

# Degradation of trace contaminants using coupled sonochemistry and Fenton's reagent

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**Abstract** The degradations of phenol in air-equilibrated aqueous media were investigated using coupled sonochemistry and Fenton's reagent for a variety of operating conditions. The decomposition yields of phenol (100–500  $\mu\text{M}$ ) were substantially enhanced due to the addition of Fenton's reagent ( $\text{FeSO}_4$ ) into the solutions irradiated at 608 kHz with 30 W and with reaction temperature  $25 \pm 1^\circ\text{C}$ . The decomposition process follows a pseudo-first-order reaction kinetics with respect to phenol concentration, and the rate constant of phenol disappearance observed increases by approximately 2–3 fold when  $\text{FeSO}_4$  concentration was between 400 and 1000 M at  $\text{pH} = 3.5 \pm 0.2$  (controlled by phosphate buffer) as a result of  $\text{Fe(II)}$  reaction with  $\text{H}_2\text{O}_2$  enabling further production of additional  $\text{OH}\cdot$  radicals. The results obtained here also indicate that the decomposition rate of aqueous phenol using coupled ultrasound and Fenton's reagent was strongly dependant on the initial concentration of reactant, the amount of  $\text{Fe(II)}$  added as well as the pH of solution. The optimal operating conditions for 100–500  $\mu\text{M}$  phenol decomposition in the air-equilibrated aqueous media were obtained when  $\text{FeSO}_4$  concentration was between 400 and 1,000  $\mu\text{M}$  with pH in the range 3.5–4.2 under ultrasonic irradiation at 608 kHz, 30 W and reaction temperature  $25 \pm 1^\circ\text{C}$ .

**Keywords** Advanced oxidation processes; Fenton's reagent; phenol degradation; sonochemistry; wastewater treatment

## Introduction

Sonochemical degradation of aqueous phenol has been examined extensively in past years (Serpone *et al.*, 1992; Petrier *et al.*, 1994; Berlan *et al.*, 1994), and ultrasonic irradiation has received considerable interest as an advanced oxidation process for the destruction of hazardous organic compounds in aqueous solution (Hoffmann *et al.*, 1996; Hua and Hoffmann, 1996, 1997; Petrier *et al.*, 1992, 1998; Petrier and Francony, 1997; Theron *et al.*, 1999; Tauber *et al.*, 2000). It is evident that the chemical effects of ultrasound are due to the phenomenon of acoustic cavitation: the formation, growth and implosive collapse of bubbles in a liquid. The collapse of cavitation bubbles induces intense localised temperatures (several 1,000 K), high pressures (several 100 atm.), electrical charges, as well as plasma effects, and produces enormous heating and cooling rates ( $>10^9$  K/sec) (Suslick *et al.*, 1986; Suslick, 1988; Flint and Suslick, 1991). Acoustic cavitation, therefore, provides a unique interaction of energy and matter causing high-energy chemical reactions to occur. The water vapour and  $\text{O}_2$  in the cavitation bubbles undergo thermal dissociation to yield  $\text{H}\cdot$  and  $\text{HO}\cdot$  radicals as well as O atoms and  $\text{HOO}\cdot$  radicals (Makino *et al.*, 1983; Riesz and Kondo, 1992). Organic solutes in the vicinity of collapsing bubbles or partitioned into the gas phase of the bubbles undergo thermal decomposition, and/or react with the highly reactive radicals (e.g.,  $\text{HO}\cdot$ ,  $\text{HOO}\cdot$ ) both within the gas–liquid interface and the bulk solution. Substrates such as phenol (Serpone *et al.*, 1992; Petrier *et al.*, 1994), chlorinated hydrocarbons (Hua and Hoffmann, 1996; Kruus *et al.*, 1997, Francony and Petrier, 1996, 1997); and various hazardous organic compounds (Hoffmann *et al.*, 1996; Theron *et al.*, 1999; Tauber *et al.*, 2000) are transformed into short-chain organic acids, inorganic ions,  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  as the final products. In particular, hydrophilic organic compounds, such

as phenol, are oxidised by highly reactive radicals (e.g., HO•, HOO• etc. formed on sonolysis) in the bulk solution and/or at the interface of liquid–gas bubbles depending on the substrate concentrations.

However, the recombination of HO• to yield H<sub>2</sub>O<sub>2</sub> both in the gas phase within the bubbles and in solution are two of the major processes that limit the amount of reactive radicals accessible to target molecules. Many efforts have therefore been devoted to improve the efficiency of sonochemical reactions (Olson and Barbier, 1994; Hua and Hoffmann, 1997; Petrier *et al.*, 1998; Theron *et al.*, 1999; Kang *et al.*, 1999; Weavers *et al.*, 2000; Joseph *et al.*, 2000), particularly in view of the fact that a substantial amount of energy employed in generating the radicals is not effectively converted into an optimum yield of the desired products.

A possible means of overcoming the generation of H<sub>2</sub>O<sub>2</sub> is to use it to produce additional HO• radicals. This could be achieved photochemically or by the addition of ferrous ions via Fenton's reagent reaction; i.e:



Fe (III) can be reduced by H<sub>2</sub>O<sub>2</sub>, via the formation of a Fe (III)-hydroperoxy complex.



HO<sub>2</sub>• can reduce Fe (III) or can instead react with Fe<sup>2+</sup>, forming H<sub>2</sub>O<sub>2</sub>:



Iron can therefore be used a catalyst, with Fe(II) being regenerated and reacting with H<sub>2</sub>O<sub>2</sub>, enabling further production of OH• (or another oxidant).

The objective of this study was to evaluate the effectiveness and the potential of the coupled sonochemistry and Fenton's reagent as an advanced oxidation process for the destruction of hydrophilic trace organic contaminants in water. Phenol was chosen as a model reactant due to its hydrophilicity and because its sonochemical degradation characteristics are well established. Its degradation rate on sonication (608 kHz, 30 W and reaction temperature 25 ± 1 °C) in the presence of Fenton's reagent (Fe<sub>2</sub>SO<sub>4</sub>) was examined and was compared with its ultrasonic irradiation alone under a variety of different operating conditions. In particular, the kinetics of phenol degradation using coupled sonochemistry and Fenton's reagent were investigated as a function of the initial concentration of phenol, the Fe(II) concentration, and the pH of solution.

### Material and methods

All chemicals were reagent grade (at least 99% purity) and used as received. Aqueous solutions were prepared by dissolving the compounds in ultra-pure deionised water obtained from a Milli-Q plus Millipore system. The pH of the solutions was established using phosphate buffer media (0.1 M) and adjusted with H<sub>3</sub>PO<sub>4</sub> (0.2 M) and NaOH (0.2 M) prior to sonication.

The instrumentation employed in this study was supplied from Radiocom Systems (France). The ultrasonic transducer (610 kHz) was constituted from a piezo-electric disc

(diameter 4 cm) fixed on a titanium plate with the specific fan to cool the transducer. Ultrasonic irradiation was performed in a cylindrical water-jacketed glass cell equipped with a Teflon holder. The ultrasonic power dissipated into the reactors was adjusted and estimated by calorimetry in order to ensure comparative ultrasonic conditions. In all cases, irradiation experiments were conducted in 250 mL air-equilibrated aqueous media. The temperature of the liquid was monitored using a thermocouple immersed in the reacting medium and was maintained at  $25 \pm 1^\circ\text{C}$  unless stated specifically.

Phenol and its primary intermediates in the course of sonochemical degradation were identified using a high performance liquid chromatograph (Waters model 600E) with an absorbance detector (Waters model 486) and equipped with a Spherisorb ODS2  $5 \mu\text{m}$  C18 column ( $250 \pm 4.6$  mm). The detection wavelength was set at 254 nm and an acetonitrile/water (45/55) mixture containing acetic acid (1%) constituted the mobile phase. Samples were injected directly into the chromatograph. The identity of intermediates was confirmed by comparing retention times with those of known standards, and their concentration determined from calibration curves.

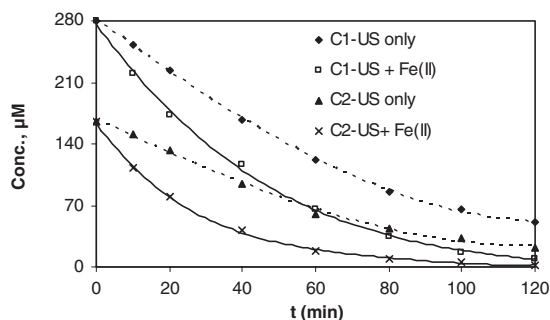
## Results and discussion

### Sonochemical degradations of phenol with and without Fenton's reagent

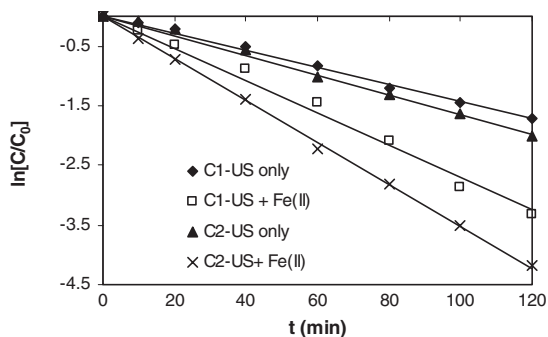
The investigations into sonolysis of phenol (608 kHz, 30 W) were carried out with 250 mL of air-equilibrated aqueous media at  $\text{pH} = 3.5 \pm 0.2$ . The decomposition yields of phenol by ultrasonic irradiation as shown in Figure 1 were significantly enhanced in the presence of Fenton's reagent ( $\text{FeSO}_4$  500  $\mu\text{M}$ ), whatever the initial concentration of target molecule present. With and without Fenton's reagent, the decomposition rates of aqueous phenol on sonication followed pseudo first-order kinetics with respect to phenol concentration, i.e:

$$-\frac{d[\text{Phenol}]}{dt} = k_{\text{obs}}[\text{Phenol}] \quad (6)$$

The rate constants of phenol disappearance ( $k_{\text{obs}}$ ) were obtained from the slopes of  $\ln(C_t/C_i)$  versus reaction time.  $C_t$  represents the concentration of phenol at time  $t$  and  $C_i$  represents the initial concentration of phenol. The resulting regression fits are compared as solid lines with the data points and can be seen in Figure 2. In coupled sonochemistry and Fenton's reagent (500  $\mu\text{M}$   $\text{FeSO}_4$ ), the apparent first-order rate constant,  $k_{\text{obs}1} = 0.0285 \pm 0.0005$  and  $k_{\text{obs}2} = 0.0355 \pm 0.0005 \text{ min}^{-1}$  at  $\text{pH} 3.5 \pm 0.2$  with respect to the initial concentration of phenol:  $C_1 = 280 \pm 10$  and  $C_2 = 160 \pm 5 \mu\text{M}$ . They are substantially higher than the rate constants obtained on US only (i.e.  $0.0125 \pm 0.0005$  and  $0.0165 \pm 0.0005 \text{ min}^{-1}$ ) by a factor of



**Figure 1** Evolution of phenol concentration with reaction time. Ultrasonic irradiation (US): 608 kHz with ultrasonic power 30 W; reaction temperature  $25 \pm 1^\circ\text{C}$ ;  $\text{pH} = 3.5 \pm 0.2$ ;  $\text{Fe(II)}$  concentration: 500  $\mu\text{M}$ ; phenol initial concentration:  $C_1 = 280 \pm 10 \mu\text{M}$ ;  $C_2 = 160 \pm 5 \mu\text{M}$



**Figure 2** Evolution of the relative concentration of phenol (shown as  $\ln(C_t/C_i)$ ) versus reaction time. Ultrasonic irradiation (US): 608 kHz, 30 W; reaction temperature  $25 \pm 1^\circ\text{C}$ ; pH =  $3.5 \pm 0.2$ ; Fe(II) concentration:  $500 \mu\text{M}$ ;  $C_t$  represents the concentration of phenol at time  $t$  and  $C_i$  represents the initial concentration of phenol. Phenol initial concentration:  $C_{1i} = 280 \pm 10 \mu\text{M}$ ;  $C_{2i} = 160 \pm 5 \mu\text{M}$

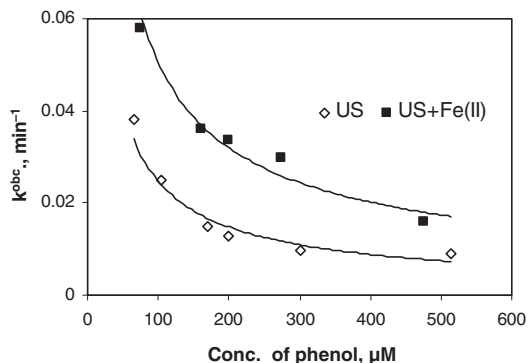
more than two. Similarly, the half-lives of phenol disappearance by ultrasonic irradiation (US) + Fe(II) irradiation are almost twice as fast as by US only.

The investigations into the effects of phenol initial concentration on rate constant were carried out with  $80\text{--}500 \mu\text{M}$  phenol solutions at pH =  $3.5 \pm 0.2$ . The apparent first-order rate constants ( $k_{\text{obs}}$ ) and the half-life ( $t_{1/2}$ ) observed for degradation of phenol on the operating conditions are given in Table 1.

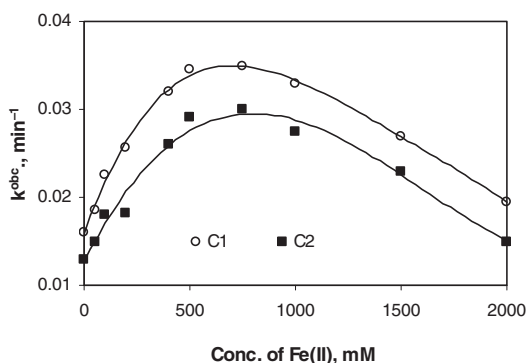
It is clear that the rate constants of phenol degradation by both US only and US + Fe(II) decrease with increasing initial concentration of the target molecule as can be seen in Figure 3. This could be explained by surmising that the intermediates of phenol degradation compete for the  $\text{OH}\cdot$  radicals with phenol itself, and some of intermediates could diffuse into the cavitation bubbles changing the condition of bubbles collapse. As a result, the more intermediates that are formed and then oxidised by  $\text{OH}\cdot$  radicals, the greater is the decrease in rate constant of phenol decomposition. The primary intermediates are identified by HPLC as hydroquinone (HQ) and catechol (CC), and occur soon after the disappearance of the initial substrate and then disappear after extended irradiation. Observation of these intermediates is in agreement with the observation of Petrier *et al.* (1994) and Serpone *et al.* (1994). It can therefore be considered that the degradation of aqueous phenol by US + Fe(II) is due to attack by hydroxyl ( $\text{OH}\cdot$ ) radicals. The results obtained here suggest that the enhancement in the rate constant of phenol degradation can be mainly due to contribution of additional hydroxyl  $\text{OH}\cdot$  radicals generated by Fenton's reagent (Eq. (1)).

**Table 1** Pseudo first-order rate constants ( $k_{\text{obs}}$ ) and half-lives ( $t_{1/2}$ ) observed for degradation of aqueous phenol in the air-equilibrated aqueous media. Fe(II) concentration:  $500 \mu\text{M}$ ; pH =  $3.5 \pm 0.2$ ; US: 608 kHz, ultrasonic power: 30 W; reaction temp:  $25 \pm 1^\circ\text{C}$

| Initial phenol conc. ( $\mu\text{M}$ ) | Irradiation | $k_{\text{obs}}$ ( $\text{min}^{-1}$ ) | $t_{1/2}$ (min) |
|--|-------------|--|-----------------|
| $80 \pm 5$                             | US only     | $0.038 \pm 0.001$                      | 18              |
|  | US + Fe(II) | $0.060 \pm 0.001$                      | 11              |
| $160 \pm 5$                            | US only     | $0.0165 \pm 0.0005$                    | 42              |
|  | US + Fe(II) | $0.0355 \pm 0.0005$                    | 20              |
| $200 \pm 5$                            | US only     | $0.0145 \pm 0.0005$                    | 48              |
|  | US + Fe(II) | $0.0335 \pm 0.0005$                    | 21              |
| $280 \pm 10$                           | US only     | $0.0125 \pm 0.0005$                    | 56              |
|  | US + Fe(II) | $0.0285 \pm 0.0005$                    | 25              |
| $500 \pm 20$                           | US only     | $0.009 \pm 0.0003$                     | 78              |
|  | US + Fe(II) | $0.018 \pm 0.0003$                     | 38              |



**Figure 3** Effect of phenol initial concentration on reaction rate constant. US: 608 kHz, 30W; Fe(II) concentration: 500 μM FeSO<sub>4</sub>; pH = 3.5 ± 0.2



**Figure 4** Effect of Fe(II) concentration on rate constant of phenol degradation. US: 608 kHz, 30W; reaction temperature: 25 ± 1°C; pH = 3.5 ± 0.2; Phenol initial concentration: C<sub>1</sub> = 150 ± 5 μM; C<sub>2</sub> = 250 ± 5 μM

#### Effect of Fe<sup>2+</sup> concentration on sonochemical degradation of phenol

As can be seen in Figure 4, the concentration of Fenton's reagent significantly affects the pseudo first-order rate constant of phenol degradation in the aqueous solutions (150 and 250 μM of phenol, pH = 3.5 ± 0.2). The rate constant of phenol degradation increases initially with increasing initial concentration of FeSO<sub>4</sub>. A maximum increase (~2.3 fold) in the measured rate constant was observed when the Fe (II) concentration was between 400 μM and 1,000 μM. This increment was due to the higher HO• radical concentration produced through Fenton's reaction (Eq. (1); Joseph *et al.*, 2000). Since phenol is predominantly oxidised and degraded by the highly reactive hydroxyl radicals (HO•) under ultrasonic irradiation (Serpone *et al.*, 1992; Petrier *et al.*, 1994; Petrier and Francony, 1997; Berlan *et al.*, 1994), the enhancement in the degradation rate of phenol resulted from the increase in HO• radicals on increasing the concentration of Fe(II) in solution by 500 μM. However, further increase in FeSO<sub>4</sub> concentration showed no further catalytic activity and, in contrast, the reaction rate of phenol degradation decreased when the Fe(II) concentration was more than 1,000 μM due to the direct reduction of HO• radicals by Fe(II) (Eq. (7)):



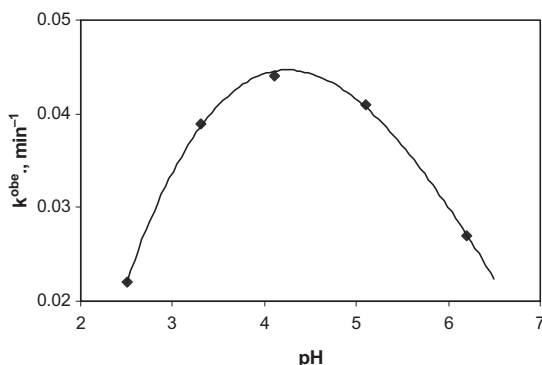
In addition, there are some reports that the maximum yield of OH• generated from Fe(II) reacting with H<sub>2</sub>O<sub>2</sub> can be obtained when an optimal ratio (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>) is used. It has been suggested to range from 5–11 at a pH of 3.5 according to the experimental investigations of Tang and Huang (1994). One can assume that the amount of H<sub>2</sub>O<sub>2</sub> produced by sonication

(at 608 kHz with 30 W and reaction temperature  $25 \pm 1^\circ\text{C}$ ) is constant. The ratio between  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  was therefore changed by increasing the concentration of  $\text{FeSO}_4$  in bulk solution. It was obvious as shown in Figure 4 that the optimal rate of phenol decomposition was obtained when the Fe(II) concentration was between 400  $\mu\text{M}$  and 1,000  $\mu\text{M}$ . Over this concentration range, the rate constant of phenol degradation decreased with increasing concentration of Fe(II). The finding that the degradation rate of the target molecule by coupled sonochemistry and Fenton's reagent depends on the Fe(II) concentration is in agreement with the results obtained from Joseph *et al.* (2000). These authors examined sonochemical degradation of azobenzene and related azo dyes in the presence of Fe(II) at 500 kHz and they demonstrated that a three-fold increase in the reaction rate was observed at optimal Fe(II) concentrations.

#### Effect of pH on rate constant of phenol sonochemical degradation

As shown in Figure 5, the decomposition rate of phenol in aqueous solution by coupled sonochemistry and Fenton's reagent was strongly dependent of pH. The lower pH (<3.0) gave the lower degradation rate, and the optimal values in rate constant of phenol degradation were obtained at pH ranged 3.5~4.5. At higher pH (>5.0), the rate constant for phenol degradation decreases rapidly with increasing pH. These experimental observations can be explained by the following pH effects on sonochemistry and Fenton's reagent.

The pH, which results in modification of the physical properties (including charges) of molecules with ionisable functional groups, plays an important role in the sonochemical degradation of chemical contaminants (Jiang *et al.*, 2001). Based on previous experimental observations, the neutral species of hydrophilic contaminants more easily diffuse to, and accumulate at, the hydrophobic liquid–gas bubbles interface to be oxidised by hydroxyl radicals ( $\text{HO}\cdot$ ). Phenol exists in protonated and uncharged form ( $\text{pK}_a = 9.99$ ) under acidic conditions, therefore, the rate constant of phenol degradation on sonication as can be seen in Figure 5 increases with decreasing pH (at least in the range of pH 4–7). There is wide experimental evidence that at pH 3–4 the radical  $\text{HO}\cdot$  is the most active species during the degradation of organic compounds (Kiwi *et al.*, 2000). An optimum in the rate constant for phenol degradation was obtained at pH 3.5–4.2 in this study. The degradation rate of phenol then decreases with further decrease in pH due to the reduced yield of hydroxyl radicals ( $\text{HO}\cdot$ ) by ultrasonic irradiation. In addition, the finding that the generation rate of  $\text{H}_2\text{O}_2$  by sonication (610 kHz, 30 W) in phosphate buffer media (0.01 M) was maximum at pH 3–4 over the range of pH 2–9 (Jiang *et al.*, 2001), is supportive of an optimal pH being observed for degradation of phenol using coupled sonochemistry and Fenton's reagent.



**Figure 5** Effect of pH on rate constant of phenol degradation. US: 608 kHz, 30W; reaction temperature:  $25 \pm 1^\circ\text{C}$ ; Fe(II) concentration: 500  $\mu\text{M}$ ; phenol initial concentration:  $C_1 = 150 \pm 5 \mu\text{M}$ ;  $C_2 = 250 \pm 5 \mu\text{M}$

The pH is also one of major factors influencing the degradation rate of chemical contaminants in the Fenton reaction. pH controls the Fe(II) speciation which affects the rate of the Fenton reaction. According to Balmer and Sulzberger (1999), the rate constant for reaction of Fe(II) with  $\text{H}_2\text{O}_2$  to produce  $\text{HO}\cdot$  radicals was low at low pH and was faster at higher pH. The authors demonstrated that the maximum rate of atrazine degradation was obtained at pH 4.3–4.6 over the range of pH 3–8 in irradiated iron/oxalate systems. An optimal pH of 3.5 was also suggested in the oxidation of chlorinated aliphatic organic contaminants by Fenton's reagent (Tang *et al.*, 1997). In addition, the solubility of Fe(III) strongly decreases with increasing pH. As a result, ferric oxyhydroxide precipitates are formed at higher pH resulting in the reduction in catalytic activity of Fenton's reagent. In the irradiated at pH 6.2 system, the rate constant obtained by coupled sonochemistry and Fenton's reagent was not enhanced significantly ( $0.025 \pm 0.001 \text{ min}^{-1}$  in comparison with  $0.023 \pm 0.001 \text{ min}^{-1}$  by ultrasonic irradiation only) because of the absence of any ferrous iron species that could be efficiently used to produce  $\text{HO}\cdot$  radicals by reacting with  $\text{H}_2\text{O}_2$ .

## Conclusion

It is apparent that the yields of phenol degradation in the air-equilibrated aqueous media are substantially enhanced in the presence of Fe(II) under ultrasonic irradiation (608 kHz, 30 W and reaction temperature  $25 \pm 1^\circ\text{C}$ ). The rate constant of phenol disappearance by the means of ultrasound increased 2–3 fold when the aqueous solutions (pH = 3.5, phosphate buffer media) were irradiated with 400–1,000  $\mu\text{M}$  of Fe(II) present. The results obtained in this study suggest that the enhancement in the yield of phenol degradation is mainly due to the contribution of additional hydroxyl radicals generated by Fenton's reagent as Fe(II) reacts with  $\text{H}_2\text{O}_2$  (formed on sonolysis) enabling further production of  $\text{OH}\cdot$ . The decomposition rate of aqueous phenol using coupled ultrasound and Fenton's reagent was strongly dependant on the initial concentration of reactant, Fe(II) concentration as well as the pH. In summary, the optimal operating conditions for degradation of 100–500  $\mu\text{M}$  phenol degradation can be achieved at 608 kHz with ultrasonic power 30 W and with reaction temperature of  $25 \pm 1^\circ\text{C}$  when  $\text{FeSO}_4$  concentrations are between 400 and 1,000  $\mu\text{M}$  over a pH range of 3.5–4.2.

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