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Intensification of sonochemical degradation of chlorobenzene using additives

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ABSTRACT

This study evaluates the application of different additives viz. H_2O_2, Fe (II), Fe metal powder, sodium bicarbonate, and t-butanol, for intensifying the sonochemical degradation of chlorobenzene. It has been observed that the degradation of chlorobenzene is controlled by the pyrolysis mechanism, and dominant zone of degradation lies around the region of cavitating bubble. Hydroxyl radicals formed during cavitation were also useful for enhancing the mineralization of intermediates formed during degradation. It has been established that the use of Fe powder, sodium bicarbonate, and t-butanol, which leads to enhancement in the cavitational effects, gives better degradation of chlorobenzene among the different additives investigated in the study, and maximum degradation is observed in the presence of Fe powder. The presence of t-butanol, a conventional radical scavenger, leading to a marginal increase in the extent of degradation confirmed that degradation mechanism is dominated by the pyrolysis effect of cavitation. The higher Henry constant pollutant was easily degraded due to pyrolysis mechanism. A three-step degradation mechanism scheme has been established on the basis of the intermediate products formed in the process such as phenols, chlorophenols, and benzene. Rate of mineralization was also quantified in terms of total organic carbon removal, and it was established that the trends in mineralization are not necessarily the same as parent compound removal confirming that both radical and pyrolysis mechanism are important for overall mineralization.

Keywords: Chlorobenzene; Additives; Sonochemical degradation; Process intensification; Pyrolysis

1. Introduction

Chlorobenzene and other halo-aromatics are widely employed as solvents, heat transfer agents, insect repellents, deodorants, degreasers, and intermediates in dye and pesticide synthesis [1]. Due to its vast range of applications, there is a significant likelihood that a substantial amount of chlorobenzene will be present in the effluent streams and pollute the natural sources, if satisfactory treatment is not provided. Chlorobenzene is listed as priority pollutant by the Environmental Protection Agency owing to higher toxicity and its potential to accumulate in the environment [2]. The exposure of chlorobenzene affects the central nervous system and can result into different effects including headache, numbness, dizziness, cyanosis, hyperesthesia, and muscle spasms [3].

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Thermal oxidation and catalytic hydrodehalogenation are generally used for the removal of chlorobenzene, but these processes have certain limitations such as lower removal rate, highly energy-intensive operation and requirement of higher operating temperature and pressure [4]. Thus, there is a need for developing efficient treatment scheme operating at ambient conditions and also resulting in efficient removal of the highly recalcitrant chlorinated aromatic hydrocarbon from polluted water. Cavitation-based sonochemical degradation is a possible imperative technique for wastewater treatment [5,6]; though, the application of sonochemical reactors for wastewater applications has been mostly successful at laboratory scale and not much processing has been possible at commercial-scale operations due to lower rates of treatment and higher costs of operation. Cavitation can be defined as the phenomena of formation, growth, and subsequent violent collapse of microbubbles or cavities occurring in extremely small intervals of time [7]. Cavitation results in release of large magnitudes of energy over a very small location and at millions of places in the reactor simultaneously. The important effects are generation of local hotspots, intense turbulence and formation of reactive hydroxyl and hydroperoxy radicals [6–8]. These conditions are extremely suitable for treatment of wastewater containing aromatic, aliphatic, and halogenated compounds. The mechanism of cavitationally induced degradation is generally in terms of the attack of the hydroxyl radicals and pyrolytic effects due to the local hot spots generated at the site of cavity collapse. During the collapse of cavity extreme temperature conditions (1,000–2,000 K) present inside the bubble, are useful for the pyrolysis of chlorobenzene (higher Henry constant, 3.58×10^{-3} atm m^3/mol [3]). The pyrolysis effect is dominant at the site of collapsing bubble and possibly also at the interface. The reaction between the $^\bullet OH$ radicals and organic compounds occurs in the bulk solution [6].

There have been studies related to the removal of chlorobenzene from water using sonochemical reactors. It has been reported that the thermal effects or pyrolysis (extreme conditions of pressure and temperature produced inside the cavity) is useful in abstracting the chloride ions from the benzene ring and the rate of removal of chlorobenzene is dominantly controlled by the pyrolytic effects [8–12]. Krus et al. [13] investigated the degradation of chlorobenzene using different types of probes (with varying tip area) operated individually (no additives) and reported that the degradation rate increased with tip area. Studies related to the effect of different frequencies (35, 74, 170, 300, and 1,000 kHz) indicated that the degradation rate was maximum at an optimum frequency as 300 kHz [14]. Stavarache et al. established the degradation mechanism of chlorobenzene using sonochemical reactors in the presence of Fenton and Pd catalyst also confirming the mechanism as the removal of chloride ions from the benzene [9,10]. Overall, it can be said that most of the earlier works reported in the literature is based on understanding the detailed mechanism of degradation at laboratory scale of operation (few ml of volume) and also on understanding the effect of individual sonochemical reactor operation in terms of the effect of intensity or the frequency of irradiation. Another aspect of degradation of chlorobenzene, is that it has very low solubility in water (466.3 ppm at 20˚C) [15]. Maximum percentage of the chlorobenzene remains in water that can be easily separated out by gravity separation, but the small quantity in dissolved state creates lots of problems especially due to lower rates of oxidation. Pyrolysis mechanism is dominating for the removal of chloride ions from the benzene ring. Considering the problems associated with large-scale operation in terms of lower rates of degradation, the important work of intensification studies using different additives for chlorobenzene degradation has been required but lacking in the open literature. This study investigates the effect of process-intensifying parameters, such as Fe (II), hydrogen peroxide, Fe metal, sodium bicarbonate, and t-butanol, using two different levels of pollutant loadings. The study presents a combination of engineering approach to intensify the extent of degradation at the same time highlighting the chemistry aspects of the degradation process with identification of reaction intermediates and also quantification of the kinetic rate constants for the reaction using the integral approach. Such type of combined engineering and mechanistic approach has not been reported in any of the earlier literature illustrations related to sonochemically induced chlorobenzene degradation to the best of our knowledge.

2. Materials and methods

2.1. Materials

Chlorobenzene, ferrous sulfate (Fe (II)), hydrogen peroxide (H_2O_2), sodium bicarbonate ($NaHCO_3$), and t-butanol (C_4H_9OH) of GR grade (Merck), and acetonitrile (HPLC grade) were procured from M/s Aranav Chemicals, Pune, India. Iron (Fe) metal powder of 100 mesh size was procured from S. D. Fine Chemicals Pvt. Ltd., Mumbai, India. Distilled water was used for the preparation of solutions and was generated fresh in the laboratory using the Millipore distillation apparatus. All the chemicals were used as received from the supplier.

2.2. Reactor configuration

The sonochemical reactor configuration used in this study is an ultrasonic bath with three transducers arranged in triangular pitch at the bottom of tank and operates at a frequency of 20 kHz with rated power dissipation of 120 W. The bath was procured from M/s Oscar Ultrasonics Pvt. Ltd., Mumbai. The ultrasonic bath has the dimensions of 25 × 17.5 × 10 cm, and an operating capacity of 2.5 L has been selected in this study. The calorimetric measurement revealed that the exact power dissipation in the reactor was 45 W for 2.5 L capacity that indicates an energy efficiency of 37.5%.

2.3. Experimental procedure

All the experiments were conducted using 100 and 502 ppm (saturation solubility of chlorobenzene at 30°C is 502 mg/l [15]) initial concentration of chlorobenzene at natural pH of solution at an operating capacity of 2.5 L. All experimental runs were conducted in homogenous phase. Additional experiments involving stirring (stirrer type: paddle impeller with diameter of 60 mm) were carried using a 2.5 L (150 mm OD × 215 mm height) reactor at a constant stirring speed of 350 rpm. The operating temperature of the solution was maintained at 30 ± 2°C using a cooling bath especially for the experiments involving sonochemical reactors. The sample for analysis was collected periodically and filtered to remove the traces of catalyst especially in the case of heterogeneous systems.

2.4. Analysis

The samples withdrawn at regular interval of time were analyzed using high-pressure liquid chromatography (HPLC) procured from Hitachi. The detection wavelength was 254 nm, and the LC column was C18 Phenomenex column (25 cm × 4.6 mm, 5 μm particle size). In all the cases, mobile phase was a mixture of water (40%) and acetonitrile (60%), with a flow rate of 0.5 ml/min and an injection volume of 20 μl. The analog signal was recorded by an integrator, which gave an indication about the area and the concentrations were established using calibration curves. The intermediate products were analyzed based on the retention times observed in the HPLC chromatograms. In addition, samples at optimized set of parameters were also analyzed to determine the total organic carbon (TOC) content using Shimadzu TOC analyzer (Model: TOCLCPH).

3. Results and discussion

3.1. Effect of initial concentration

The effect of initial concentration of chlorobenzene was investigated at two different levels of pollutant loading as 100 and 502 ppm. The obtained results for the extent of degradation have been shown in Fig. 1. It has been observed that the extent of degradation increased with a decrease in the initial concentration of chlorobenzene from 502 to 100 ppm (66.4% for 502 ppm and 77.4% for 100 ppm). A more detailed analysis revealed that the decrease in the extent of degradation was marginal considering that the initial concentration was increased 5 times. Also, the net moles of chlorobenzene removed using the sonochemical treatment increased with an increase in the initial concentration. During the sonolysis of aqueous solution of chlorobenzene, pollutant is subjected to the hot spots formed due to the rapid adiabatic collapse. At the final stage of collapse, the temperature inside the bubble or in thin shell of liquid (immediately surrounding the bubble) is around 1,000 to 2,000 K [6]. At this temperature, more volatile component of chlorobenzene with higher Henry's law constant is transferred to the bubble, where it degrades quickly due to the hot spots generated from the cavity collapse. An increase in the concentration of chlorobenzene resulted into the enhanced degradation in terms of net moles degraded. The temperature of the collapsing cavitation bubble also depends on its contents

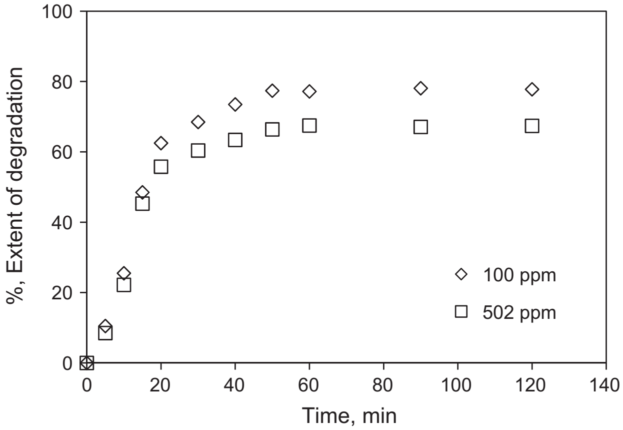


Fig. 1. Effect of initial concentration on extent of degradation of chlorobenzene.

and is determined by the average specific heat ratio (γ) of the gases present in the collapsing cavity. At higher concentration of chlorobenzene, γ value of the bubble content is lowered resulting in decreased collapse temperature of bubble. Pseudo-first-order rate constant is 3.3×10^{-2} and 2.3×10^{-2} min^{-1} for 100 and 502 ppm concentration, respectively. It shows that the counteracting effects result in marginally decreased rates of degradation, and hence, the overall extent of degradation is lower for the 502 ppm concentration. Though, net degradation rate was lower for the 502 ppm concentration, net moles degraded for 502 ppm was more compared with 100 ppm concentration. TOC measurements indicated that 41.3% and 46% reduction was observed for 100 and 502 ppm initial concentration of chlorobenzene, respectively.

Similar effects have been reported in the literature for the degradation of mixture of chlorobenzene and trichloroethylene, where it has been observed that the first-order kinetic rate constant of trichloroethylene lowered from 0.0617 to 0.0194 min^{-1} for increased initial concentration from 1.67 to 6.68 mM and from 0.0243 to 0.0057 min^{-1} for change in chlorobenzene concentration from 0.86 to 3.44 mM [16]. Another study reported that the first-order kinetic rate constant for the degradation of aqueous solution of chlorobenzene decreased from 0.0365 to 0.0025 min^{-1} for an increase in the initial concentration from 1 to 3,440 μM [14]. In all the studies, it can be easily seen that the decrease in the extent of degradation or the kinetic rate constant is not directly proportional to the degree of change in the initial concentration confirming the counteracting effects of the presence of chlorobenzene and decreased cavitational activity.

3.2. Effect of addition of ferrous sulfate, Fe (II)

The cavitational activity (i.e. the rate of formation and collapse of bubbles) increases in the presence of the gases, solid particles, and radical promoters [6]. Considering this fact, different additives have been used in this study to investigate the dependency of degradation of chlorobenzene on the type of additive.

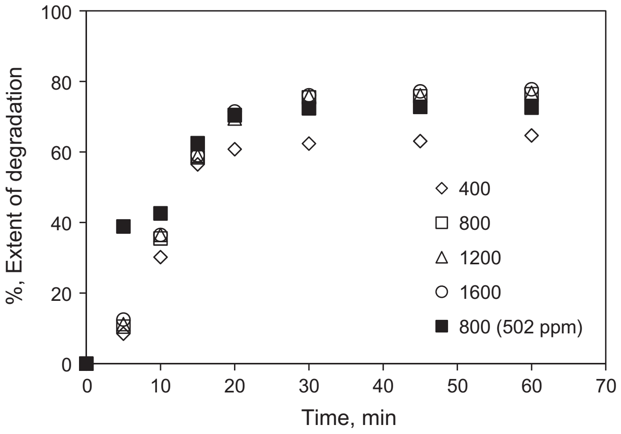


Fig. 2. Effect of Fe (II) addition on extent degradation of chlorobenzene.

The results for the variation in the extent of degradation of chlorobenzene with addition of Fe (II) have been presented in Fig. 2, and it can be seen that the extent of degradation marginally changes with an increase in the concentration of Fe (II). The maximum extent of degradation of chlorobenzene (using optimum concentration of Fe (II) as 800 ppm) was 75.5 and 70.4% for 100 and 502 ppm initial concentration of chlorobenzene, respectively, which is quite similar to that obtained in the absence of Fe (II). Also further increase in the concentration of Fe (II) does not show any increase in the degradation rate. The time of the desired degradation, however, considerably decreased from 50 to 30 min. The abstraction of chloride ions from benzene ring is a pyrolytic process, which occurs inside the cavity of bubble and depends on the cavitational intensity produced in the reactor. Addition of Fe (II) is likely to intensify number of cavitational events and the presence of Fe (II) may alter the physical effects of cavitation. Also, it provides the additional oxidizing radicals in bulk solution (from the Fenton like reaction with the *in situ* generated hydrogen peroxide) enhancing the rate of degradation of the compounds (chlorobenzene or the intermediate products) present in the bulk [9]. Similar results have been reported in the literature for the degradation of chlorobenzene in the presence of ferrous sulfate, and degradation rate (61.4% in 30 min) was the maximum for ferrous sulfate concentration of 450 mg/l. Any further increase in the concentration of Fenton's reagent reduced the rate of degradation [10]. The generated radicals in the bulk solution may be helpful for the enhanced mineralization of chlorobenzene as the intermediates formed from the initial pyrolytic mechanism can react with the hydroxyl radicals in the bulk solution. TOC measurements indicated that 97.5 and 92.8% reduction was obtained for 100 and 502 ppm concentration, respectively. TOC analysis confirms that the enhanced production of the hydroxyl ions in bulk of the solution (reaction of Fe (II) with the *in situ* generated hydrogen peroxide due to the cavitating conditions) was useful for further oxidation of benzene, phenol, chlorophenols, and other intermediate products.

3.3. Effect of H_2O_2

The purpose of using hydrogen peroxide is to increase the number of cavitational events and to provide additional source of hydroxyl radicals for the complete mineralization of chlorobenzene. The results for different concentrations of hydrogen peroxide have been presented in Fig. 3, and it can be seen that the rate of degradation of chlorobenzene increases at lower loadings of hydrogen peroxide, and any further increase in the concentration of hydrogen peroxide has marginal effect on the degradation of chlorobenzene. The extent of degradation was not increased for both the initial concentrations of chlorobenzene loadings, but there was a reduction in the process time requirement from 50 to 30 min. At lower concentration, hydrogen peroxide increased the cavitational activity (by altering the concentration of $^{\bullet}$OH radical) which can possibly contribute to enhanced rate of chlorobenzene degradation especially at the high energetic conditions inside the cavity. At higher concentrations of hydrogen peroxide, the rate of $^{\bullet}$OH formation is increased; however, due to the presence of large quantum of hydrogen peroxide inside the cavity, the effectiveness of chlorobenzene degradation is decreased due to the fact that cavitational energy is utilized for the dissociation of hydrogen peroxide present inside the cavity suppressing the pyrolysis effect for the abstraction of the Cl$^{\bullet}$ ions from the benzene ring [17]. The possible dissociation of hydrogen peroxide can be represented as follows:

$$H_2O_2 \rightarrow {}^{\bullet}OH + {}^{\bullet}H \qquad (1)$$

Similar results have been reported for the removal of chlorobenzene in the presence of hydrogen peroxide; the degradation rate decreased with an increase in the concentration of hydrogen peroxide from 10 to 25 μM. The pseudo-first-order rate constant for the initial concentration of chlorobenzene as 2.4 μM decreased from 6×10^9 to 1.2×10^9 $M^{-1}s^{-1}$ over the change in the hydrogen peroxide from 10 to 25 μM [18].

TOC measurements confirmed the higher removal of TOC and 89.9 and 80.2% reduction was observed for 100 and 502 ppm concentration, respectively. Similar to Fe (II), TOC analysis confirms that the hydroxyl ions produced in the bulk of the solution are useful for the enhanced mineralization of chlorobenzene.

3.4. Effect of Fe powder

The results for the extent of degradation of chlorobenzene in the presence of 100 mesh size Fe powder have been shown in Fig. 4. The rate of degradation increased significantly with an initial increase in the concentration of Fe powder, especially for the higher loading of pollutant. The maximum degradation obtained was 96.9 and 93.8% for 1,200 mg/l concentration of Fe powder in 30 min for 100 and 502 ppm concentration of chlorobenzene, respectively. Any further increase in the concentration of additive showed only marginal increase in the degradation rate. The presence of the solid particles in reactor provides additional surface for the production of nuclei which results in more cavitational events in the reactor [19]. Thus, there will be a net increase in rate of degradation of chlorobenzene due to higher overall cavitational intensity. Pagano et al. studied the effect of addition zero-valent iron on the degradation of chlorobenzene and reported that 99% degradation of chlorobenzene (initial concentration = 18.3 ppm) is achieved in 10 min for 1,000 ppm concentration of zero-valent iron [19].

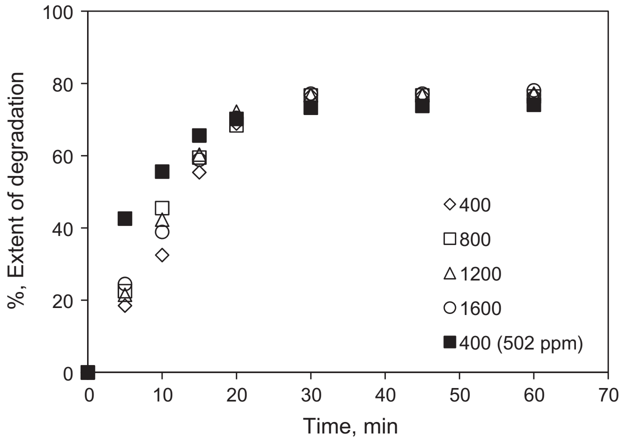


Fig. 3. Effect of H_2O_2 addition on extent degradation of chlorobenzene.

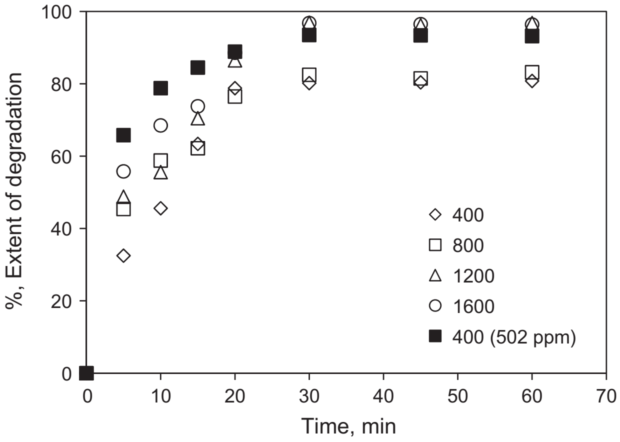


Fig. 4. Effect of Fe mesh powder addition on extent degradation of chlorobenzene.

The TOC measurements also indicated that maximum TOC reduction was obtained for the combination of Fe powder and ultrasound, and 98.8 and 97.9% reduction was obtained for 100 and 502 ppm concentration, respectively. TOC analysis confirms that in addition to the enhanced cavitational activity leading to higher chlorobenzene removal, the enhanced hydroxyl radical produced in the bulk of the solution (from the advanced Fenton-type mechanism) contribute to near complete mineralization of chlorobenzene. The studies have confirmed that the combination of Fe powder and ultrasound is the best hybrid approach resulting in beneficial results for both chlorobenzene removal and mineralization.

3.5. Effect of addition of H_2O_2 combined with Fe (II)/Fe powder

The results for the combination approach of hydrogen peroxide with Fe (II)/Fe powder have been presented in Fig. 5, and it can be seen that the extent of degradation of chlorobenzene is lower for the combination mode as compared to the individual addition indicating that combination does not favor the desired reaction of abstraction of $Cl^{\bullet}$ ion from the ring. The combination of hydrogen peroxide and Fe (II) increases the rate of radical formation in the bulk of solution on multifold basis in short span of interval. The rate of radical formation for combination of hydrogen peroxide with Fenton is more compared with Fe mesh powder [9,10]. The overall mechanism increased the rate of radical formation in the bulk of solution and hence enhanced quantum of hydrogen peroxide is likely to occupy the cavity and thus reduces the rate of abstraction of $Cl^{\bullet}$ ion from the benzene ring. In the bulk solution, combination of hydroxyl radicals leads to the formation of hydroperoxyl radicals ($^{\bullet}OOH$) and subsequently hydrogen peroxide. Thus, there will be a decrease in the rate of degradation of chlorobenzene in bulk and inside the cavity. TOC removal for the combination of Fe (II) + H_2O_2 was 65.1 and 62% and for the combination of Fe powder + H_2O_2 TOC removal was 65.1 and 62% and for the combination of Fe powder + H_2O_2 was 68.4 and 65.4% for 100 and 502 ppm concentration, respectively. This analysis confirms that the combination of Fe (II) and Fe powder with hydrogen peroxide reduced the rate of degradation. The results confirm that the abstraction of chloride ion from chlorobenzene was dominated by pyrolysis mechanism and little amount of the chlorobenzene have been degraded via hydroxyl radicals at the gas-liquid interface due to the lower concentration of hydroxyl ions. Also, the concentration of formed intermediate products was lower for the combination of additives compared with individual addition. The formation of higher amount of hydroperoxyl ($^{\bullet}OOH$) radical reduced degradation of the chlorobenzene and thus reduced the formation of intermediate products. Most of the intermediate products were chlorophenol, phenol or oxidation products of the chlorobenzene (hydroxyl radicals). The reported results for chlorobenzene degradation in presence of Fe powder (1 g/l) and Fe^{2+} (167 mg/l) indicate that the extent of degradation was 99.1 and 98.2%, respectively, and this is higher as compared to the combination approach of Fe^{2+} + H_2O_2 (93.7%) and Fe powder + H_2O_2 (91.5%) [19].

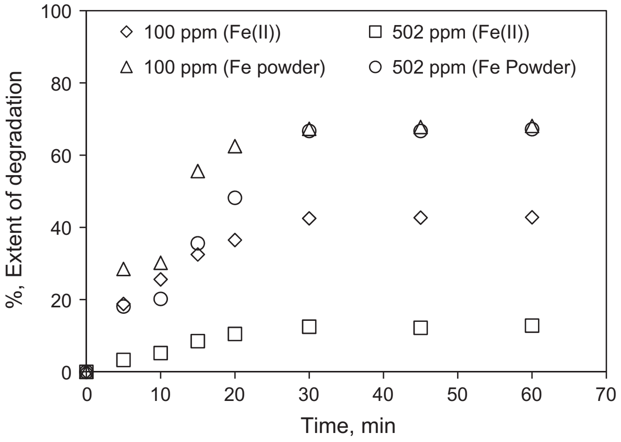


Fig. 5. Effect of combination of H_2O_2 (400 ppm) with Fe (II) (800 ppm) and Fe powder (1,200 ppm) addition on extent degradation of chlorobenzene.

3.6. Effect of sodium bicarbonate

Addition of sodium bicarbonate enhances the rate of degradation by changing the distribution of aqueous and organic phases. Molecules with relatively large Henry's constants will be occupied in the cavitational bubble, while nonvolatile molecules or with lesser Henry's constant remain in the bulk of solution (benzene ring) [20]. Thus, the effect of salt in changing the partition coefficient pushes the chlorobenzene from the bulk of solution toward interfacial region of cavitational enhancing the degradation [21]. Carbonate radicals (CO_3^-) is a strong electron oxidant, and these radicals result from the reaction of hydroxyl radical (produced from cavitation) with carbonate ions. These radicals have no protonation effect for pH range 0–10 and migrate in bulk of solution, like $^{\bullet}OH$ radicals and useful for further degradation of compound [20]. Thus, the presence of radical species in the liquid bulk enhanced the rate of degradation

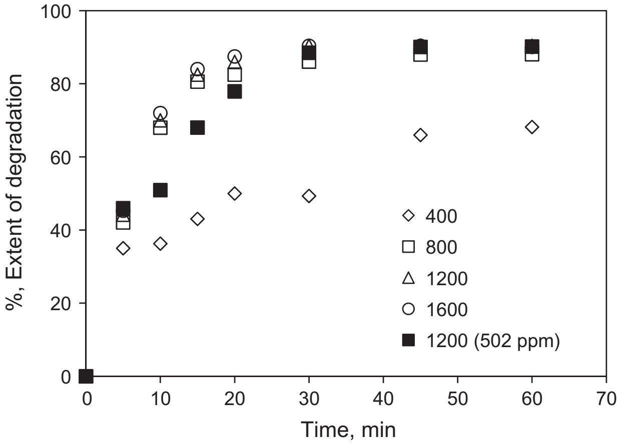


Fig. 6. Effect of sodium bicarbonate addition on extent degradation of chlorobenzene.

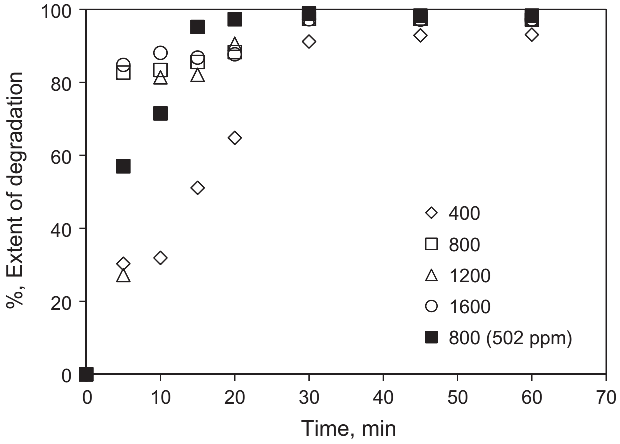


Fig. 7. Effect of t-butanol addition on extent degradation of chlorobenzene.

of compounds present in the bulk. The result of extent of degradation of chlorobenzene is shown in Fig. 6. The maximum degradation was 90.4 and 90.1% in 30 min for 1,200 mg/l concentration of sodium bicarbonate for 100 and 502 ppm concentration of chlorobenzene, respectively. Any further increase in concentration of sodium bicarbonate shows a marginal increase in the rate of degradation. Similar to the earlier results of Fe powder, the maximum removal of $Cl^{\bullet}$ ions take place in the cavity and further oxidation of benzene ring occurs in the bulk solution. TOC results confirm that the pyrolysis and hydroxyl radical attack in bulk are useful for the complete mineralization of chlorobenzene (99.6 and 99.1% TOC was removed for 100 and 502 ppm concentration, respectively). Similar results have been reported for sonochemical degradation of bisphenol-A (loading of 0.022 μmol/l) where it was established that the degradation rate was increased by a factor of 3.2 in the presence of bicarbonate addition (500 mg/l) compared with initial bicarbonate present in the water [20]. Thus, the observed enhancement in the degradation of chlorobenzene in the presence of bicarbonate can be attributed to a change in partition coefficient which is useful for the quick removal of $Cl^{\bullet}$ ions, whereas the production of oxidizing radicals from the reaction of carbonate ions and $^{\bullet}OH$ radicals in the liquid bulk helps in enhanced mineralization.

3.7. *Effect of addition of t-butanol*

The results for the addition of t-butanol have been presented in Fig. 7, and it can be seen that the extent of degradation of chlorobenzene increases with initial increase in the concentration of t-butanol till an optimum loading. Maximum extent of degradation was 97.4 and 98.5% at a loading of t-butanol as 800 mg/l for the 100 and 502 ppm initial concentration of chlorobenzene, respectively. Further increase in concentration of t-butanol showed marginal effect on degradation. The rate of degradation is higher due to the quick defragmentation of t-butanol. The defragmentation occurs due to the pyrolysis/thermal effect produced in sonication and through a combination of hydroxyl radical-induced reaction at the gas/liquid interface. Pyrolysis effect occurs inside the cavitation bubble, which degraded most of $Cl^{\bullet}$ ions. The scavenging effect is produced due to the interaction of defragmented radicals from t-butanol and $^{\bullet}OH$ radicals in bulk of solution [22]. This interaction between the radicals hindered the rate of formation of $^{\bullet}OH$ radicals in the bulk of the solution affecting the further mineralization of chlorobenzene. TOC analysis confirms that the mineralization was drastically reduced in the bulk of the solution (2.6 and 2.8% TOC was removed for 100 and 502 ppm concentration, respectively). The work on sonodegradation of bisphenol in the presence of varying concentration of t-butanol (10–100 μl) indicated that the rate of degradation was increased at lower concentration of t-butanol and decreased at higher concentration. Quantitatively, the rate of degradation decreased by 10-fold basis at t-butanol loading of 100 μl as compared to the 10 μl concentration of t-butanol [23]. The sonolytic degradation of benzene, chlorobenzene, dichlorobenzene, and biphenyl is lower in the presence of t-butanol [24].

3.8. *Effect of stirring for addition of Fe (II)*

The results for effect of Fe (II) in the presence of stirring have been presented in Fig. 8, and it can be

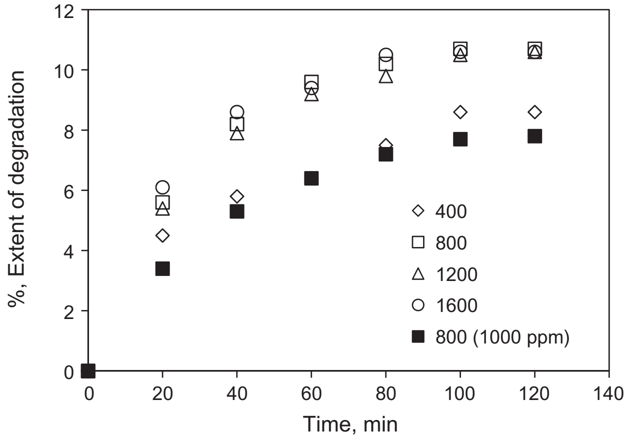


Fig. 8. Effect of stirring for the addition of Fe (II) on extent degradation of chlorobenzene.

seen that the extent of degradation of chlorobenzene is increased with an increase in the concentration of Fe (II) till 800 mg/l, whereas any further increase in concentration shows only marginal increase in the degradation. The maximum degradation of 10.7 and 7.8% was obtained for 100 and 502 ppm initial concentration, respectively, in 120 min of treatment, which is lower as compared with sonolysis and also the total treatment time, is about 4 times than that required in sonication. During stirring, reactions between the Fe (II) ions and chlorobenzene resulted into intermediates products. The product distribution also confirms that the presence of $^{\bullet}$OH radicals or complete abstraction of chloride ions is not observed. TOC analysis also confirms that degradation and mineralization of chlorobenzene is not possible in the presence of Fe (II) (2.6 and 2.8% TOC reduction for 100 and 502 ppm concentration respectively).

3.9. Effect of addition of H_2O_2 in the presence of stirring

The results for addition of hydrogen peroxide in the presence of stirring have been presented in Fig. 9, and it can be seen that the extent of degradation of chlorobenzene increased with an increase in the concentration of hydrogen peroxide up to 800 mg/l and further increase in concentration showed a marginal decrease in the degradation. The maximum degradation of 61.4 and 55.6% was observed in 120 min for 100 and 502 ppm concentration, respectively, which is lower as compared with the sonolytic degradation of 76.7 and 74.3% in 30 min at 120 ppm concentration of hydrogen peroxide. Another advantage of sonolysis process is in terms of lower energy requirement for the degradation, it was reduced from 8.64 x 10^2 to 2.16 x 10^2 kJ. TOC removal was definitely not significant enough for this approach (4.5 and 2.3% TOC reduction for 100 and 502 ppm concentration, respectively).

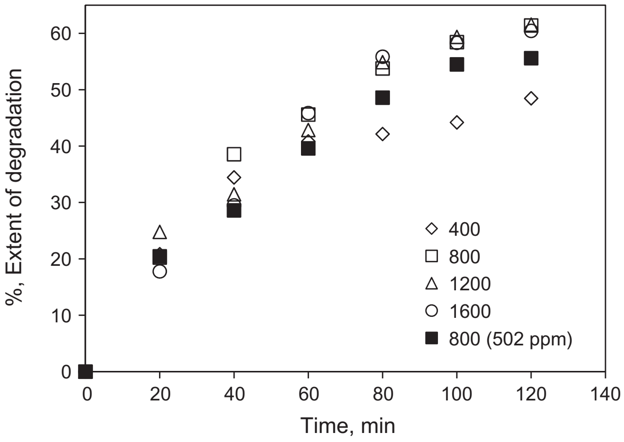


Fig. 9. Effect of stirring for the addition of H_2O_2 on extent of degradation of chlorobenzene.

The degradation of chlorobenzene in the presence of Fe (II) and hydrogen peroxide was observed to be 35.6 and 18.5% for 100 and 502 ppm concentrations, respectively. The rate of $^{\bullet}$OH radical formation increased in the presence of Fe (II) and H_2O_2 [17–20]. Thus, rate of degradation of chlorobenzene decreases in the presence of combination of Fe (II) + H_2O_2 compared with individual addition of hydrogen peroxide possibly attributed to the dissociation of hydrogen peroxide into hydroxyl radicals which are not that reactive as compared to the chemical oxidation action of hydrogen peroxide specifically for chlorobenzene. TOC analysis confirms that TOC removal rate decreased for the combinational effect compared with individual effect of radicals (3.9 and 1.3% TOC reduction for 100 and 502 ppm concentration, respectively).

4. Comparison of degradation rate based on different additives and kinetic data analysis

The effects of different additives on the extent of degradation of chlorobenzene have been given in Table 1. It has been observed that the rate of degradation increases with an increase in the concentration of additive. The overall rate of degradation is decided mainly by the number of cavitational events produced in the reactor. The pyrolysis effect of cavitation is responsible for the removal of $Cl^{\bullet}$ ions from the benzene ring. The rate of degradation was observed to be the maximum in the presence of Fe powder (96.9%, k = 11.9 min^{-1}) followed by sodium bicarbonate (90.4%, k = 12.1 min^{-1}). TOC analysis confirms that $Cl^{\bullet}$ ions

Table 1
Optimized concentrations of radical promoters based on extent of degradation of chlorobenzene

Catalyst	Catalyst concentration, ppm	Process time, min	% extent of degradation		TOC removed, %	
			100 ppm	502 ppm	100 ppm	502 ppm
Based on sonochemical effect						
No catalyst	–	50	77.4	66.4	41.3	46.0
Fe (II)	800	30	75.5	70.4	90.4	82.8
H_2O_2	400	30	76.7	74.3	89.5	80.2
Fe powder	1,200	30	96.9	93.8	98.8	97.9
$NaH(CO_3)_2$	1,200	30	90.4	90.1	99.6	99.1
t-butanol	800	20	99.4	98.5	2.6	2.8
$H_2O_2 + Fe(II)$	400+800	30	42.5	12.5	65.1	62
H_2O_2 + Fe powder	400+1,200	20	67.3	66.7	68.4	65.4
Stirring on stirring effect						
Fe (II)	1,200	120	10.7	7.8	1.9	0.8
H_2O_2	800	100	61.4	55.6	4.5	2.3
Fe (II) + H_2O_2	1,200+800	100	35.6	18.5	3.9	1.3

Table 2
Kinetic parameters

Catalyst	Catalyst concentration, ppm	Kinetic parameters, k x 10^{-2}, min^{-1}	
		100 ppm	502 ppm
Effect of sonochemical			
No catalyst	–	3.3	2.3
Fe (II)	800	5.2	5.1
H_2O_2	400	6.1	5.1
Fe powder	1,200	11.9	8.4
$NaH(CO_3)_2$	120	12.1	8.5
t-butanol	800	11.8	8.6
H_2O_2 + Fe (II)	400 + 800	2.1	0.5
H_2O_2 + Fe powder	400 + 1,200	4.2	3.3
Effect of stirring			
Fe (II)	800	0.1	0.08
H_2O_2	800	0.9	0.7
Fe (II) + H_2O_2	1,200 + 800	0.5	0.1

abstraction took place inside the cavity and $^{\bullet}OH$ radicals produced in bulk of solution are responsible for the mineralization of chlorobenzene. TOC removal rate was highest in the presence of Fe powder (98.8%) and lowest in the presence of t-butanol (2.6%). The $^{\bullet}OH$ radical produced from the cavitation effect, which is further enhanced in the presence of other radical promoters such as Fe (II) and H_2O_2 showed marginal effect on the final extent of degradation though the treatment time was reduced. The hydroxyl radicals generated due to the action of ultrasound had significant controlling effect on the extent of mineralization as some of the intermediate products of chlorobenzene degradation have suitable affinity and reactivity towards the hydroxyl radicals.

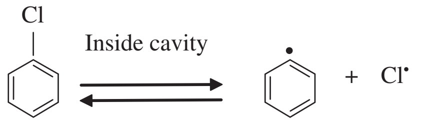
The kinetic rate constant was evaluated assuming the first-order kinetics, and the obtained data have been given in Table 2. It has been observed that the kinetic rate constant for lower concentration of chlorobenzene is higher as compared to that obtained for the higher concentration. The degradation rate depends on the rate of removal of $Cl^{\bullet}$ ion from the benzene ring. Abstraction of $Cl^{\bullet}$ occurred inside the cavity, which depends on the concentration of volatile matter and specific heat capacity ratio. At higher concentration of chlorobenzene, specific heat capacity ratio decreased reducing the collapse temperature, and thus, there is a decrease in the rate of degradation [14,16,25]. Kinetic rate constant for the approach of presence of Fe (II) and H_2O_2 with only stirring is significantly lower as compared to the sonolytic process. During stirring, oxidation of chlorobenzene is observed and enhanced production of aromatics (chlorophenol) was observed. The complete removal of chloride from benzene ring has not been observed during stirring operation.

5. Mechanistic details for sonochemical degradation of chlorobenzene:

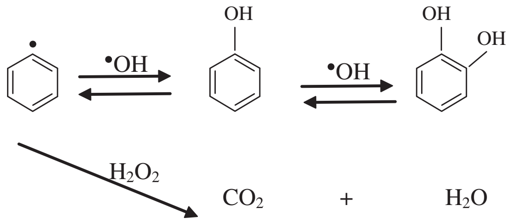
The mechanistic studies based on the analysis of bubble dynamics and the presence of pollutants at the different locations where degradation is expected to occur confirmed that degradation of chlorobenzene occurs prominently inside the collapsing cavity and also the pyrolysis mechanism is dominant in deciding the extent of degradation of chlorobenzene [26,27]. Bubble dynamics studies have confirmed that during the collapse of bubble, extreme temperature conditions are generated which result into thermal decomposition (pyrolysis) of both the pollutant under question and water (generates hydroxyl radical). The relative contribution of these degradations by pyrolysis will depend on the type of the pollutants and its location in the mixture [26–32]. Not only the degradation of parent compound is affected, but also the degradation of intermediates like dichlorophenol, phenol etc. will be affected, and hence, the net mineralization rates will be dependent on the relative contributions of these mechanisms that have also been confirmed based on the experimental studies presented in the current work. The degradation of chlorobenzene (or in general the organic pollutant) will be dependent on the diffusive flux of pollutant molecules across the bubble bulk interface. The diffusion flux of pollutant depends on the partial pressure of chlorobenzene (1,598 Pa at 25℃) at the bubble/bulk interface, which in turn depends on the concentration of pollutant in the interfacial region [26,27].

$$\frac{dN}{dt} = 4\pi R^2 D_p \frac{\partial C}{\partial r}\Big|_{r=R} \tag{2}$$

where D_p is the effective diffusion coefficient for chlorobenzene, N is number of chlorobenzene molecules, R is radius of bubble, C is the concentration of chlorobenzene, and r is radius of bubble at any time t. The mole fraction of chlorobenzene at the collapsing bubble is given as: $x_{pR} = x_p K_{\text{interface-bulk}}$, Where x_p is the overall mole fraction of chlorobenzene, and $K_{\text{interface-bulk}}$ is the interfacial partition coefficient that increases with salt/additive addition which alters the partition coefficient. As chlorobenzene is hydrophobic nature, interfacial region is always saturated with the chlorobenzene for all experimental conditions. The diffusion flux and the entrapment of chlorobenzene remain practically unchanged irrespective of change in the initial concentration of chlorobenzene or the addition of different additives [26–28], which also confirm the obtained trends for degradation rate of chlorobenzene. Additives play an important role in enhancing the number of cavitational events and formation of hydroxyl radicals, especially when radical enhancers are used in the system. These effects are useful for increasing rate of degradation and also mineralization (increased probability of reaction between the hydroxyl and intermediate products). Rate of degradation of chlorobenzene also depends on the collapse conditions of cavity, that is, the number of water and pollutant molecules trapped in cavity and the peak temperature reached in the cavity along with the equilibrium composition of various intermediate products that are formed from dissociation of water, additives if they are present and chlorobenzene molecules trapped in cavity [26–31].



Scheme 1. Removal of •Cl ion from benzene ring.



Scheme 2. Attack of •OH radical promoters on benzene ring in bulk solution.

Considering the fact that the pyrolytic mechanism removes the Cl• from the chlorobenzene ring, benzene will be formed as indicated in Scheme 1 (the bond dissociation energy of C–Cl (400 kJ/mole) is less than C–H (463 kJ/mole) and H–OH (424 kJ/mole) [18]. Hence, most of chlorobenzene will be dissociated by Scheme 1). The •OH radicals produced by sonolytic process or produced in the presence of •OH radical promoters oxidizes the carbon and hydrogen ring of benzene as indicated in Scheme 2. The suggested degradation mechanism is as follows.

The percentage distribution of the intermediate products of chlorobenzene degradation viz. benzene, phenol, and chlorophenol in the presence of optimized concentrations of different additives as depicted in Table 1 has been shown in Fig. 10(a–k). The products were analyzed based on the obtained peaks at different retention time as compared with the standard peaks of samples. The maximum part of chlorobenzene degraded into phenol and part of chlorobenzene is converted into chlorophenol and further mineralized to carbon dioxide and water in the presence of hydroxyl radicals present in the bulk of solution. Pyrolytic mechanism results in enhanced concentration of Cl•, which can disappear by way of any of the following mechanisms (i) reacting with the hydroxyl radical and (ii) reacting with benzene oxidized products such as phenol shown by Scheme 3 [9]. Table 1

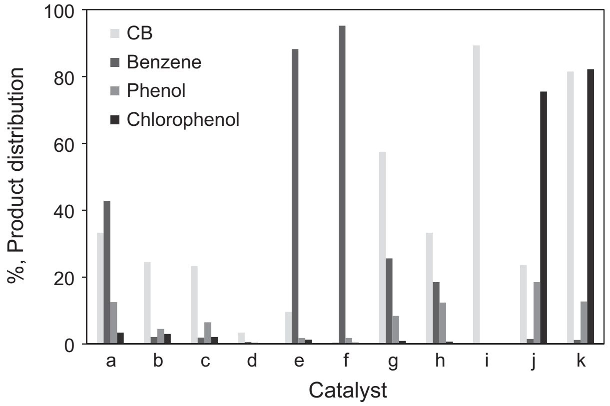
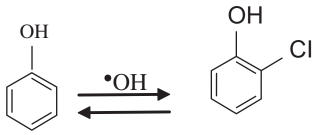


Fig. 10. Product distribution based on 30-min run at optimized concentration of catalyst (a) No catalyst, (b) Fe (II), (c) H_2O_2, (d) Fe powder, (e) $NaH(CO_3)_2$, (f) t-butanol, (g) Fe(II)+H_2O_2, (h) Fe powder + H_2O_2, (i) Fe (II) Stirring, (j) H_2O_2 Stirring, (k): Fe (II) + H_2O_2 Stirring.



Scheme 3. Combination of phenols and $^{\bullet}$Cl ions.

shows that the complete degradation and mineralization of chlorobenzene is increased with addition of additives compared with the absence of additives. Use of additives increases the cavitational events, which is useful for the removal of Cl$^{\bullet}$ and complete mineralization ($^{\bullet}$OH radicals present in bulk). It has been observed that rate of mineralization increases with the addition of Fe powder, sodium bicarbonate, and H_2O_2, and it is the maximum in the presence of Fe powder (attributed to simultaneous increase in the number of cavitational events due to enhanced deformity in the medium and generation of hydroxyl radicals due to the advanced Fenton's mechanism [33,34]). Combination of H_2O_2 with Fe (II) and Fe powder results in lower removal of the pollutant as compared with individual addition. Addition of t-butanol confirms that removal of Cl$^{\bullet}$ by pyrolysis is the dominant mechanism, and scavenging action of the t-butanol (interaction of decomposed of t-butanol and $^{\bullet}$OH radical) has no effect on the removal of chlorobenzene, but it strongly hinders the rate of mineralization of compounds present in the bulk of solution. The results confirm that addition of heterogeneous catalyst (Fe powder) gives the better degradation and mineralization results compared with the addition of homogeneous catalyst (Fe(II), H_2O_2, sodium bicarbonate, and t-butanol), and it depends upon the number of cavitational events occurring in the reactor. In the presence of stirring, degradation, and mineralization rate are significantly lower as compared to sonolysis process. Stavarache et al. reported that the hydroxyl radical present in the bulk of solution or outside the cavity reacts with benzene ring and formed different phenol derivatives by similar reactions as shown by Scheme 2, and some polyphenol reacts with the part of $^{\bullet}$Cl to form chloro derivates of phenol as per Scheme 3 [9,10].

The reported work on sonolysis of chlorobenzene in the presence of Fenton, and Pd (II) confirmed that chlorobenzene degraded into phenol and benzene. The rate of phenol formation from benzene depends on the cavitational activity produced in the presence of Fenton [9]. The work on sonolysis of chlorobenzene in the presence of Pd salts such as $PdSO_4$, $PdCl_2$, and Pd^0 confirmed that Cl$^{\bullet}$ removal from benzene ring is only due to the pyrolysis effect of cavitation [10]. Based on the product distribution obtained in this study, it is also confirmed that the removal of Cl$^{\bullet}$ from benzene ring is only due to the pyrolytic action, and it strongly depends on the number of cavitational events produced in the reactor. Thus, the extent of chlorobenzene removal enhanced in the presence of solid particles such as Fe powder, and also salts that alter the distribution of pollutants favorably toward the site of cavity collapse. The increase in the cavitational activity in the presence of solid particles, dissolved gases, and inert material has also been confirmed by Pang et al. [21].

6. Conclusions

This study confirms that the rate of degradation of the chlorobenzene is driven by the pyrolysis mechanism, which removes the Cl$^{\bullet}$ from the benzene ring and the degradation strongly depends on the number of cavitational events occurring in the reactor. The rate of degradation increased with a decrease in the initial concentration of chlorobenzene. The intensification was significantly benefitted by the addition of Fe powder, sodium bicarbonate and t-butanol. TOC analysis confirms that production of $^{\bullet}$OH ions from the cavitation in bulk of solution plays significant role in mineralization of chlorobenzene. The rate of degradation and mineralization was observed to be maximum in the presence of Fe powder. The combination of H_2O_2 with Fe (II) showed negative effect on the rate of degradation and also use of stirring in combination with Fe (II)/H_2O_2 resulted in lower rates of degradation confirming the requirement of cavitating conditions.

The established three-step degradation mechanism, based on the identification of the intermediate products, consists of removal of •Cl from the chlorobenzene, attack of •OH radical on benzene ring producing phenol and polyphenols and the combination of phenols and •Cl ions producing the chlorophenol.

Overall, the study has clearly established the beneficial application of ultrasonic irradiations for the degradation of chlorobenzene and has highlighted the efficient approaches based on the proper selection of additives to enhance the removal of the parent pollutant as well as the intermediate products that can give efficient mineralization.

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