organic compounds with ozone can be split into two individual steps, i.e., direct and indirect. The direct ozone oxidation of organic compounds (M+O<sub>3</sub>) is a selective reaction with slow rate constants, whereas in the indirect reaction, the first step is the decomposition of ozone which is accelerated at high pH leading to formation

of secondary and powerful oxidants such as HO• which react non-selectively with solutes [35].

### 3.4.2 Preliminary studies with the ZOO Process

The key Fenton reagents are H<sub>2</sub>O<sub>2</sub> and a mixture of iron salts-oxides-ZVI, which are relatively inexpensive and the Fenton process is efficient only at pH 2–4 and usually most efficient at pH 2.8 and the process is inefficient in the range of pH 5–9, particularly due to the tendency for ferric oxyhydroxide precipitation (which has a low catalytic activity) to occur at pH >3–4 [36]. However, literature on ozone oxidation of organic compounds reveals that pH 9–11 supports high degradation rates of various organic compounds [34, 37]. In order to see the influence of pH (3 and 9) and ozone dose (2 and 6 g O<sub>3</sub> m<sup>-3</sup>), a combination of conditions (pH 3 and 6 g O<sub>3</sub> m<sup>-3</sup> at 0.25 LPM and pH 9 and 2 g O<sub>3</sub> m<sup>-3</sup> at 0.75 LPM) on the ZOO process was tested for enhanced phenol removal in the 300 kHz US reactor over 60 min in the presence of ZVI and ZVCs.

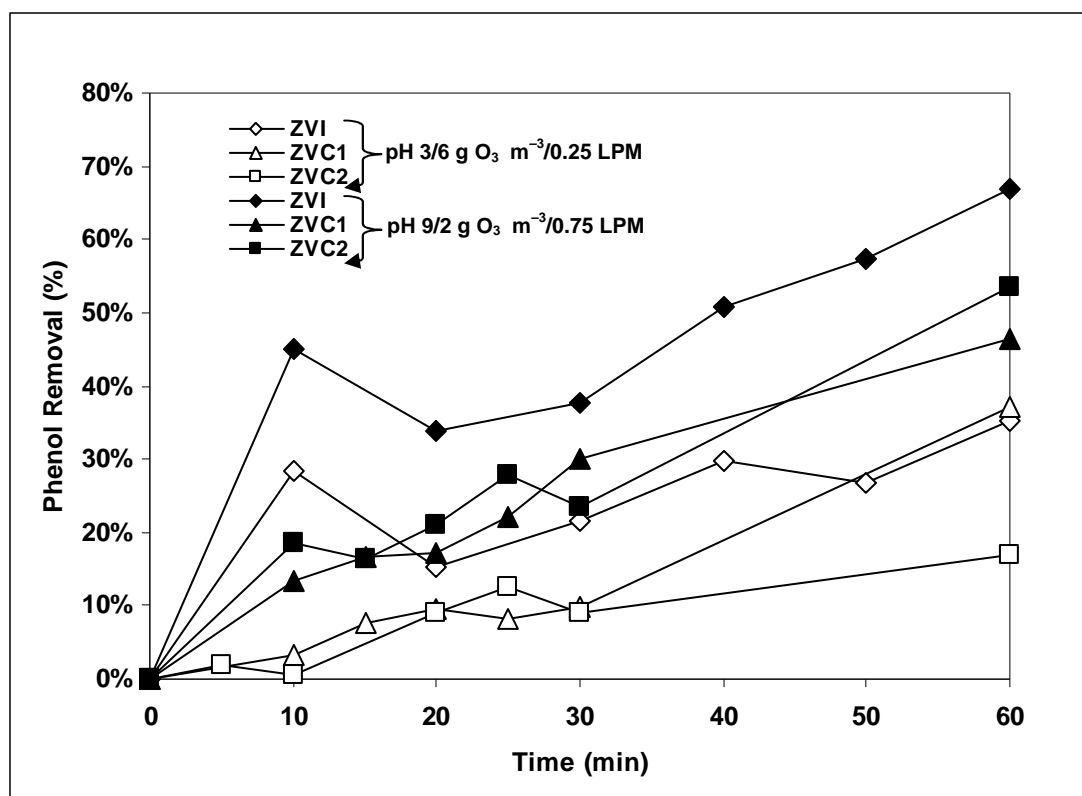


Figure 9: Optimisation of pH and ozone dose for phenol removal (%) in the presence of ZVI and ZVCs in a 300 kHz US reactor. Filled symbols

represent: pH 9 and  $2 \text{ g O}_3 \text{ m}^{-3}$  at 0.75 LPM and hollow symbols represent: pH 3 and  $6 \text{ g O}_3 \text{ m}^{-3}$  at 0.25 LPM.

Fig. 9 shows that pH 9 and  $2 \text{ g O}_3 \text{ m}^{-3}$  at 0.75 LPM has a much better rate of phenol removal in a 300 kHz US reactor than pH 3 and  $6 \text{ g O}_3 \text{ m}^{-3}$  at 0.25 LPM with respect to all chosen zero valent metals, especially with ZVI. At higher pH, two cross effects are seen where on the one hand, ozone quickly decomposes into free radicals which are responsible for other chain reactions as discussed above and reacts with the phenol, leading to degradation (Eq. 7–12). On the other hand, the dissolved ozone equilibrium concentration in water decreases when the pH is increased, since high pH values induce ozone decomposition [34]. Therefore, at alkaline pH the reaction mechanism follows a radical pathway while at low pH, ozone reacts in the molecular form by selective and sometimes relatively slow reactions. Furthermore, at both pH 3 and 9, it is notable that during the first 30 min of continuous ozonation, only 10–30% of phenol removal was observed; however, at the end of the reaction time removal percentages range from 15% (ZVC2) to 65% (ZVI). Moreover 40–65% of phenol removal with all three catalysts at alkaline pH 9 is associated with the presence of competing intermediate species and hydroxyl and perhydroxyl radicals.

#### **4. US/Air/ZVI/H<sub>2</sub>O<sub>2</sub> vs US/ZOO systems**

The conditions of pH 9 and  $2 \text{ g O}_3 \text{ m}^{-3}$  at 0.75 LPM were chosen to study the relative effectiveness of phenol removal in the 300 and 520 kHz US reactors and a comparison was carried out between US/ZOO and US/Air/ZVI/H<sub>2</sub>O<sub>2</sub> systems (Fig. 10). Ozone is activated by metal ions in solution and heterogeneous catalytic ozonation in the presence of metal oxides or metals on support, and also activated carbon [38]. At the same time, the catalytic ozonation oxidation is quite compound-selective and depends on various experimental factors. For example under acidic conditions (pH 3), iron, molybdenum and cobalt oxides were found to be potent catalysts in *m*-dinitrobenzene ozonation [39] and in the photo-Fenton-assisted ozonation of *p*-coumaric acid, the contribution of the radical pathway to the overall reaction was 77% at pH 2, 53% at pH 9 and only 4% with a single ozonation [34]. A

similar observation was noted here in the US/ZOO reaction where in the absence of catalyst, a low mineralization rate was observed as compared to reactions where the presence of ZVI and ZVCs lead to 3–12% phenol degradation in the 300 and 520 kHz US reactors.

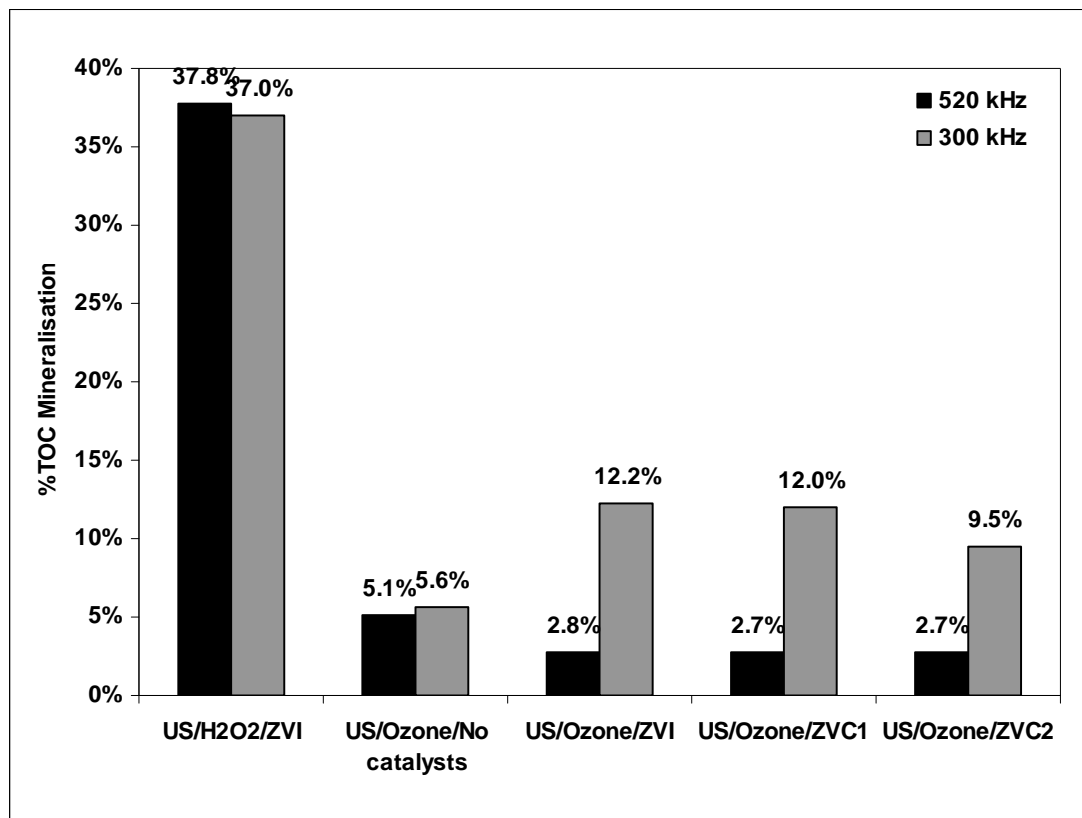
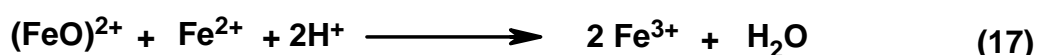
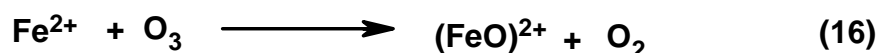


Figure 10: Comparative overall TOC mineralization using US/ZOO and US/Air/ZVI/H<sub>2</sub>O<sub>2</sub> systems in 300 and 520 kHz US reactors. Experimental conditions: pH 9 with 2 g O<sub>3</sub> m<sup>-3</sup> at 0.75 LPM. (Black bars, 520 kHz; grey bars, 300 kHz).

Very low level of TOC mineralisation was observed in US/ZOO when compared to US/Air/ZVI/H<sub>2</sub>O<sub>2</sub> integrated system. Reactions of molecular ozone with reduced metals have been discussed in detail by Legube and Leitner [40] who reported that molecular ozone exhibits a low rate constant in acidic medium and a significant increase of reactivity as pH increases and they summarised the background on ozone and hydroxyl radical reactivities as (Eq. 13–17):



Therefore, ozone does not favour high carbon mineralization due to insufficient radical formation through oxygen-transfer from ozone lead pathways. However, hydrogen peroxide, in the presence of ultrasound forms hydroxyl radicals that participate in chain reactions to form hydroperoxyl and other radical species produced due to air as sparge gas, and this probably accounts for enhanced degradation. However, no literature thus far has discussed the mechanism of the reaction of ozone with copper under the current conditions. Moreover, it can also be proposed that ozone decomposition due to ultrasonic irradiation influences the catalyst and oxidant concentration, which hinders direct pollutant destruction, whereas in the case of hydrogen peroxide, simultaneous decomposition and synthesis of the oxidant occurs in the reaction system and/or additional free radicals/iron species also react with the pollutant. Thus, hydrogen peroxide proves to be the most effective oxidant in conjunction with zero valent metals, especially ZVI, in high frequency US reactors.

## 5. Conclusions

Phenol oxidation was carried out under various US frequencies (20, 300 and 520 kHz) and it can be concluded that 300 kHz offers the maximum phenol degradation and overall TOC removal followed by 520 kHz when coupled with external overhead stirring and in case of 20 kHz US reactor, effective degradation was observed only with US/Air/ZVI/H<sub>2</sub>O<sub>2</sub> system. Moreover, among the three catalysts (ZVI, ZVC1 and ZVC2) used for the study, the highest phenol oxidation was observed with ZVI under the US/Air/ZVI/H<sub>2</sub>O<sub>2</sub> system. The zero valent ozone oxidation (ZOO) process works efficiently

under basic pH 9. Finally, from the above study, it can be deduced that Fenton-like processes in conjunction with zero valent catalysts, work more efficiently with US/Air/H<sub>2</sub>O<sub>2</sub> than US/O<sub>3</sub> for high pollutant removal.

### **Acknowledgements**

The authors thank COST D32 and the European Science Foundation for financial support to carry out an STSM. R Chand thanks Bogazici University, Istanbul, Turkey for the provision of laboratory facilities and the research staff for their support and also thank the administration staff at the University of Abertay Dundee.

### **References**

1. V. Uberoi, S.K. Bhattacharya, *Wat. Environ. Res.* 69 (1997) 146-156.
2. K.C. Namkung, A.E. Burgess, D.H. Bremner, H. Staines, *Ultrason. Sonochem.* 15 (2008) 171-176
3. D.H. Bremner, A.E. Burgess, D. Houlemare, K-C. Namkung, *Appl. Catal. B: Environ* 63 (2006) 15-19.
4. R. Molina, F. Martinez, J.A. Melero, D.H. Bremner, A.G. Chakinala, *Appl. Catal. B: Environ.* 66 (2006) 198–207.
5. M.H. Entezari and C. Petrier, *Appl. Catal. B: Environ.* 53 (2004) 257-263
6. S.T. Kolaczowski, F.J. Beltran, D. B. McLurgh, F.J. Rivas, *ICHEME*, 75 (1997) 257–265
7. K.S. Suslick, *Ultrasound: Its Chemical, Physical and Biological Effects*, VCH Publishers Ltd., 1998.
8. N.H. Ince, G. Tezcanli, R.K. Belen, I.G. Apikyan, *Appl. Cat. B: Environ.* 29 (2001) 167–176.
9. P.R. Gogate, S. Majumdar, A.B. Pandit, *Adv. Environ. Res.* 7 (2003) 283–299.
10. P.R. Gogate, S. Majumdar, J. Thampi, A.M. Wilhelm, A.B. Pandit, *Sep. Purif. Technol.* 34 (2004) 25–34.
11. M.H. Entezari, C. Petrier, P. Devidal, *Ultrason. Sonochem.* 10 (2003) 103–108.



12. H. Nakui, K. Okitsu, Y. Maeda, R. Nishimura, *Ultrason. Sonochem.* 14 (2007) 191–196
13. V. Kavitha, and K. Palanivelu, *Chemosphere* 55 (2004) 1235–1243.
14. J. Rima, E. Aoun, J. Hanna, Q.X. Li, *J. Phys IV France* 124 (2005) 81–89.
15. R. Rangsvivek and M.R. Jekel, *Water Res.* 39 (2005) 4153–4163.
16. S.-Y. Oh, P.C. Chiu, B.J. Kim, D.K. Cha, *Water Res.* 37 (2003) 4275–4283.
17. A. Ghauch, C. Gallet, A. Charef, J. Rima, M. Martin-Bouyer, *Chemosphere* 42 (2001) 419–424.
18. A. Ghauch, J. Rima, C. Amine, M. Martin-Bouyer, *Chemosphere* 39 (1999) 1309–1315.
19. S.-F. Cheng and S.-C. Wu, *Chemosphere* 41 (2000) 1263–1270.
20. J.-L. Chen, S.T. Al-Abed, J.A. Ryan, Z. Li, *J. Haz. Mater.* B83 (2001) 243–254.
21. C.J. Lin, S.L. Lo Y.H. Liou, *Chemosphere* 59 (2005) 1299–1307.
22. S. Nam, P.G. Tratnyk, *Water Res.* 34 (2000) 1837–1845.
23. L. Mcdowall, DSTO Report, Commonwealth of Australia (2005).
24. P.G. Tratnyk, T. Johnson, A. Schattauer, I&EC Special Symposium, Atlanta, 1995.
25. J.T. Nurmi, P.G. Tratnyk, V. Sarathy, D.R. Baer, J.E. Amonette, K. Pecher, C. Wang, J.C. Linehan, D.W. Matson, R.L. Penn, M. D. Driessen, *Environ. Sci. Technol.* 39 (2005) 1221–1230.
26. N.V. Klassen, D. Marchington, H.C.E. McGowan, *Anal. Chem* 66 (1994) 2921–2925.
27. C. Petrier, A. Francony, *Ultrason. Sonochem.* 4 (1997) 295–300.
28. R. Kidak, N.H. Ince, *J. Haz. Mater.* B137 (2006) 1453–1457.
29. R. Kidak, N.H. Ince, *Ultrason. Sonochem.* 13 (2006) 195–199.
30. P.R. Gogate, *Adv. Environ. Res.* 7 (2003) 283–299.
31. Z. Guo, Z. Zheng, S. Zheng, W. Hu, R. Feng, *Ultrason. Sonochem.* 12 (2005) 461–465.
32. J.K. Lim, F. Martinez, I.S. Metcalfe, *Catal. Today* 124 (2007) 224–231.
33. C. Gottschalk, J.A. Libra, A. Saupe, *Ozonation of Water and Wastewater.* Wiley-VCH, 2000

34. J.M. Monteagudo, M. Carmona, A. Duran, *Chemosphere* 60 (2005) 1103–1110.
35. J. Hoigne, H. Bader, *Water Research* 17 (1983) 185–194.
36. S. Parsons, *Advanced Oxidation Processes for Water and Wastewater Treatment*, IWA Publishing (2004).
37. J.H Suh, M. Mohseni, *Water Res* 38 (2004) 2596–2604.
38. KB. Kasparzyk-Hordern, M. Ziolk, J. Nawrocki, *Appl. Catal. B: Environ* 46 (2003) 639–726.
39. M. Trapido, Y. Veressinina, R. Munter, J. Kallas, *Ozone Sci. Eng.* 27 (2005) 359–363
40. B. Legube, N.K.V. Leitner, *Catal Today*, 53 (1999) 61–72.