



Understanding acoustic cavitation for sonolytic degradation of p-cresol as a model contaminant



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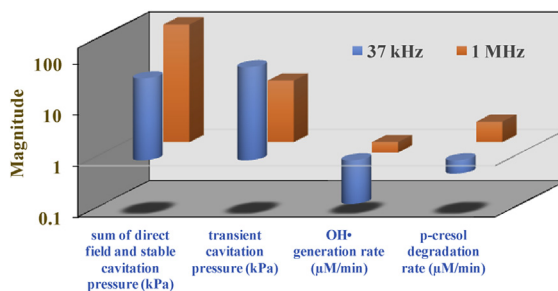
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HIGHLIGHTS

- Examined acoustic cavitation using hydrophone and chronoamperometry measurements.
- Stable cavitation prevalent at 1 MHz while transient cavitation dominant at 37 kHz.
- Higher generation rate of OH[•] at 1 MHz than at 37 kHz.
- p-cresol degradation rate faster at 1 MHz compared to 37 kHz.
- Addition of H₂O₂ or Cu²⁺/H₂O₂ significantly improved the p-cresol degradation rate.

GRAPHICAL ABSTRACT



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ABSTRACT

Many modern techniques exist for the degradation of organic pollutants in water. Numerous treatment processes which utilize the formation of hydroxyl radicals for oxidation of pollutants have been studied thoroughly. In this study, a three pronged approach has been used to characterize and understand the effect of two distinct acoustic frequencies (37 kHz and 1 MHz) on cavitation behavior. Correlation of this behavior with sonolysis of a target phenol pollutant is described. Hydroxyl radical capture, hydrophone, and microelectrode studies in this work show that megasonic frequencies are more effective for generation of hydroxyl radicals and stable cavitation events than ultrasonic frequencies. UV absorption and fluorescence measurements confirm that the combination of ultrasonic sonolysis with a Fenton reagent achieved complete degradation of p-cresol at 50 mg/L in about 30 min. Cost estimates have been made for different sonication processes and compared with traditional advanced oxidation processes.

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1. Introduction

Sonolysis is one of the techniques used for the degradation of

organics in water (Gonzalez-Garcia et al., 2010; Chowdhury and Viraraghavan, 2009). As an acoustic pressure wave from a transducer propagates through the aqueous medium, the oscillation between high and low pressure causes cavitation bubbles to form, oscillate and subsequently collapse (Awad et al., 2010). Cavitation events are described as either stable or transient, and both cases generate highly localized temperature (thousands of Kelvin) and

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pressure (hundreds of atmospheres) elevations (Flint and Suslick, 1991; Margulis and Margulis, 2004). The energy of the event is dependent on the intensity of cavitation which in turn depends on the amplitude and frequency of the acoustic wave among other factors (Entezari et al., 2005). The frequency determines growth time of the bubble. Lower frequencies give longer growth periods and produce fewer but larger cavitation events for a given time period. These cavitation events have greater likelihood of more violent transient cavitation. Higher frequencies produce more but smaller cavitation events due to a faster cycle. Events at higher frequency have a greater likelihood of stable cavitation in which the bubble does not collapse entirely but grows and shrinks periodically. Transient cavitation generates higher temperatures which are more ideal for the pyrolytic degradation of volatile hydrophobic organics, but stable organics, such as aromatics, are degraded by cavitation indirectly (Entezari et al., 2005; Petrier and Francony, 1997). Researchers have been successfully able to fundamentally study and characterize the cavitation effects by means of chemical and electrochemical methods (Mason et al., 1994, 2012).

Organics undergo sonolytic degradation in two possible ways, pyrolytic degradation and oxidative degradation. Besides heat, the cavitation event causes the short lived formation of hydroxyl radicals which can react with organic species to oxidatively degrade them. Many studies have been performed in the ultrasonic range to determine the most appropriate frequency for various organic species. Petrier et al. (Petrier and Francony, 1997; Petrier et al., 1992; Petrier et al., 1994) have elucidated the role of acoustic frequency on sonolytic degradation of organic compounds in aqueous solutions. Their work on phenol degradation indicates that 200 kHz is the most effective frequency for degradation among a range of frequencies (20, 200, 500 and 800 kHz) investigated. About 50% degradation of phenol ($C_0 = 1$ mM) was observed in about 100 min at 200 kHz. Another such study showed that with volatile organic species, reaction rate increased with increasing frequency from 20 to 800 kHz, but the reaction efficiency decreased with each cycle (Petrier and Francony, 1997). This implies that there is an energy threshold for degradation of the volatile organic, carbon tetrachloride in this case, which is met on average by cavitation events in the frequency range of 20–800 kHz but that as frequency increases a greater proportion of those cavitation events did not meet that energy threshold and so efficiency per cycle decreased. There is undoubtedly a similar duality in the acoustic frequency effects on OH^\bullet formation, but it is known that the energy threshold in this case is much lower. This suggests that the megasonic frequency range may be more effective for the degradation of stable aromatic type compounds.

In the current work, focus has been laid on the sonolytic degradation of p-cresol, an organic compound which is present in waste water from coal conversion plants, textile industry, paper pulp treatment facilities, refineries, pharmaceutical plants and others (Jiazhen et al., 2007). Although present in small quantities (several ppm) (Nakhla and Suidan, 1995), p-cresol is prevalent in wastewaters originating from refineries, petrochemicals, polymeric resins, pharmaceuticals, and various chemical industries (Rojas et al., 2010). One of the primary mechanisms behind degradation of phenolic compounds is by oxidation through reaction with a strong oxidant such as OH^\bullet . Advanced oxidation processes (AOP's) such as UV, photocatalysis, $\text{O}_3/\text{H}_2\text{O}_2$, $\text{UV}/\text{H}_2\text{O}_2$, and UV/O_3 are some common methods used to treat such pollutants (Esplugas et al., 2002). Among all the available oxidative processes, the use of O_3 has been identified to be the most effective and economical due to large oxidation rate constant of 4.42 hr^{-1} (pseudo first order), which is about an order of magnitude higher than that observed in the presence of UV and photolysis (Hoigne and Bader, 1983). It has also been established that other combinative processes are not as

effective as using just O_3 (Esplugas et al., 2002). On the contrary, ultrasound has been given much attention due to its relatively high efficiency of oxidation through homolytic cleavage of water during cavitation. However, complete degradation through sonolysis alone takes much more time than when combined with other oxidative techniques (Bagal and Gogate, 2014; Gogate, 2008). Addition of hydrogen peroxide increases hydroxyl radical formation during sonication because it is a direct precursor. Another technique is the addition of Fenton's reagent such as iron/copper ions with H_2O_2 that react with each other to form hydroxyl radicals in parallel with sonication. The Fenton's reagent is a very effective formulation for catalyzing hydroxyl creation especially when irradiated with light or acoustic power, but even individually at higher concentrations (Kubo et al., 2004). Aside from the influence of solution parameters, the work of Gogate et al. (Sutkar and Gogate, 2009; Gogate and Pandit, 2004a, 2004b) shows the importance of the dynamics and non-linearity of acoustics. Design aspects such as shape and configuration of the transducer, liquid height, and reactor geometry play a key role in the development of a sonochemical reactor for commercial applications. In order to capture the bubble cavitation dynamics, a variety of measurement techniques have been used in the past. Some of these include hydrophone (pressure), calorimetry (temperature), iodide dosimetry (von Sonntag et al., 1999), terphenathal acid dosimetry, sonochemiluminescence and electrochemical sensors (Zhou and Maisonhaute, 2013).

Petrier et al. have reported that with 50 W of acoustic power, higher frequencies, from 20 to 500 kHz, cause better generation of hydroxyl radicals (Petrier and Francony, 1997). However, the study also showed a greater rate of phenol degradation with addition of a Fenton's reagent at a much lower frequency, 35 kHz, but equal acoustic power, which demonstrates that additives and the geometry of the transducer and vessel play a significant role as well. There may be a unique frequency of maximum efficiency or reaction rate for every set of conditions and geometries. However, the general consensus is that hydroxyl formation due to acoustic cavitation is greater at higher frequencies within the ultrasonic range (Didenko et al., 1994). A study by Namkung et al., in 2008 found that in advanced Fenton processing of phenols in solution, total organic carbon (TOC) content removal was not significantly increased by changing the intensity of sonication from 2.4 to 4.7 W in an acid solution containing ferrous and zero valent iron as a Fenton's type reagent. However, increasing the hydrogen peroxide flow rate from 14 ml/h to 60 ml/h increased the TOC removal by almost 4 times from about 11 to 38% (Namkunga et al., 2007).

A study by Entezari et al. (2005) found that ultrasonic acoustics increased the effectiveness of 2-chlorophenol degradation in a solution containing a Fenton's reagent (iron II), hydrogen peroxide and inorganic catalyst (titanium dioxide) at 6 mM, 10 mM and 0.01–0.06 (wt. %) respectively. The combination of inorganic catalyst, Fenton's reagent and sonication with 20 kHz at 11–45 W/cm^2 was far more effective than any individual technique. The original concentration of 2-chlorophenol, 50 μM , was completely degraded in approximately 100 min in the most ideal case.

The ultrasonic frequency range of sonolysis has been studied extensively with many papers reporting effective conditions for the degradation of phenols below 800 kHz (Kidak and Ince, 2006), however, the megasonic frequency range is yet to be explored. In this study, characterization of the cavitation activity was conducted by means of a microelectrode, a hydrophone, and hydroxyl radical capture measurements at two contrasting frequencies of 37 kHz and 1 MHz. Further, we have been able to separate out stable cavitation from transient cavitation at ultrasonic and megasonic frequencies using the acoustic emission technique and correlate the effect of these frequencies on generation rate of OH^\bullet and sonolytic degradation of a model compound such as p-cresol in the presence

and absence of peroxide and Fenton's reagent.

2. Materials and methods

2.1. Reagents

De-ionized water (18 M Ω -cm) was used for preparation of solutions. p-cresol, copper sulfate, potassium ferricyanide, potassium chloride and sodium hydroxide of purity greater than 99% were procured from Fisher Scientific Inc. Terephthalic acid (98%) and 2-hydroxyterephthalic acid (97%) were purchased from Sigma Aldrich. Semiconductor grade hydrogen peroxide (30%) was purchased from Honeywell Inc.

2.2. Experimental setup

Ultrasonic and megasonic systems with operating frequencies of 37 kHz and 1 MHz were manufactured by Elma Ultrasonics and PCT Systems Inc., respectively. The reactor consisted of a flat bottomed glass beaker (total volume = 1.5 L) containing about 1 L of p-cresol solution (Fig. 1). The beaker was immersed in the ultrasonic tank and placed about 1 cm above the transducer. To maintain a constant bath temperature (30 \pm 2 $^{\circ}$ C), the water was recirculated through a heat exchanger.

2.3. Analysis

Hydroxyl radical capture studies were conducted with air saturated solutions containing 2 mM terephthalic acid and 4.1 mM sodium hydroxide (pH \sim 9.5). Samples were collected in regular intervals and the OH $^{\bullet}$ was quantified by means of fluorescence spectroscopy (Keswani et al., 2014). The OH $^{\bullet}$ generated during acoustic exposure reacts with the terephthalic acid to form 2-hydroxyterephthalic acid that exhibits emission at 425 nm, when excited at 318 nm. Microelectrode studies were performed in argon saturated solutions containing 50 mM potassium ferricyanide (electroactive species) and 100 mM potassium chloride (supporting electrolyte). The setup consisted of a 25 μ m diameter platinum disc as the working electrode along with 500 μ m diameter and 1 cm long platinum wires as counter and reference electrodes. Electrochemical investigations were conducted at an applied potential of -0.6 V to the working electrode (vs Pt reference), which was achieved by means of a potentiostat (Gamry Interface 1000). Pressure measurements were conducted at sampling rates of 50 million samples per second for total duration of 1 s using a HCT-0310 hydrophone (Onda. Corp.) and an oscilloscope (NI USB 5133). LabVIEW 2012 (version 12.0) was used to acquire the data and Matlab 7.3 was used to process the spectral information. The

net acoustic pressure (root mean square, rms) delivered into the aqueous solution (air saturated) was estimated to be about 70 kPa and 80 kPa at 1 MHz and 37 kHz, respectively.

Degradation studies were carried out under two different frequencies (37 kHz and 1 MHz) and varied parameters such as concentration of components (0.6–150 ppm Cu and 10–60 mM H $_2$ O $_2$) of Fenton's reagent in solutions containing 50 ppm of p-cresol. Generally, iron is used for Fenton's system. However, we have used copper since the standard reduction potential for the equilibrium reaction of Cu $^+$ /Cu $^{2+}$ is lower (0.18 V) than that of the Fe $^{2+}$ /Fe $^{3+}$ couple (0.77 V) and therefore Cu $^+$ would be easier to oxidize (thermodynamically) compared to Fe $^{2+}$ at low concentrations of H $_2$ O $_2$ and likely to generate OH $^{\bullet}$ more readily. The concentration of p-cresol was determined mainly by fluorescence spectroscopy, but also with limited studies conducted using UV–Vis spectroscopy. Fig. S1 shows the calibration curves obtained for different p-cresol (1–50 ppm) standards. When excited at a wavelength of 277 nm, p-cresol shows peak emission at about 305 nm. The intensity at this emission wavelength was used to calculate p-cresol concentration in actual degradation samples. UV–Vis characterization was achieved by calculating the area under the absorbance peak at 277 nm using OriginPro software. The UV–Vis characterization served as a confirmation to the fluorescence measurements and a good correlation was observed between the results obtained using the two methods.

3. Results and discussion

In this section, characterization of acoustic cavitation through hydroxyl radical measurements, hydrophone and microelectrode studies are discussed. Then an attempt is made to relate cavitation to degradation of p-cresol at ultrasonic and megasonic frequencies.

3.1. Hydroxyl radical measurement

Terephthalate dosimetry has been a well-established technique to quantify cavitation activity in acoustically irradiated solutions. Literature suggests that volume of solution, shape of the container (Mason et al., 1994), concentration and type of dissolved gas, transducer power, and acoustic frequency (Hua and Hoffman, 1997; Lida et al., 2005) are some of important parameters that affect OH $^{\bullet}$ generation. It has been established that for the frequency range of 20–500 kHz and in the presence of various dissolved gases (Kr, Ar, He, O $_2$), the generation rate of OH $^{\bullet}$ is maximum (3.17 μ M/min) at 500 kHz and solutions saturated with Kr. In this study, a similar approach has been adopted, but with the exception of investigating this behavior at a much higher frequency of 1 MHz. Fig. 2 shows the concentration of the generated OH $^{\bullet}$ as a function of sonication time

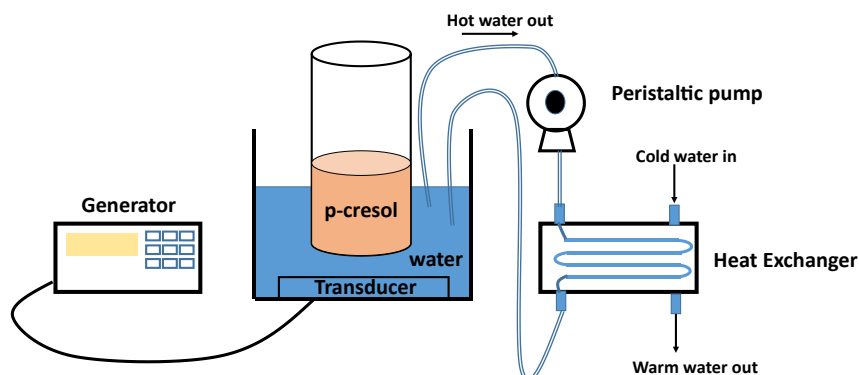


Fig. 1. Schematic of the experimental setup used for degradation experiments.

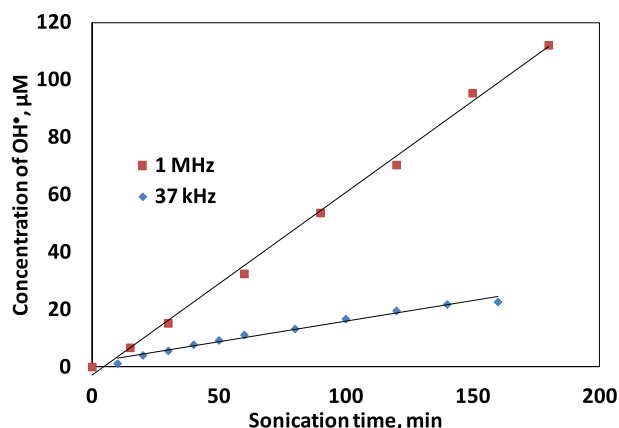


Fig. 2. Concentration of OH^* as a function of sonication time, Solution: 2 mM terephthalic acid and 4.1 mM sodium hydroxide, pH = 9.5, Excitation wavelength = 318 nm, Emission Wavelength = 425 nm.

for two different frequencies, 37 kHz and 1 MHz. The figure shows that OH^* concentration increases linearly with time at both frequencies suggesting a constant rate of generation due to relatively uniform and steady sonochemical activity. At 37 kHz, the measured OH^* concentration increased to about 20 μM in 150 min, an average generation rate of about 0.14 $\mu\text{M}/\text{min}$. Interestingly, at higher frequency of 1 MHz, the measured OH^* was about 100 μM after 150 min, about 5 times greater ($\sim 0.63 \mu\text{M}/\text{min}$) than measured at 37 kHz. This increased generation of OH^* at higher frequencies could possibly be attributed to increased number of stable cavitation cycles that a bubble undergoes, about 25 times more at 1 MHz than at 37 kHz. The extreme temperatures at the end of each cycle provide conditions for the breakdown of water into radicals. Although lower frequencies are known to generate more intense transient cavitation due to the larger size of cavities prior to collapse, the occurrences of total cavitation (stable and transient) events with high temperature conditions are much lower at these frequencies, which reduces the overall generation rate of OH^* .

3.2. Microelectrode studies

Fig. 3(a) and (b) show the current versus time at acoustic frequencies of 37 kHz and 1 MHz, respectively. The measured current is a result of electrochemical reduction of ferricyanide species (to ferrocyanide) at the electrode surface. As the species is consumed, it is continuously being replenished by transport due to diffusion (in the absence of sound field) or combination of convection and diffusion due to acoustic streaming and/or stable and transient cavitation. The figures display a steady baseline current of about $-0.4 \mu\text{A}$ in the absence of sonication, under an applied potential of -0.6 V . This limiting current corresponds to the reduction of ferricyanide to ferrocyanide. In the presence of an acoustic field, current peaks were observed. The current peaks pertain to the effects produced by the collapsing or oscillating cavities near the microelectrode. Transient cavities grow in size and collapse, which causes accumulation of ferricyanide ions at the bubble–liquid interface by advection (Keswani et al., 2013a, 2013b). The concentrated ferricyanide diffuses radially after collapse and reaches the electrode surface where it is electrochemically reduced, which causes the current to increase in magnitude. The current continues to increase with more transport of ferricyanide towards the electrode and reaches a peak value and starts dropping as ferricyanide disperses by diffusion and finally attains the baseline value. Similar effect is observed during the compression phase of a stable

oscillating cavity, although in this case, the peak magnitude will be much smaller due to lower degree of advection and smaller ferricyanide accumulation. Examples of current peaks at 37 kHz and 1 MHz is illustrated in Fig. 3(c) and (d), respectively. A peak was defined as due to cavitation when the maximum current reached 0.6 μA or higher in magnitude. Below this threshold, any increase in current from the baseline is attributed to reduction in the boundary layer due to acoustic streaming. The rise and fall times of peaks were in the range of 10–30 ms and 30–80 ms and 3–10 ms and 12–20 ms at 37 kHz and 1 MHz, respectively. The average peak rise and fall times were higher (~ 3 times) at 37 kHz indicating that the average time per cavitation event is much larger at lower frequencies. As the time per cavitation event increases, the frequency of occurrence of high temperature conditions goes down, possibly reducing the OH^* generation rate and the oxidative power of the solution.

At 37 kHz, several current peaks with magnitudes greater than 3 μA were observed, the greatest at about 5.5 μA . At 1 MHz, most of the current peaks were less than 1 μA , with a limited number of peaks in the range of 1 and 2 μA . The larger magnitude of current peaks seen at ultrasonic frequency is likely due to the fact that the bubble grows into a larger transient cavity thereby yielding a more violent collapse at this frequency. At megasonic frequency, the overall amplitude of current peaks significantly reduces indicating predominance of stable cavitation at higher acoustic frequency. During 12 s of acoustic exposure, 80 peaks exceeding 0.6 μA were observed at 1 MHz but only 30 at 37 kHz. These results clearly demonstrate that although the maximum intensity of cavitation at 1 MHz is lower than that at 37 kHz, the total number of significant cavitation events is higher at megasonic frequencies leading to more frequent generation of conditions sufficient to achieve release of active radicals (Keswani et al., 2013a).

3.3. Hydrophone studies

The results from hydrophone measurements at 37 kHz and 1 MHz are shown in Fig. 4. The root mean pressure values for direct field, stable cavitation, and transient cavitation are plotted for the two frequencies in this figure. The methodology for obtaining the different pressure fields has been described in Zhao et al. (2015); Balachandran et al. (2015). The pressure-time data computed after application of hydrophone calibration to the acquired voltage–time curves was converted into the frequency domain using a Discrete Fourier Transform (DFT). The resulting plot consisted of line spectrum representing direct field and stable cavitation pressure and broadband spectrum (white noise) denoting transient cavitation. The direct field has contribution from pressure wave emanating from the transducer at the driving frequency as well as that from resonant bubbles oscillating at that frequency. The stable cavitation pressure includes contributions from non-linearly oscillating stable bubbles at harmonic and sub-harmonic frequencies, while transient cavitation pressure results from random collapses of cavities that produce shock waves and microjets. The integral under the fundamental peak (above the background) was used for computing the direct field pressure while collective integral under the line spectra (above the background) at harmonics, sub-harmonics, and ultraharmonics provided the stable cavitation pressure. The transient cavitation pressure was obtained by fitting a curve to the continuous broadband spectrum or white noise (on which the line spectra are superimposed) and taking the integral under this curve. As one may note from Fig. 4, the direct field pressure at 37 kHz is $\sim 15 \text{ kPa}$ and increases to 160 kPa at 1 MHz. Similarly, the stable cavitation pressure is about 1.5 times higher at 1 MHz compared to 37 kHz. On the other hand, the trend in transient cavitation activity is reversed where transient cavitation

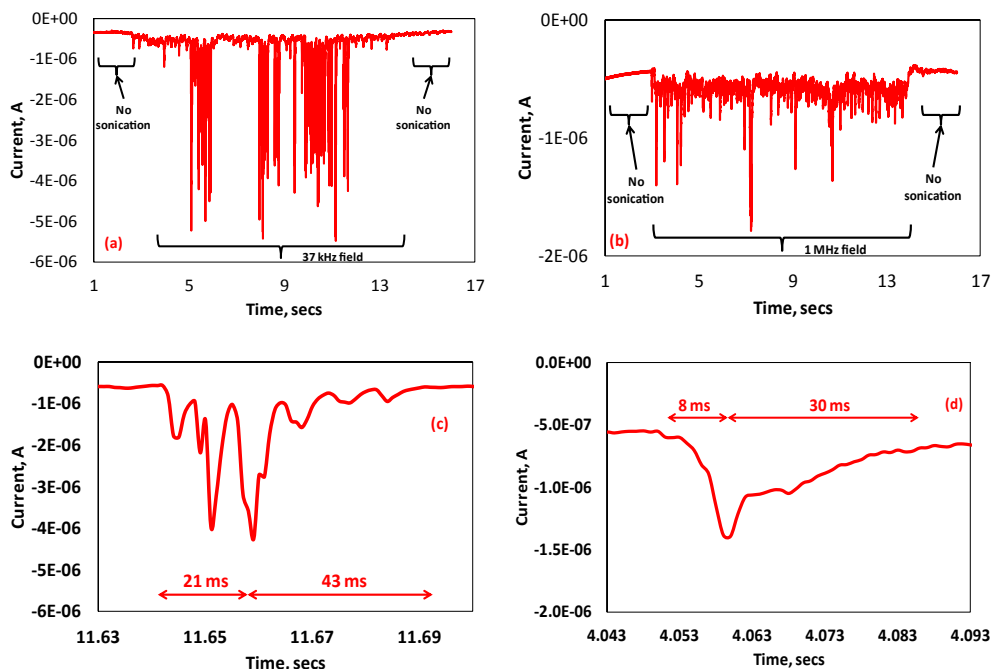


Fig. 3. Current as a function of time (chronoamperometry curves) for solutions containing 50 mM potassium ferricyanide and 100 mM potassium chloride at (a) 37 kHz and (b) 1 MHz, Expanded time scale to illustrate the shape of a representative current peak at (c) 37 kHz and (d) 1 MHz. Applied potential = -0.6 V (vs Pt reference).

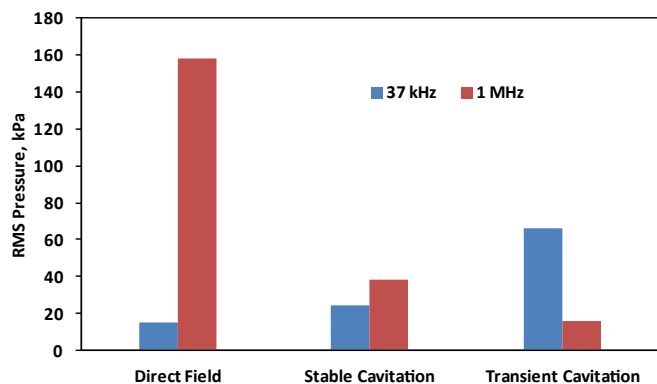


Fig. 4. Direct field, stable cavitation and transient cavitation pressures at 37 kHz and 1 MHz.

pressure is much lower at 1 MHz (~ 20 kPa) than that at 37 kHz (~ 70 kPa). These results suggest that the frequency of occurrence of stable cavitation event is higher at megasonic frequency of 1 MHz and that of transient cavitation is lower compared to ultrasonic frequency of 37 kHz. Additionally, the pressure field at 1 MHz and 37 kHz increases in the following order direct > stable > transient and transient > stable > direct, respectively. This indicates that predominantly all the cavitation generated at 1 MHz occurs as a result of stable resonating bubbles which is in contrast to that observed at 37 kHz. Overall, hydrophone measurements in combination with OH^\bullet capture and microelectrode studies reveal that stable cavitation dominates at megasonic frequencies.

3.4. Degradation of p-cresol

Fig. 5(a) through (c) show degradation results obtained from fluorescence spectroscopy under a variety of conditions, while Fig. 5(d) was acquired using data from UV–Vis spectroscopy. The

presence of hydrogen peroxide, Fenton's reagent at several concentrations and the application of acoustic field at 37 kHz and 1 MHz were studied individually and in some combinations. The concentration of p-cresol remaining was normalized with respect to the original concentration and plotted as function of time.

In the absence of sonication (Fig. 5(a)), the percent degradation proceeds slowly with time when the solution contains 60 mM of hydrogen peroxide. At the end of about 3 h, the degradation is only about 20%. When 150 ppm of copper ion as CuSO_4 was introduced into the solution, more than 85% degradation was achieved in less than 10 min and only about 2% of the original concentration remained after 3 h. The initial sudden drop in p-cresol concentration in these solutions is likely due to high OH^\bullet release rate with immediate addition of Fenton's reagent followed by a slow degradation with equilibrium progression of the Fenton's reaction. These results also emphasize the importance of hydroxyl radicals in enhancing oxidation of aromatics as indicated by the increase in the p-cresol degradation rates for solutions containing hydrogen peroxide and Fenton's reagent both.

The effect of application of sonication at 37 kHz on p-cresol degradation is illustrated in Fig. 5(b). In the absence of any additives, the p-cresol degrades only 10% in 150 min. In the presence of 60 mM peroxide, degradation in 150 min was only about 20%, but with the same concentration of peroxide combined with sonication about 80% p-cresol was degraded in 150 min. Degradation increases from continuous generation of OH^\bullet when peroxide containing solutions are irradiated with a sound field. The most effective degradation of p-cresol was achieved by the following combination of Fenton's reagent, 60 mM peroxide and 150 ppm copper ion exposed to a 37 kHz sonication field. Under this condition, complete degradation of p-cresol was achieved in 30 min. In comparison, about 98% of p-cresol was degraded in 180 min using the Fenton's reagent but in the absence of sound field. Reducing peroxide concentrations to 10 mM (keeping Cu at 150 ppm) or copper concentration to 2.5 ppm (keeping H_2O_2 at 60 mM) increased the sonication time required for complete degradation to

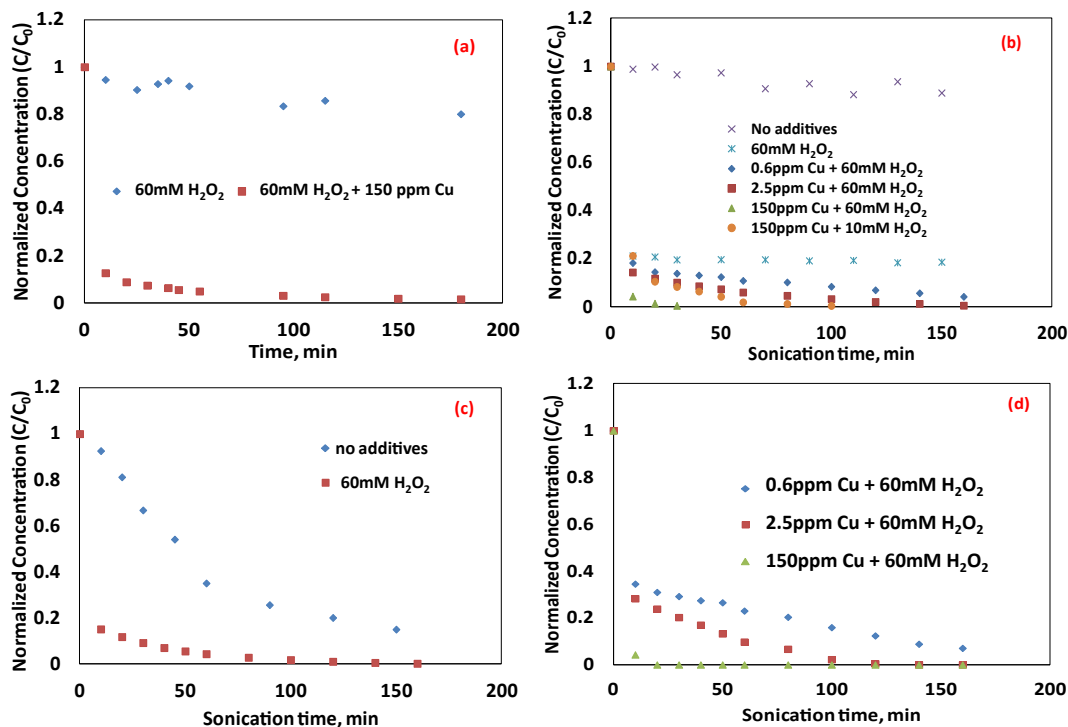


Fig. 5. Fluorescence results for degradation of p-cresol under (a) no sonication, (b) 37 kHz, (c) 1 MHz and UV–Vis results under (d) 37 kHz.

100 min and 160 min respectively. However, further lowering the copper concentration to 0.6 ppm (with 60 mM H_2O_2) did not yield complete degradation of p-cresol in the investigated time of 160 min. Increased degradation rates with the combination of sonication and Fenton's reagent possibly arises from the catalytic effect of acoustic cavitation induced localized thermal and pressure increases on enhancing the Fenton's reaction and therefore OH^\bullet generation rates.

At 1 MHz of sonication, the percent degradation of p-cresol, shown in Fig. 5(c), was much higher than at 37 kHz. When sonicated at 1 MHz, without any additives, as much as 85% degradation was attained in 150 min. With just the addition of hydrogen peroxide at 60 mM, 100% p-cresol degradation was measured in less than 160 min, while the percent degradation was only 80% when 37 kHz frequency was applied for the same time. Although megasonic frequencies were not explored in combination with peroxide and Fenton's reagent, these results clearly suggest that megasonic frequencies are more effective than ultrasonic for degradation of p-cresol and perhaps many, if not all aromatics.

Further confirmation for the degradation of p-cresol was achieved by means of using UV–Vis spectroscopy (Fig. 5(d)). For solutions containing 60 mM H_2O_2 and irradiated with 37 kHz, complete degradation was observed in about 20 min and 140 min in the presence of 150 ppm and 2.5 ppm copper respectively, whereas about 90% degradation was measured after 160 min with 0.6 ppm copper. These trends are similar to those observed using fluorescence spectroscopy and confirm the reproducibility of the data and improve the reliability of the results obtained in this study. It may be noted that the quenching of fluorescence and loss of UV absorbance indicates the degradation of the aromatic structure. We are not claiming mineralization here, but rather, the loss of the parent compound as measured by intrinsic spectroscopic properties.

3.5. Cost estimate

Fig. 6 shows the comparison of the cost estimates obtained for different sonolysis processes for the degradation of p-cresol. The cost of chemicals and electricity were included in the estimated cost calculations. Calculations were performed using 1 m^3 of effluent as the basis. Electrical energy required for ultrasonic and megasonic processes were computed based on the power transmitted into the solution during acoustic exposure using the following electrical energy per order (EE/O) equation (Mahamuni and Adewuyi, 2010).

$$\text{EE/O} = \frac{P \cdot t \cdot 1000}{V \cdot 60 \cdot \log\left(\frac{C_0}{C}\right)} \quad (1)$$

Where, P = electrical power in kilo Watts transmitted to the solution, t = time (in minutes) needed to degrade p-cresol concentration to a concentration C , V = volume of solution in liters, C_0/C = ratio of initial to final concentration of p-cresol. The measured

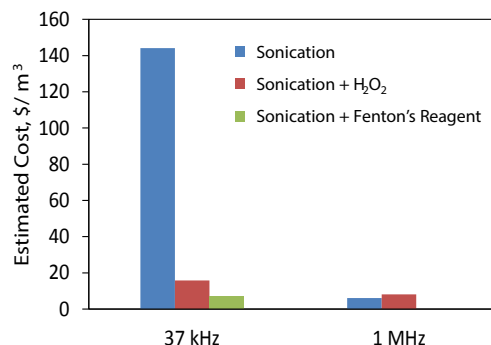


Fig. 6. Cost estimates of different degradation processes for p-cresol.

pressure rms values of 70 and 80 kPa for ultrasonic and megasonic field respectively were converted to power density (I_{rms}), using equation (2), from which the power (rms) was calculated by multiplying with the area of the exposed solution ($\sim 78 \text{ cm}^2$) in the container.

$$I_{\text{rms}} = p_{\text{rms}}^2 / (2 * c * \rho) \quad (2)$$

where, c is the speed of sound in water (1490 m/s) and ρ is the density of water (1000 kg/m^3)

The EE/O was calculated to be roughly 1000 and 90 kWh/m^3 -order for ultrasonic and megasonic processes, respectively. Electrical cost is the product of electrical energy (kWh) and rate per unit of energy consumed ($\sim \$0.08/\text{kWh}$). The cost of hydrogen peroxide and copper sulfate were estimated at about \$ 4 per gallon and \$ 2.2 per kg (Mahamuni and Adewuyi, 2010), respectively. For 1 m^3 of effluent solution about 6 L of H_2O_2 and 0.15 kg of CuSO_4 was required. Therefore, total chemical costs were computed to be about \$6.35 and \$0.33 for H_2O_2 and CuSO_4 , respectively.

In the presence of only the acoustic field, megasonic frequency clearly seems to be much more cost effective as the cost is lower by an order of magnitude (\$6 in comparison to \$144 at 37 kHz). In the case of added peroxide, cost of operation for the ultrasonic process reduces to \$16 while it increases slightly for megasonic process to \$8. However, it may be noted that megasonic process with peroxide requires much lower time for degradation than ultrasonic or megasonic only and ultrasonic with peroxide. When Fenton's reagent was added to ultrasonic process, the estimated cost was \sim \$7 and the degradation time was the lowest. However, the disadvantage with use of Fenton's reagent is that the process leaves behind metallic impurities in the solution at the end of degradation. In comparison, the costs for UV/ O_3 and UV/ H_2O_2 processes have been estimated to be \$10 and \$80, respectively, for degradation of phenol (Mahamuni and Adewuyi, 2010).

4. Conclusion

This work explores the use of a combinative technique employing sonication with conventional oxidizing agents such as hydrogen peroxide and Fenton's reagent for destruction of p-cresol. It was successfully shown that the acoustic systems utilized in this work produced greater concentrations of hydroxyl radicals at higher frequencies. At 1 MHz, complete degradation of p-cresol was achieved in about 160 min with only the presence of 60 mM H_2O_2 . The effect of a lower acoustic frequency, 37 kHz, was also studied to understand the effects of cavitation and achieve conditions that would yield complete degradation. Complete p-cresol degradation was observed at 37 kHz in about 30 min in the presence of 150 ppm copper and 60 mM H_2O_2 . Rate of generation of OH^\bullet and the number of cavitation peaks were observed to be 5 and 3 times higher, respectively, at 1 MHz than those at 37 kHz. The combinative technique involving sonication and Fenton's reagent is clearly much more effective than any part individually for the elimination of p-cresol. Greater hydroxyl generation at megasonic frequencies using Fenton's reagent may improve this combinative technique yet further. Cost estimates showed that the most suitable conditions for achieving complete degradation of p-cresol were 1 MHz sonication with peroxide and 37 kHz with Fenton's reagent.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2015.12.066>.

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