



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



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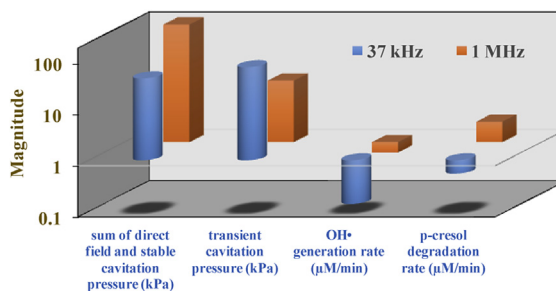
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HIGHLIGHTS

- 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), terphenathic 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

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