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A study on the enhancement of sonochemical degradation of eosin B using other advanced oxidation processes

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Effects of process parameters during the sonochemical degradation of benzene and toluene in water

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Effects of process parameters during the sonochemical degradation

of benzene and toluene in water

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Abstract

This work describes the sonochemical (chemical effects of ultrasound) degradation of aqueous solution of benzene and toluene using ultrasonic probe (20 kHz frequency). The process variables studied include initial concentrations, temperature, and type of saturated gas. The effect of addition of H_2O_2 and chloride ions was also examined. The results were explained based on the hot spot theory. The reaction rate showed a reverse proportionality to the initial concentration, which may be attributed to the decrease in specific heat ratio with increase in initial concentration, thereby causing the decrease in temperature inside the cavitation bubbles and hence reduction in the reaction rate. However, H_2O_2 concentration and the type of the dissolved gas did not seem to affect the reaction rates.

Key words: Sonication; Cavitation; Chemical Processes; Reaction Engineering; Pollution; Remediation

1. Introduction

The rapid industrialization in the present society is leading to severe air, water and soil pollution. The disposal of huge amount of wastes in the aquatic streams has especially caused massive water degradation. These adverse effects are substantially affecting human health. The presence of even trace amount of dangerous chemicals like volatile organic compounds (VOCs) is sufficient to render water unusable for reasons of long term associated health risks [1, 2]. In fact, the Environmental Protection Agency (EPA) in the USA has listed more than 100 toxic pollutants present in water [3, 4]. Although clean and safe drinking water is indispensable for the sustained and healthy progress of the society, yet, the present set up precludes the possibility of avoidance of the generation of these wastes altogether.

Numerous water treatment technologies have been developed to eliminate toxic chemicals from water. An ideal waste water treatment technique should not only mineralize all the toxic species present in the water stream without leaving any hazardous residues, but also be cost effective. Since sonication is a chemical-free technology, there has been a growing interest in the sonochemical destruction of organic contaminants in water, especially in recent times. Several studies have been reported in the literature in this regard [5-7].

Mechanism of sono-chemical treatment is fairly well-agreed upon among researchers. The process of cavitation has been identified to be the primary mechanism for ultrasonic degradation. In fact, cavitation is the outcome of the expansion and contraction of

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cavitation nuclei due to the presence of compression and rarefaction cycles in the ultrasonic wave. Subsequent effects include bubble formation, rapid growth and finally implosive collapse. The implosion of cavities causes an unusual reaction environment in the vicinity of the bubbles [8, 9], resulting in intense heat and local hot spots. Thus, the sound energy is converted into thermal energy, which is one of the major causes behind much of the observable sonic degradations. Based on the pioneering study by Suslick et al. [10], the temperature inside the cavity is expected to reach as high as 5,200 K, the interfacial region (i.e., between the solution and the collapsing bubble) being maintained at about 1,900 K or so. In essence, sonochemical effect does take place either due to the pyrolytic decomposition at the gas-liquid interface or by the reduction and oxidation due to the generation of H$^{\bullet}$ and OH$^{\bullet}$ radicals [11].

The purpose of this work was to examine the effect of process variables such as temperature, initial concentration, types of dissolved gas and addition of H_2O_2 on the sonochemical reaction. The chemical compounds studied were benzene and toluene.

2. Experimental Section

2.1 Materials

Reagent-grade benzene (from Aldrich), toluene (from Merck) and H_2O_2 (from Merck) were used as received. Aqueous solutions were prepared by dissolving the compounds in deionized water.

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2.2 Analytical Methods

Quantitative analysis of benzene and toluene were determined with HP 6890 (Hewlett-Packard Inc.) purge and trap Gas Chromatography (GC), equipped with an auto sampler, flame ionization detector and a column (HP-624, 30 m x 0.53 mm x 3 μm). The analysis was conducted under the following conditions: injector temperature and detector temperature were both kept at 250°C, whereas the oven temperature was held steady at 110 ^{o}C. Samples (5.0 ml each) were drawn at various time intervals and transferred to GC sampling vial for analysis.

2.3 Apparatus

Sonication was done using an ultrasonic source (VC-750, Sonics and Materials), with the probe tip measuring 19 mm (in diameter) and the ultrasonic source (of frequency 20 kHz) employed at 50% amplitude. A water jacketed glass vessel (with Teflon cover) was used as reaction vessel. The volume of the solution taken for study was 200 ml, with almost practically no head-space (Fig. 1). The temperature was monitored periodically with the help of a thermocouple immersed in the reacting medium.

3. Results and Discussion

3.1 Influence of initial concentration

Air saturated aqueous solution of benzene and toluene were sonicated at four different initial concentrations (viz. 50, 100, 150 and 200 ppm, by volume). In all cases, the concentration was found to decrease exponentially with time, indicating first order or pseudo first order kinetics. In all cases, the experimental run was performed for 150 minutes. The degradation curve for benzene is shown in Fig. 2. Based on the results

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obtained, the first order reaction rate seems to depend upon the initial concentration. Accordingly, a decrease in rate constant (k) was observed with increase in the initial concentration. A similar trend was also observed for toluene degradation. This observation is very much similar to the reports by other investigators, as well. Jiang et al. [12] found that the rate constants of chlorobenzene and 1,4-dichlorobenzene decrease with the increase in initial concentration. They found that the reaction rate constant (k) decreased from k = 0.035 min^{-1} (for initial chlorobenzene concentration of 40 μM) to k = 0.020 min^{-1} (for initial chlorobenzene concentration of 500 μM).

The reaction condition showed distinct changes with change in concentration of the organic compound. De Visscher et al. [9] derived the relationship between specific heat ratio (γ) and initial concentration. For relatively small mole fractions of volatile compounds in the cavitation bubble, they found that:

$$\gamma = \gamma_0 - KC_i \tag{1}$$

where γ is the specific heat ratio for pure gas-water mixture and K is a proportionality constant. Since the specific heat ratio of gas-water mixture is larger than that of the volatile compounds, K must be positive. Thus, specific heat ratio is expected to decrease with the increase in initial concentration. Furthermore, according to hot spot theory, the degradation rate is function of the temperature and pressure inside the bubble. It is given by Noltingk and Neppiras [13], as follows:

The maximum temperature, T_{max}, obtained is:

$$T_{\max} = T_0[(\gamma - 1)\frac{p_a}{p_0}] \qquad (2)$$

and, maximum pressure, p_{max}, obtained is:

$$p_{\max} = p_0[(\gamma - 1)\frac{p_a}{p_v}] \qquad (3)$$

where, p_a is the acoustic pressure, p_0 is ambient pressure, p_v is the pressure in the bubble at its maximum size and T_o is the ambient temperature.

The decrease in γ will cause the decrease in temperature inside the bubble according to equation 2 and hence reaction rate is expected to be lower. Fig. 3 compares the degradation rates for benzene and toluene for 50 ppmv initial concentration. Both being volatile and of similar nature, degradation follows the same pattern, as indicated by the plot (Fig.3).

3.2 Influence of dissolved gas

In addition to the vapors of volatile compound, the cavitation bubbles contain other gases, which are likely to have a significant effect on the cavitational collapse. To determine the effect of dissolved gas, the experiments were also carried out in argon saturated solution. Both the gases (Air and Argon) were bubbled for 1 hour before sonication (with intermittent shaking, to achieve proper mixing). No gas was added during the sonication, because of volatile nature of organics themselves. The reaction

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was observed to be almost independent of the type of dissolved gas. In an argon saturated solution, k_1 was estimated to be 0.0148 min^{-1} for benzene and 0.0125 min^{-1} for toluene (at 50 ppmv).

The average specific heat ratio γ of the gas is an important parameter for the degradation of organic compounds. In general, monoatomic gases like helium, argon, krypton etc. are known to have the highest specific heat ratio $(\gamma = 1.67)$ [14]. The final collapse temperature for a monoatomic gas could be as much as twice the collapse temperature for a triatomic gas. In fact, such wide variation in temperature makes the specific heat of the gas a critical parameter. Besides, the sensitivity of the gas to sonochemical degradation is also dependent on other factors such as thermal conductivity and gas solubility.

The hot spot theory assumes adiabatic collapse of the bubbles. However, departure from adiabatic collapse is likely to take place due to the heat conduction from the hot bubble contents to the bulk liquid. The gas with low thermal conductivity is likely to reduce the heat dissipation from cavitation site, thereby favoring high collapse temperature. A highly soluble gas is expected to diffuse more easily into the bubbles and cushion the implosion. Studies carried out herewith suggest that the reaction rate is independent of the gas dissolved. This anomalous behavior might be due to the higher solubility of argon (5.60 ml/100 ml H_2O) compared to the solubility of air (2.89 ml/100 ml H_2O) in water.

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3.3 Influence of hydrogen peroxide

As seen in the fig. 4, the addition of hydrogen peroxide showed slight increase in the degradation rates for toluene, although it did not seem to alter the rate constant for benzene (Table 1). De Visscher and Langenhove [15] (1998) observed similar results for trichloroethylene (TCE) degradation, where they observed an increase in TCE degradation with the increase in H_2O_2 concentration. Teo et al. [16] also noted the increase in p-chlorophenol degradation with the addition of H_2O_2.

This observation may be explained by the fact that benzene, toluene and TCE are highly volatile and hence have a strong tendency to diffuse into the gaseous bubbles. Thus, they are mostly degraded either in the interior of the bubbles or in the interfacial sheath, as supported by findings of Mahamuni and Adewuyi [17]. Therefore, the degradation does not seem to necessarily require $OH^\bullet$ radicals, generated by the decomposition of hydrogen peroxide. On the other hand, since chlorophenol has a lower vapor pressure, it tends to remain in water and undergo oxidative degradation. Furthermore, the increase in hydrogen peroxide concentration would increase the concentration of hydroxyl radicals as well, which can attack the aromatic structures, thereby increasing the rates of reaction.

3.4 Influence of temperature

Generally for a chemical reaction following Arrhenius rate law, reaction rate increases with increase in temperature. However, sonochemical reaction rate depends on many factors, which causes irregularity in reaction rates. The material properties (namely,

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viscosity, gas solubility, vapor pressure and surface tension) would also be affected by the temperature. In literature also, there is hardly any report claiming consistency in effects, caused by the impact of temperature on the decomposition of organic compounds. Ku et al. [18] observed that decomposition was slightly lower at high temperatures. Similarly, Ondruschka and Hoffmann [19] also indicated the increase in sonochemical degradation of chlorobenzene with increase in temperature. On the other hand, however, Jiang et al. [20] noted that p-chlorophenol degradation showed that above 40°C the degradation rate and temperature were inversely proportional whereas below 40 °C the degradation rate increases with temperature. The present study clearly indicated an increase in the degradation rate with increase in temperature. Fig. 5 and 6 present the decomposition of benzene and toluene respectively in the temperature range 10-40 °C. The k_1 value is compared in Table 2.

The increase in temperature is known to increase the vapor pressure of the solution. Consequently, the cavitation bubbles formed would be filled with water instantaneously, leading to cushioning in the adiabatic collapse of the bubbles, and subsequent reduction in the intensity of collapse (and hence reduction in the extremes of pressure and temperature generated) [21]. This would cause the decrease in degradation rates. However, according to Arrhenius law, the rate should increase with the increase in temperature. Also, we know, the increased temperature is likely to result in the reduction of gas solubility, which can have positive effect on degradation rate. In this context, the experiments were chosen to be conducted at low concentration (50 ppmv) because at higher concentrations, cavitation bubbles would be filled with large number

of gas molecules. This state of increase in size and number of bubbles, coupled with the increased vapor pressure is likely to dampen the cavitation efficiency. On the other hand, at low concentrations the decrease in cavitation efficiency could be offset by increase in k.

3.5 Influence of chloride ions

As per the literature, sonochemical degradation has been known to be accelerated in the presence of ions [22, 23]. In fact, ultrasonic irradiations normally result in the higher mass-transfer, which is a function of specific parameters (viz. type and geometry of reactors used for irradiation, gas flow rate, and power dissipation into the system) [24]. The presence of a salt (say sodium chloride) necessarily leads to enhanced mass transfer rates (due to its non-combining nature in aqueous systems), thereby leading to the formation and maintenance of smaller bubbles. The presence of salt has also been found to decrease the vapor pressure of the medium and to increase the surface tension, both resulting in more violent collapse of the cavities [24]. Besides, the improvement in rate is also reported by Kumar et al. [23]. In fact, the use of Cl^- and NO^{2-} result in two to eight-fold enhancement in the rates of degradation of phenol and p-nitrophenol. However, Gultekin and Ince, [25] had reported that the presence of ions is less likely to increase the sonochemical degradation of bisphenol-A. Besides, the addition of salt would also increase ionic strength of the aqueous phase, which can drive the organic compounds to the bulk-bubble interface. Furthermore, dissolved electrolytes also affect other properties such as viscosity and heat capacity. Thereby, the resultant effect on degradation rate is observed to be non-linear and thus difficult to

estimate. Fig. 7 shows the effect of chloride concentration on degradation of benzene and toluene, wherein a minor increase in the degradation rates was observed for volatiles. This may possibly be due to volatile degradation taking place in the interior of bubbles rendering the merit of presence of anion to be poor.

4. Conclusion

The application of ultrasound was studied for the decomposition of benzene and toluene. The following conclusions can be drawn from the above study:

1) The reaction rate was observed to be a function of the initial concentration. It decreased with the increase in initial concentration. The volatile nature of compound causes the lowering of adiabatic collapse temperature at higher concentration.

2) The reaction rate was independent of the gas dissolved. The rate constant remains same for both argon and air saturated solution.

3) The addition of hydrogen peroxide did not seem to alter the reaction rates appreciably. It was almost constant for benzene, whereas toluene showed slight increase.

4) The reaction rate was found to be temperature dependent in the range 10-40 $^{\circ}$C. Both, benzene and toluene showed increase in rate constant with respect to temperature.

5) The addition of anions like chloride results in minor increase in the degradation rate.

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Nomenclature

p_a Acoustic pressure (bar)

p_v Pressure in the bubble at its maximum size (bar)

p_{max} Maximum temperature generated inside the bubble (bar)

T_{max} Maximum temperature generated inside the bubble ($^{)}$C)

k First order rate constant (min^{-1})

T_0 Ambient temperature (^{0}C)

C_i Initial concentration (mol/l)

K Proportionality constant

Greek letters
γ Specific heat ratio

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Table 1 First order rate constant at different H_2O_2
concentration for benzene (T = 20°C)

System	k_1 (min^{-1})	r^2
50 ppmv Benzene (Bn)	0.0146	0.985
50 ppmv Bn + 200 ppmv H$_2$O$_2$	0.0147	0.982
50 ppmv Bn + 400 ppmv H$_2$O$_2$	0.0147	0.0.98
50 ppmv Bn + 1000 ppmv H$_2$O$_2$	0.0146	0.984

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Table 2. First order rate constant at different temperature
(Initial concentration = 50 ppmv)

Temperature ($^{\circ}$C)	Benzene		Toluene	
	k_1 (min^{-1})	r^2	k_1 (min^{-1})	r^2
10	0.0092	0.986	0.0087	0.982
20	0.0101	0.985	0.00906	0.979
30	0.0109	0.983	0.0102	0.98
40	0.012	0.983	0.0118	0.979

Figure Captions

Fig. 1 Experimental set up.

Fig. 2 Effect of initial concentration on degradation of benzene at 20°C.

Fig.3 Comparing the degradation rate for benzene and toluene for 50 ppmv

   initial concentration.

Fig. 4 Effect of hydrogen peroxide on degradation of toulene at 20°C.

   (initial conc. = 50 ppmv)

Fig.5 Effect of temperature on degradation of benzene at 50 ppmv initial

   concentration

Fig.6 Effect of temperature on degradation of toluene at 50 ppmv initial

   concentration

Fig. 7 Effect of Cl$^-$ ions concentration on the degradation of benzene and toluene

   (initial conc. = 50 ppmv)
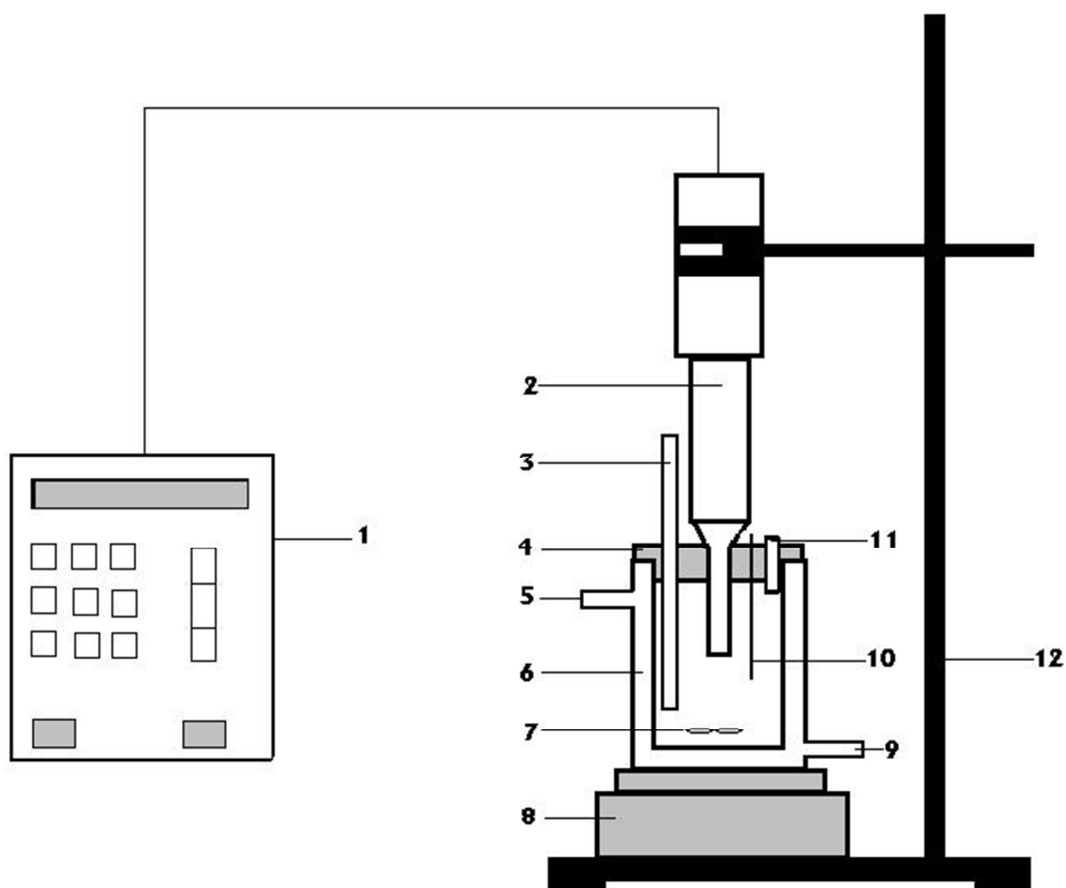
1. Probe system display   7.   Stirrer
2. Ultrasonic probe   8.   Magnetic stirrer
3. pH probe   9.   Cooling water inlet
4. Teflon cover   10.Thermocouple
5. Cooling water outlet   11. Septum for Sampling
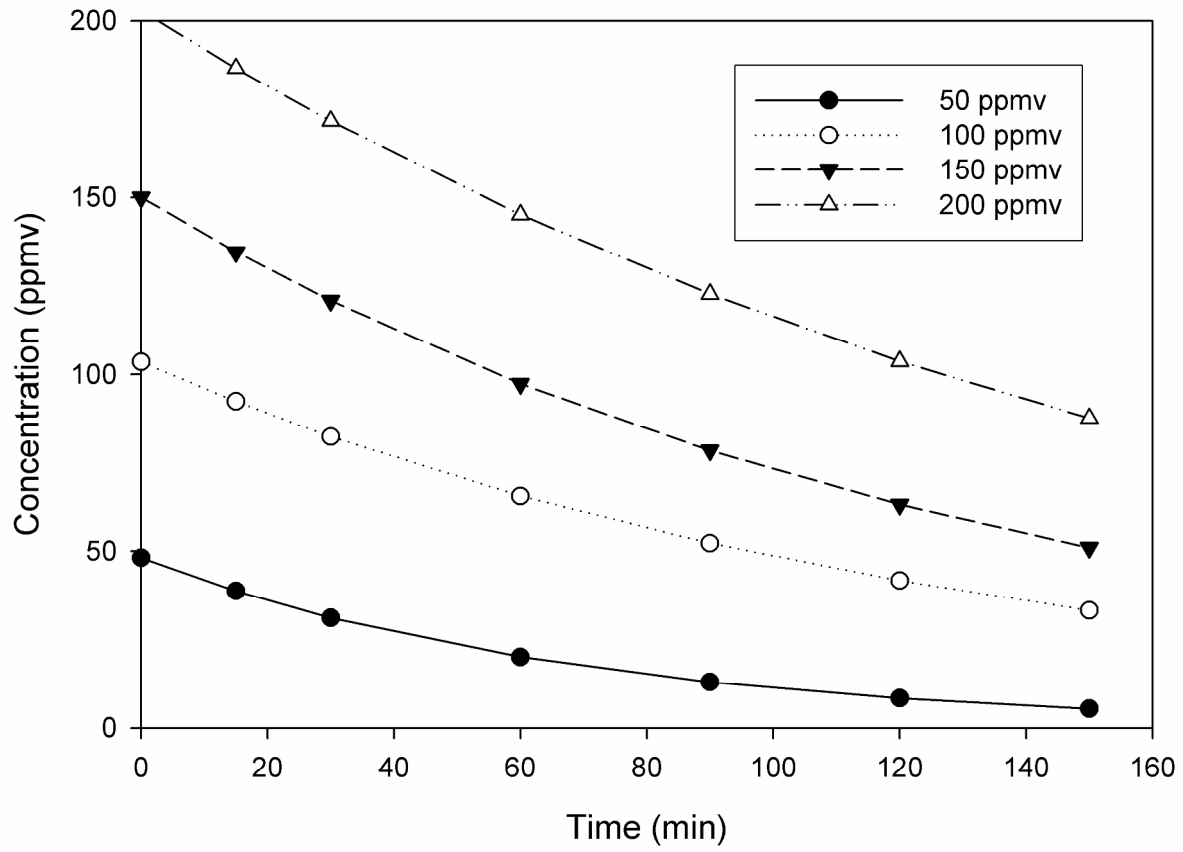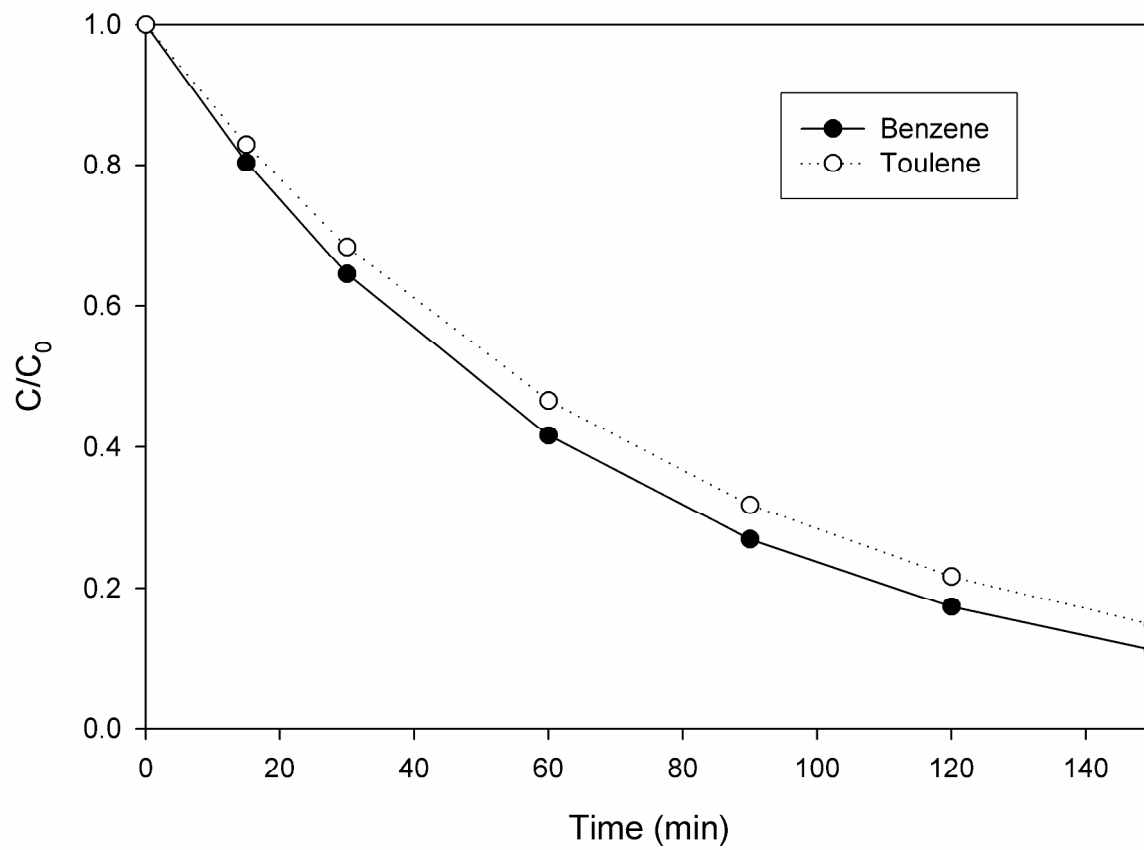6. Water jacket   12. Steel stand

Fig. 1

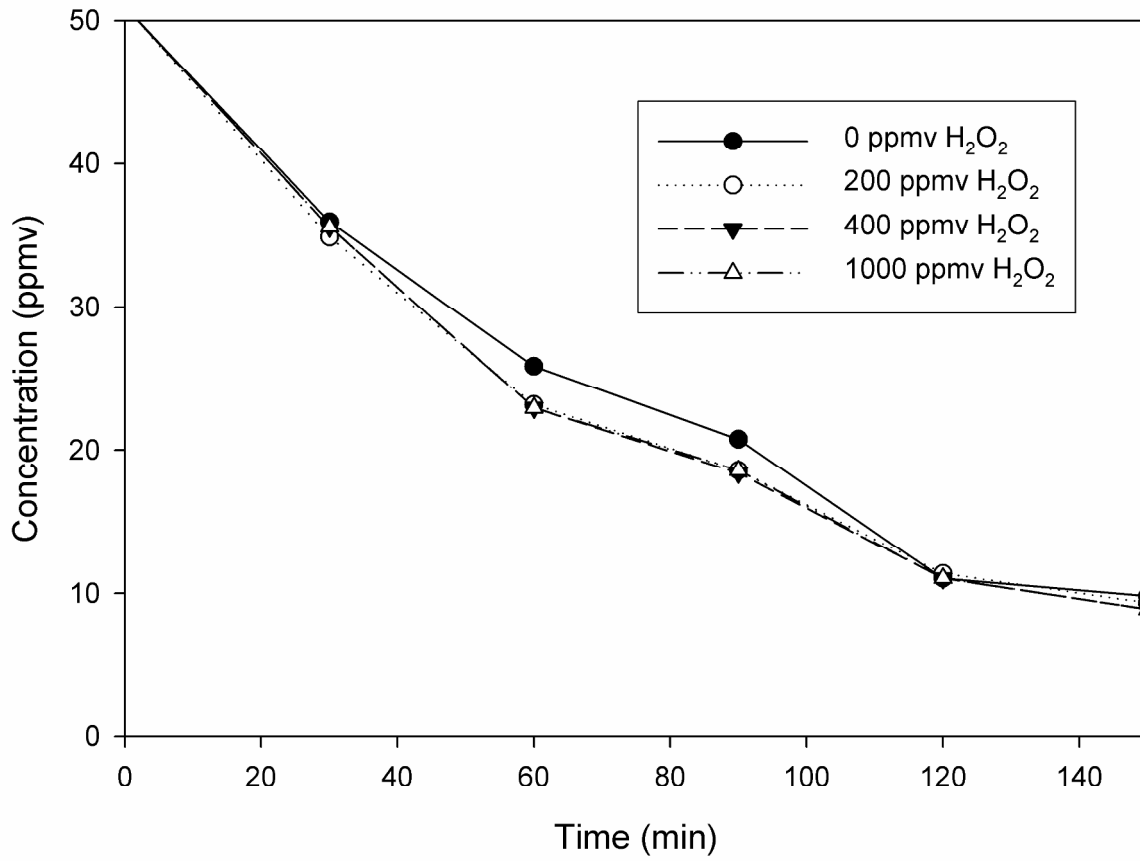**Fig. 2**

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7