Kinetics, Thermodynamic and Mechanism of Ultrasonic Degradation of Benzene in Aqueous Solution

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Received on:20/2/2013 & Accepted on:15/8/2013

ABSTRACT

Ultrasonic technology, as an innovative technology,was used for degradation of benzene in an aqueous solution under ultrasound frequency of 20 kHz at different temperatures with initial concentration of 100 and 200 mg/L. Kinetic and thermodynamic of benzene degradation in aqueous solution were investigated. While the mechanism of benzene sonolysis was discussed. The degradation rate of benzene increased with increasing electric power, sonication time and by decreasing liquid volume, temperature and initial concentration of benzene. The beneficial effect of which power electrical or ultrasound on removal rates is believed to be due to increased cavitational activity occurring at higher levels of power. As power increases, the number of collapsing (effective) cavities also increases, which is leading to enhanced degradation rates. Thermodynamic parameters indicated that benzene degradation was spontaneous and exothermic in nature. The obtained data was fitted through the pseudo-first order model.

Keywords: Ultrasonic; Benzene; Degradation; Water Treatment; Kinetic; Thermodynamic.

خصائص الثرموداينمك والحركية باستخدام الموجات فوق الصوتية من تحليل محاليل البنزين المؤمن

الخلاصة

تعتبر تكنولوجيا الموجات فوق الصوتية أحد الطرق المعتمده للأستخدام في تحلل محاليل البنزين المائية ، فقد تم أستخدام هذه التكنولوجيا لهذه المحاليل تحت تردد مقداره 20 كيلوهرتز لدرجات حرارية مختلفة وللتراكيز100و200 ملغم / لتر. كما تم دراسة حركية وثرموديناميكية تحلل المحاليل المائية للبنزين وتم مناقشة ميكانيكية التحلل الصوتي للبنزين و تشير النتائج الى زيادة معدل سرعة تحلل البنزين مع زيادة القدرة الكهربائية وزمن تعرض المحاليل للموجات فوق الصوتية ، كما أن هذا المعدل يزداد مع الأنخفاض بحجم السائل ودرجة الحرارة والتركيز الاولي للبنزين .أن زيادة قدرة الموجات فوق الصوتية سيؤدي الى زيادة عدد الفجوات الفعالة والتي تقود

https://doi.org/10.30684/etj.32.1A.4
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الى زيادة معدل سرعة التحلل . كما تشير النتائج الثرموديناميكية الى أن تحلل البنزين يكون بطبيعته تلقائياً وباعثاً للحرارة ، في حين تؤشر نتائج الحركية لهذا التحلل الى أنه تفاعل من الرتبة الاولى الكاذبة.

INTRODUCTION

Benzene is one of the major volatile organic compounds that are widely used in many industries [1]. However, it has some health concerns such as cancer, irritation of mucosal membranes, hematological changes, impairment of the centralnervous system, respiratoryproblems and disruption of liver and kidney[2]. Therefore, the removal of this pollutant has a highly potential research in environmental treatments.

Techniques of organic pollutants removal from aqueous systems have been developed. These techniques includes microbial degradation[3,4], chemical oxidation[5], photo catalytic degradation [6], ultrasonic degradation [7], enzymatic polymerization [8], membrane separation [9], solvent extraction [10] and adsorption [11]. Ultrasound is a source of high energy vibrations that produces mechanical waves with frequencies above the human hearing upper limit .The considerable interest has been shown in the application of an innovative treatment for hazardous chemical destruction, including the degradation of volatile organic compounds based on the use of ultrasound. Although ultrasonic irradiation is employed in a variety of industrial processes (*i.e.* welding of metals, homogenization of emulsions, dispersion of paints, cleaning and degreasing, synthesis, catalysis, improved extraction, crystallization, modification of enzyme and material processing. [12]. The chemical effects of ultrasound derived from acoustic cavitation (*i.e.* the formation, growth and implosive collapse of cavitation bubbles in liquid) cannot result from a direct interaction of sound with molecular species [13, 14].

Extreme temperatures of the order of 5000 K has been experimentally obtained and pressures of the order of 1000 atm are developed locally within the bubbles during their collapse with these bubbles serving as hot spot micro reactors in an otherwise cold liquid. It is generally believed that there are three potential sites for chemical reactions in ultrasonically irradiated aqueous solutions, to yield radicals, such as hydroxyl and atomic hydrogen[12].These sites are the bubble itself where pyrolysis of volatile species takes place in the gas phase, while water decomposes thermally to form hydrogen and hydroxyl radicals, second the interface between the bubble and the surrounding liquid where the temperature is lower than that in the bubble but is still high enough to cause thermal decomposition. Moreover, reactive radicals formed through water decomposition in the bubble accumulate at high concentrations in this site and may mediate free radical decomposition reactions, and finally the solution bulk, where reactions of hydrogen or hydroxyl radicals, which escape from the interface, may occur. Organic compounds may be destroyed either at the first two sites upon combined effects of pyrolytic decomposition and hydroxylation, or in the solution bulk via oxidative degradation by hydroxyl radicals and hydrogen peroxide.

In previous studies, the beneficial effect of ultrasonic irradiation on the removal of several target compounds from model aqueous solutions has been demonstrated. Such compounds include phenol, chloro-phenols, nitro-phenols, polychlorinated

biphenyls, pesticides, polycyclic aromatic hydrocarbons and surfactants [15-20]. Other studies report the use of ultrasound in combination with thermo chemical and advanced oxidation processes, such as wet air oxidation [21], ozonation [22], electrochemical oxidation [23] and UV irradiation [24]. Typical treatment conditions include relatively dilute aqueous solutions of initial concentrations, low to medium ultrasound frequencies and irradiation times .

The scope of this work is to study the effect of ultrasound frequencyon the removal of benzene compound typically found in wastewaters produced by chemical processes. In particular, the effect of various operating conditions (electric power, liquid volume, liquid bulk temperature, initial substrate concentration) on degradation rates have been investigated.

EXPERIMENTAL

Degradation experiments

Benzene supplied by sigma-Aldrich (99.5%) was used for degradation.Aqueous benzene solutions of 100 ppm and 200 ppm were prepared .Ultrasonic irradiation of the benzene solutions were carried out continuously with a sonicators (U.S.A) probe-type sonicator capable of operating either continuously or in a pulse mode at a fixed frequency of 20 kHz and maximum electric power output of 100WFigure (1).A sample of 100mlbenzene solution was placed in 250ml conical flask and placed in water bath at temperatures of (283, 293, 313 and 333K)under a sonication for 150 min.Four milliliters samples were withdrawnevery 10 min for kinetic study. The amount of residual concentration of benzene in the solution was measured considering the wavelength of (204 nm) using a UV-Vis spectrophotometer. The value of the absorbance obtained has been used to determine the equilibrium concentration of calibration curve according to Beer-Lambert law. The degradation percentage(%R) of benzene was calculated as follows:

$$\mathbf{R = (C_o - Ce) / C_o \times 100\%\%} \qquad \mathbf{\ldots(1)}$$

Where C_o and Ce is the initial and remained concentration of *Benzene*

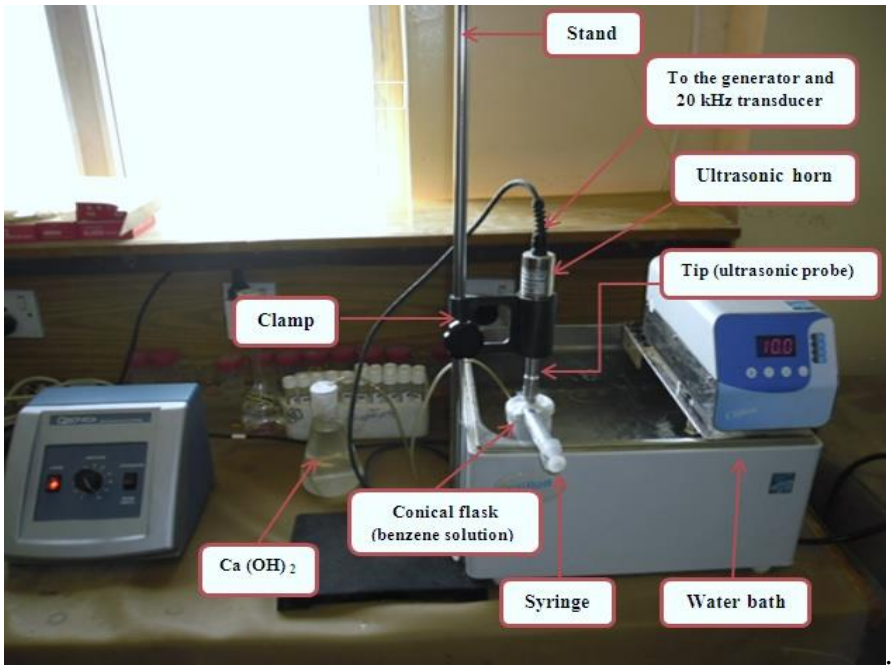


Figure (1) Experimental setup of ultrasonic probe.

Measurements of pH

The pH value of benzene solutions was determined using pH meter before and after degradation.

Qualitative tests

Aromatics and aliphatics were identified. Ignition of aromatics produces a smoky soot while the aliphatic give unsmoky blue flame.

Nitration was used to distinguish between aromatic and aliphatic compounds according to the following reaction

$$\text{Ar-H} + HNO_3 + H_2SO_4 \longrightarrow \text{Ar-}NO_2 + H_2O \downarrow$$

1ml1mlYellow coloured compounds

The yellow coloured products indicate the aromatictype while the disappearance of thecolour reflects the aliphatic ones.

Detectionof carbon dioxide produced from benzene after oxidation via clear water-lime gaveturbid in thepresence of CO_2according to the equation.

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$$

RESULTS AND DISCUSSIONS

Effect of initial concentration

Experiments were conducted at various times to see if there was any synergistic effect on the degradation of benzene. Increasing the concentration from 100ppm to 200ppm showed a decrease in degradation of benzene. Experiments showed that with sonochemical reactor, about 100% and 97.94% degradation of benzene occurred after 150 min at 283K.But only 89.48% and 68.39% degradation of benzene was observed within 10 min, as shown in Table (1).Therefore, results obtained from the sonochemical degradation of benzeneat various concentrations indicated that removal rates were found to be decreased with increasing of benzeneconcentration.

Table (1) The degradationof *Benzene* byultrasonic percentage with concentrationsof100ppm,200ppm at different temperature.

Time	*% of degradation at temperature (K)*							
	283K		293K		313K		333K	
	100ppm	200 ppm	100ppm	200 ppm	100ppm	200 ppm	100ppm	200 ppm
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10	89.48	68.39	76.26	63.77	70.75	59.32	61.01	54.78
20	90.50	76.35	78.47	70.33	73.89	64.49	65.75	57.07
30	91.43	82.45	79.82	71.78	77.79	67.67	69.06	59.57
40	93.05	85.29	82.62	77.62	80.67	73.43	72.62	61.69
50	93.47	88.30	85.33	80.55	82.11	76.27	75.75	67.54
60	93.67	89.70	87.36	85.33	84.48	82.33	77.11	74.02
70	93.95	94.74	89.82	87.67	87.36	84.87	79.74	78.00
80	94.49	96.10	93.16	90.55	90.08	86.86	82.96	81.22
90	95.05	96.63	94.33	93.56	92.28	88.81	86.94	87.50
100	95.54	96.77	95.37	95.08	93.65	91.78	89.82	89.61
110	96.42	96.98	96.23	96.60	94.49	93.77	92.28	91.44
120	97.47	97.30	97.35	96.94	95.28	95.59	93.86	92.79
130	98.84	97.49	98.09	97.24	96.28	96.59	94.65	94.15
140	99.86	97.78	99.79	97.51	97.19	97.07	95.38	95.30
150	100.00	97.94	100.00	97.79	98.02	97.31	96.63	96.02

Effect of sonication time

In order to observe the effect of sonication time on the benzene degradation rate during treatment, sonodegradation (sonication time) for aqueous benzene concentrations was performed in 150 min. As clearly seen, by increasing of the sonication time, considerable levels of benzenedegradation can be expected after150 min. It was observed that removal percentage and the degradation efficiency of acoustic frequency was increased when sonication time increased, as shown in table (1). This effect is due to the increase in the exposure time between

the benzene solution and the acoustic cavitation process as the time of sonication is increased[25, 26].

Effect of temperature and pH

Increasing the temperature causing a decrease in degradation ratios of benzene Table (1). The reason is possibly coming from the decrease of the surface tension and viscosity of the solution, so that the generation of bubbles become easier. However, the increase in solution temperature results in a dramatic increase of the vapor pressure of the liquid, which gives a higher vapor content of the cavitating bubble. In general, increased temperatures are likely to facilitate bubble formation due to an increase of the equilibrium vapor pressure. However, the sonochemical effect of such bubbles may be reduced. During the bubble growth, complete collapse may not occur and the bubble may oscillate in the appliedfield if some gas or vapor has diffused into the bubble [27, 28, 29, 30].

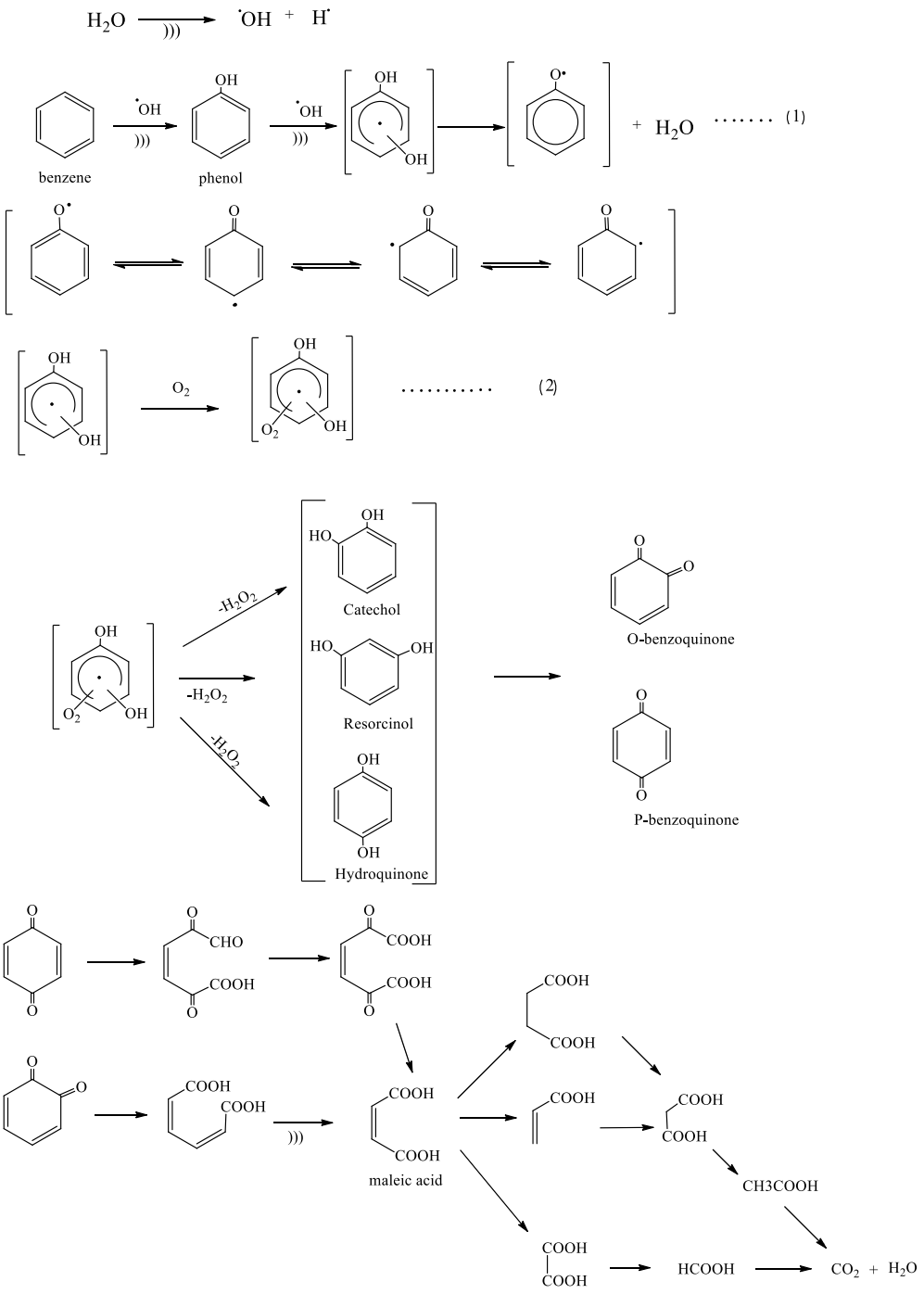
Experiments showed that pH valuehasbeen affected through degradation of benzene. The pH values during the sonodegradation are shown in Table (2). These values indicated that a surfactant will accumulate on a surface independent of whether it is protonated or deprotonated, the effect of pH value on degradation[23]. Also, this conclusion was confirmed by other researchers[31]who predicted that the pH value was a key parameter affected by the sonodegradation of surfactant.

Table (2) The effect of temperature on pH values for degradation of *Benzene* by sonication .

Time (min)	Temp.(K)	pH	
		100 ppm	200 ppm
0	Standard	6.33	6.21
150	283	6.90	5.19
150	293	6.84	5.34
150	313	6.72	5.50
150	333	5.16	5.67

Mechanism of benzene sonolysis

The sonolytic benzene was involved in the degradation pathways and the primary degradation products of phenol. The reaction of phenol with OH radicals leads to the formation of dihydroxyl cyclohexadienyl radicals as shown in equation (1). (sketch 1).In the presence of oxygen, subsequent reaction of the dihydroxyl cyclohexadienyl radicals leads to the formation of peroxyl radicals by the addition of molecular oxygen as indicated by equation (2)(sketch 1). Peroxyl radicals are known to form hydroquinone and catechol after eliminating superoxide radicals and rearranging the aromatic system [32]. These compounds further degraded into biodegradable products, such as carboxylic acids, which is finally complete mineralized into CO_2 and H_2O [33].



Sketch (1) Mechanism of benzene

Pyrolysis of benzene inside the cavities formed in the ultrasonic field has also given a minor contribution, because acetylene, which is a product of sonochemical destruction of volatile aromatic compounds, was detected in a low yield [34].

Thermodynamic parameters

The thermodynamic parameters ΔG^0, ΔS^0, and $\Delta H^0$for thedegradation processes are determined by using following equations[35].

$$\Delta G^0 = -RT \ln K \quad \text{... (3)}$$

Where K is the thermodynamic equilibrium constant. The effect of temperature on thermodynamic constant is determined by:

$$d \ln K/dt = \Delta H^0/RT^2 \quad \text{… (4)}$$

$$\text{Log } K = \Delta S^0 / 2.303\ R - \Delta H^0/2.303\ RT \quad \text{... (5)}$$

Gibbs free energy ΔG^0 is given by:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad \text{… (6)}$$

Where ΔG^0 is the free energy change (kJ/mol); R is the universal constant (8.314 J/mol K) and T the absolute temperature (K);ΔH^0 change in enthalpy;$\Delta S^0$is thechange in entropy.

The ΔH^0 and ΔS^0 values were calculated from slope and intercept of the linear plot, of log K vs. 1/T as shown in Figure (2).

The corresponding values of thermodynamic parameters are presented in Table (3). The negative values of ΔG^0 indicate that the benzene degradation process is spontaneous and feasible, while the negative value of ΔH^0 shown an exothermic degradation process in nature. The positive ΔS^0 indicatedthe increase in randomnessduring degradation of benzene.

Table (3) Thermodynamic functions of the degradation process using ultrasonic at the concentration of 200 ppm.

T(K)	K	ΔH^0 kJ.mol^{-1}	ΔS^0 J.mol^{-1}.k^{-1}	ΔG^0 kJ.mol^{-1}
283K	47.591	-8.006	3.827	-9.089
293K	44.259		4.184	-9.232
313K	36.230		4.268	-9.342
333K	28.656		3.853	-9.289

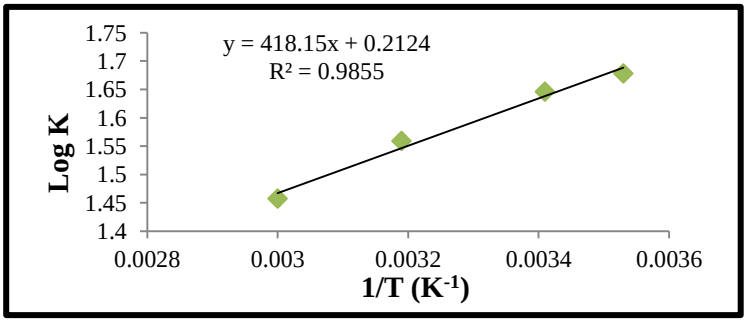


Figure (2) The plot of Log K vs. the reciprocal of Temperature by ultrasonic.

Degradation kinetics

Degradation kinetic models can be useful to determine the mechanism of degradationand the efficiency of the removal of pollutants. In this study, the degradationdata of benzene by ultrasonic was fitted through kinetic model including ***pseudo-first order kinetic***[36].

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad \ldots (7)$$

Whereq_e (mg/g)is the amount of benzene at equilibrium timewhile q_t (mg/g) is the amount of benzene at any time (t),k, min^{-1} is the pseudo-first order rate constant.k and q_e was determined from the slope and intersection of the linear plot of ln (q_e-q_t) against t, respectively see Figures (3 and 4).

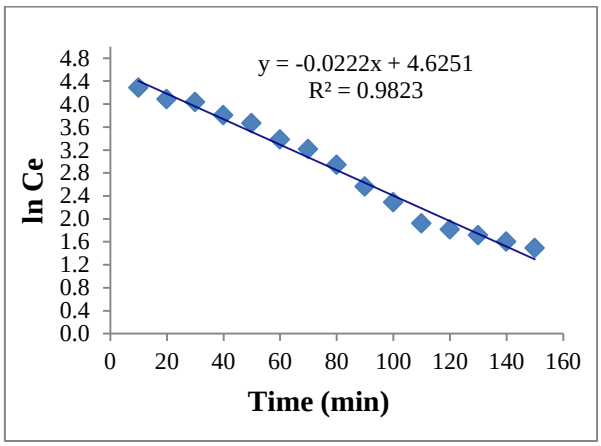


Figure (3) Linear relationship between Ln Ce vs. time for *Benzene* solutions at temperature 293K and Con. (200mg/L) using ultrasonic.

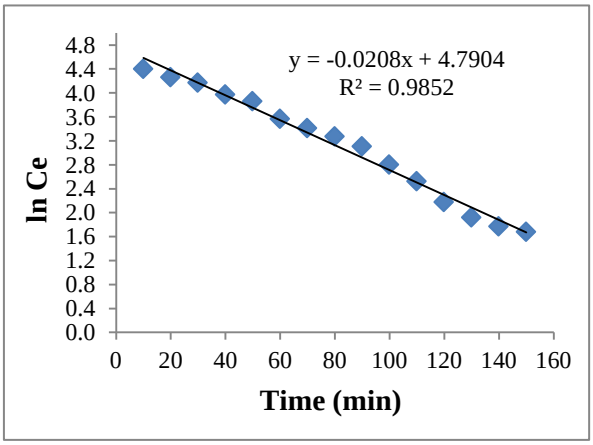


Figure (4)Linear relationship between LnCe vs. time for *Benzene* solutions at temperature 313K and Con. (200mg/L) using ultrasonic.

CONCLUSIONS

Results obtained from this research demonstrate that sonochemical reactor at a frequency of 20 kHz and a power of 100 W is capable to some degree of benzene degradation in aqueous synthetic solutions. The potential of sonochemical reactors for benzene degradation are evaluated with emphasis on the effect of sonication time and initial concentration. Experiments showed that sonication time is one of the most important parameters for benzene degradation.

Sonochemical reactors alone may not be useful for reducing completely complex wastewaters of high surfactant load. Hence, effectiveness be improve coupling acoustical reactors with other treatment processes including ozone, UV, chlorination and H_2O_2. Alternatively, acoustical processor reactor could be used as a pretreatment stage in a sequential chemical and biological treatment process.

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