

Ultrasonic degradation of Rhodamine B in aqueous solution: Influence of operational parameters

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Abstract

The aim of the study was to investigate decolorization of Rhodamine B (RB) in aqueous solution using ultrasonic degradation. The results showed that decolorization follows pseudo-first-order reaction kinetics. The apparent reaction rate constant (k_{ap}) was found to increase with decreasing pH and decreases with increasing initial RB concentration. Power density was very important parameter and increasing it causes a considerable increase of removal efficiency. UV–vis spectral changes of RB indicate that in the sonolysis of RB, the cleavage of aromatic chromophore ring structure and the *N*-deethylation take place, but decomposition of aromatic structure is predominant.

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1. Introduction

Wastewaters generated by the textile, paper, leather and pharmaceutical industries are one of the major environmental pollutants. The disposal of these colored wastewaters poses a major problem for the industry as well as a threat to the environment [1]. Generally, adsorption on activated carbon, coagulation by a chemical agent or reverse osmosis were applied to such effluents [2]. Nevertheless, they are non-destructive methods, and merely transfer contaminants from water to sludge [3].

Advanced oxidation processes (AOPs) are promising alternatives to non-destructive methods, owing to their potential to generate hydroxyl radicals in solution [4–8]. The hydroxyl radicals are short-lived and highly reactive chemical species which react non-selectively with organic matter present in wastewater. Among many ways of producing hydroxyl radicals in AOPs, ultrasound is a novel method [9]. In recent years considerable interest has been shown on the application of ultrasonic degradation for the removal of hazardous contaminants from water [9–11]. Sonochemical degradation methods are relatively new and involve exposing aqueous solutions containing the organic pollutant to ultrasound and the effect of different operational

parameters on degradation could be found [12–16]. Sonochemical decomposition of organic compounds is resulted from the formation, growth and collapse of high-energy cavitation bubbles, which releasing large quantities of energy over a small location [17].

When water is sonicated, $\bullet\text{H}$ and $\bullet\text{OH}$ are produced. A simple mechanism for radical formation and depletion, during sonication of water is given below [11]:



On the other hand, organic compounds in the vicinity of a collapsing bubble may undergo pyrolytic decomposition due to the local high temperatures and pressure [12]. Many researchers investigated the sonochemical degradation of dyes during the last few years. Ince and Tezcanli-Güyer [11] reported that decolorization of two azo dyes with 300 kHz emitter was first order with respect to the maximum absorption of the dye in the visible band and was accelerated with increasing acidity. Vinodgopal et al. [10] showed that 65% the Remazol Black B (a reactive textile azo dye) was mineralized under 6 h sonolysis with a

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640 kHz ultrasonic system. Vončina and Majcen-Le-Marechal [18] reported that the efficiency of decolorization of azo dyes with ultrasound significantly enhanced in the presence of H_2O_2 .

The purpose of this study was to investigate the effects of operational parameters such as initial concentration of dye, power density, pH, NaCl, BuOH and H_2O_2 concentrations on the rate of decolorization. Also kinetics and mechanism of the process were subjects of the present research.

2. Experimental

2.1. Materials

RB (Fig. 1), NaOH, HCl, H_2O_2 , EtOH and BuOH were purchased from Merck (Germany). *N,N*-Dimethyl-*p*-nitroso-aniline (RNO) was purchased from Fluka (Switzerland). Solutions were prepared by dissolving the requisite quantity of the dye (RB) in double distilled water.

2.2. Ultrasonic bath (T 460/H)

The ultrasonic bath was purchased from Elma (GmbH) with the operating frequency of 35 kHz and with a rated output power of 170 W. The bath has the dimensions of 240 mm × 137 mm × 100 mm. The total internal body is made from stainless steel. Efficiency of the bath was determined by calorimetric method and Table 1 gives the values of actual power dissipated and the corresponding efficiency in the bath. A cooling coil was kept inside the reactor and water was pumped at desired temperature from a thermostatic bath in order to maintain the temperature at the selected value within $\pm 2^\circ C$.

2.3. Experiments

In each experiment, certain volume of the RB solution at desired concentration was transferred to ultrasonic bath and then the sonication was switched on to initiate the reaction. At certain

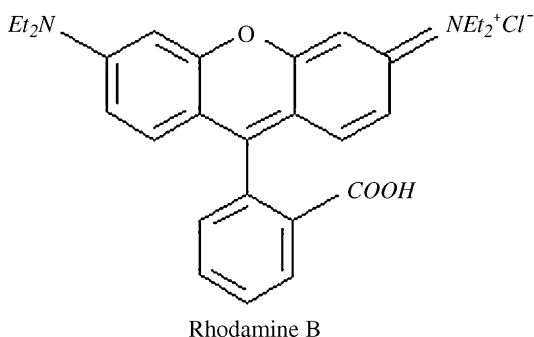


Fig. 1. Chemical structure of RB.

Table 1
Actual power dissipation and the corresponding efficiency of ultrasonic bath

Area of dissipation (cm^2)	329
Actual power dissipated in the given volume P (W)	49
Efficiency (%) $\eta = \left(\frac{P}{170}\right) \times 100$	28.8

reaction intervals, 5 ml of sample was withdrawn and the concentration of RB was determined by means of a spectrophotometer (Ultrspec 2000, Biotech pharmacia, England) at 554 nm. A calibration plot based on Beer–Lambert's law was established by relating the absorbance to the concentration.

2.4. Chemical oxygen demand (COD)

The closed reflux colorimetric method was used to determine COD values. Each time the appropriate amount of sample was introduced into commercially available digestion solution (WTW, Germany) and the mixture was then incubated for 120 min at $150^\circ C$ in a COD thermoreactor (model CR 3000, WTW, Germany). COD concentration was measured colorimetrically using a Photolab Spectral (WTW, Germany).

3. Results and discussion

3.1. The effect of initial concentration of RB

It is important from an application point of view to study the dependence of removal efficiency on the initial concentration of the dye. Therefore the effect of RB concentration on the dye removal efficiency was investigated at different concentrations in the range from 1 to $10\ mg\ l^{-1}$. Decolorization percent decreases with increasing initial concentration of RB as shown in Fig. 2a. An explanation to this behavior is that as the initial

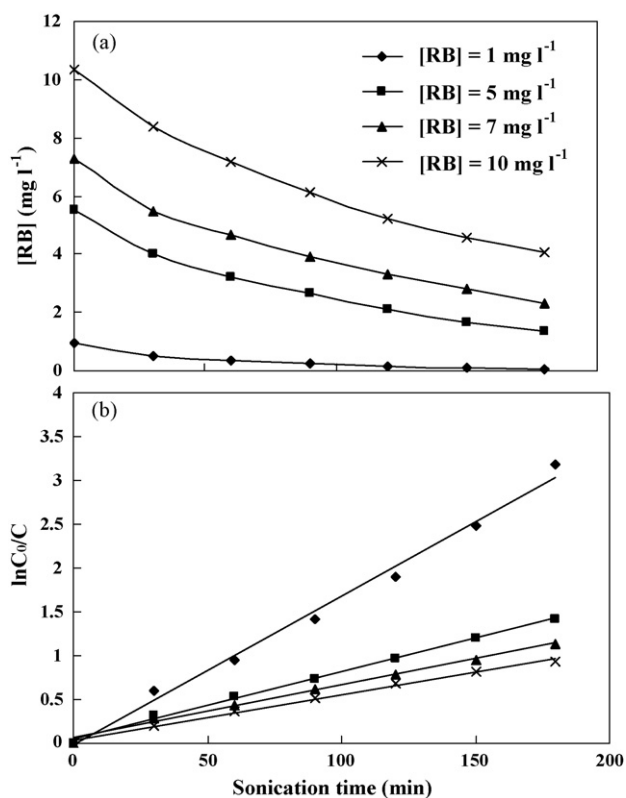


Fig. 2. Effect of initial RB concentration on RB sonochemical degradation (a), the semi-logarithmic plot of RB concentration vs. sonication time at different initial RB concentration (b). $V = 500\ cm^3$, $T = 25 \pm 2^\circ C$.

concentration of RB increases, higher concentrations of intermediates form. Assuming most of the reactions take place at the bubble–liquid interface, with increasing initial concentration of RB and correspondingly intermediates, the RB degradation has been limited by the available interfacial area [17]. Kinetics of the sonochemical degradation of RB is a pseudo-first-order:



$$-\frac{d[\text{RB}]}{dt} = k[\text{RB}][\bullet\text{OH}] \quad (6)$$

As $\bullet\text{OH}$ is a very reactive species, it not only is accumulated in solution, but its concentration takes on a steady value during the process.

$$\ln \frac{[\text{RB}]}{[\text{RB}]_0} = -k_{\text{ap}} \times t \quad (7)$$

$$k_{\text{ap}} = k[\bullet\text{OH}] \quad (8)$$

where $[\text{RB}]_0$ and $[\text{RB}]$ are the initial concentration and concentration of RB (mg l^{-1}) at time t , respectively. k_{ap} and t are the pseudo-first-order (min^{-1}) and sonication time, respectively. The semi-logarithmic graphs of the concentration of RB for various initial concentration of this compound versus sonication time (Fig. 2b) yield straight lines, which confirm the proposed pseudo-first-order kinetic for decolorization of RB with ultrasonic technique. Fig. 3 shows the plot of k_{ap} versus RB initial concentrations.

3.2. The effect of power density

One important factor that influences the performance of the ultrasonic degradation is the power density. The effect of power density on the extent of removal rate has been studied with varying the power density of RB solution (5 mg l^{-1}) in the range of $0.049\text{--}0.163 \text{ W ml}^{-1}$. Fig. 4 shows the effect of power density on the final concentration of RB. As can be seen from this figure final concentration of RB decreases with increasing the power density. This may be due to the fact for the same energy input, if the volume of solution is decreased, it results in delivering much higher energy to the system. Results show that k_{ap} is a function

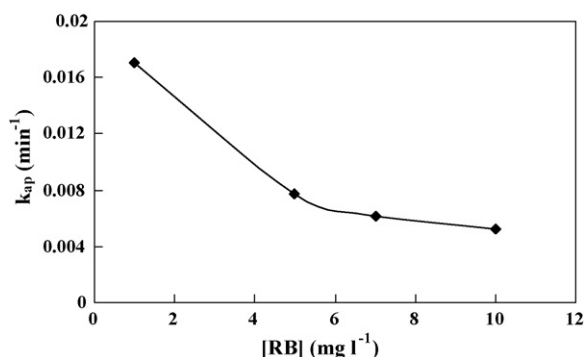


Fig. 3. Pseudo-first-order degradation rate constant of RB as a function of RB initial concentration. For experimental details refer to Fig. 2.

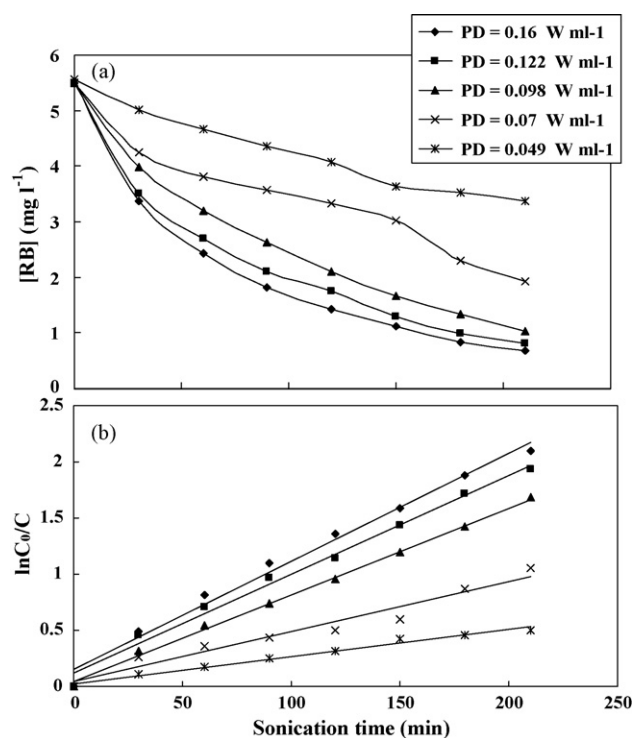


Fig. 4. Effect of power density on RB sonochemical degradation (a), the semi-logarithmic plot of RB concentration vs. sonication time at different power densities (b). $[\text{RB}]_0 = 5 \text{ mg l}^{-1}$, $T = 25 \pm 2^\circ\text{C}$.

of power density (Fig. 5) as following:

$$k_{\text{ap}} = 0.058 \left(\frac{P}{V} \right)^{0.94} \quad (9)$$

3.3. The effect of pH

The influence of pH on the ultrasonic degradation of RB was studied in the range of pH between 2 and 10 and results were shown in Fig. 6. It was found that the RB removal rate constant increases with decreasing pH values. Hence, the efficient treatment of organic water contaminants with molecular structure like RB with ultrasonic technique should be performed in acidic medium. Decreasing of decolorization rate by increase of pH is due to dissociation of RB at $-\text{COOH}$ sites, so that retards it to

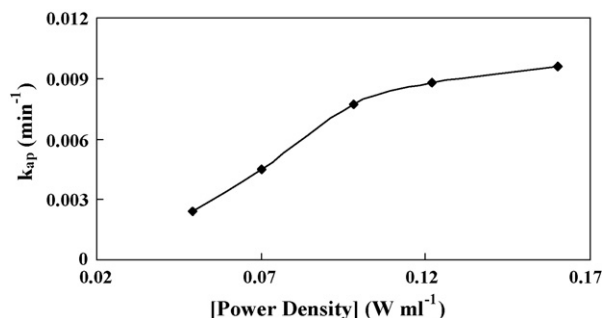


Fig. 5. Pseudo-first-order degradation rate constant of RB as a function of power density. For experimental details refer to Fig. 4.

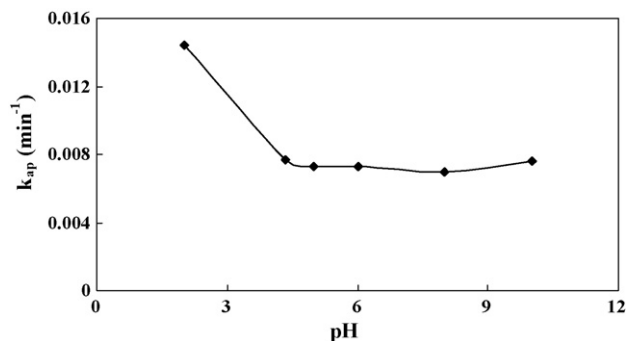


Fig. 6. Effect of pH on RB sonochemical degradation. $[RB]_0 = 5 \text{ mg l}^{-1}$, $T = 25 \pm 2^\circ \text{C}$, $V = 500 \text{ cm}^3$.

diffuse into the reactive zone (bubble–liquid interface), where uncombined $\bullet\text{OH}$ concentration is maximum [9].

3.4. Spectral changes of RB and COD measurements during ultrasonic degradation

The changes in absorption spectra of RB during ultrasonic degradation at 30 min sonolysis intervals were shown in Fig. 7. The decrease of the absorption peak of RB at $\lambda = 554 \text{ nm}$ in Fig. 7 indicates degradation of the dye.

As can be seen from Fig. 7, concomitant with decreasing of absorption band at 554 nm, a hypsochromic shift occurred with increasing sonolysis time and the maximum absorption wavelength shifts from 554 to 547 nm at 180 min of sonolysis time. The hypsochromic shift process is an *N*-deethylation process [19]. Therefore both *N*-deethylation and degradation of RB chromophore structure take place under sonolysis. In fact the degradation of RB chromophore structure and *N*-

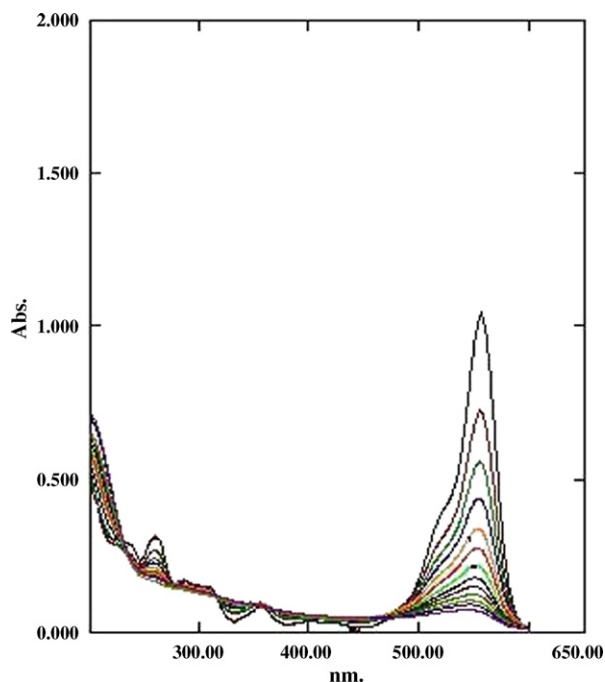


Fig. 7. UV–vis spectral changes of RB, recorded during the dye degradation at 30 min sonication intervals. $[RB]_0 = 5 \text{ mg l}^{-1}$, $T = 25 \pm 2^\circ \text{C}$, $V = 500 \text{ cm}^3$.

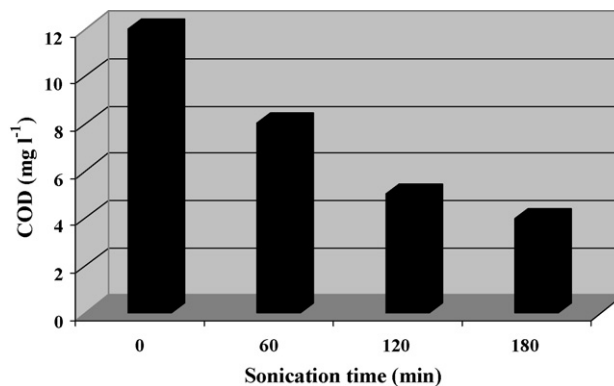


Fig. 8. COD change vs. sonication time for RB sonochemical degradation. $[RB]_0 = 5 \text{ mg l}^{-1}$, $T = 25 \pm 2^\circ \text{C}$, $V = 500 \text{ cm}^3$.

deethylation are two competitive reactions during the RB degradation (Scheme 1). The spectral changes of RB under sonolysis (Fig. 7) showed that the absorption decreased with the concomitant small wavelength shift of band to the shorter wavelengths. These results indicate that in the sonolysis of RB, the cleavage of aromatic chromophore ring structure (pathway 1) and the *N*-deethylation take place (pathway 2), but decomposition of aromatic structure is predominant. As shown in Scheme 1, from second pathway *N*-deethylated products are formed at degradation of RB under sonolysis. With increasing sonolysis time a new band started to form at 335 nm. It may be interpreted that poly-aromatic rings are destroyed at initial stages of the process and the produced aromatic rings display absorption in UV region, which gradually decreases by increasing sonolysis time.

The measurement of COD values can be related to the total concentration of organics in the solution and the decrease of COD reflects the degree of mineralization.

As can be seen from Fig. 8 the amount of COD decreases with increasing sonolysis time and almost 67% of the COD was removed after 180 min of sonolysis.

3.5. The effect of sodium chloride on the sonochemical degradation of RB

It is important from an application point of view to study the dependence of removal rate on the presence of salts such as NaCl, since wastewater usually contains various types of salts. As can be seen from Fig. 9 the k_{ap} increased with increasing NaCl con-

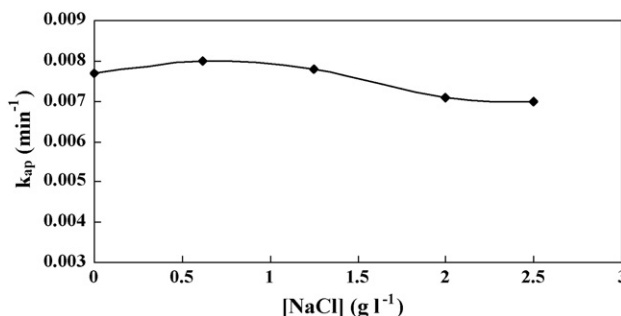
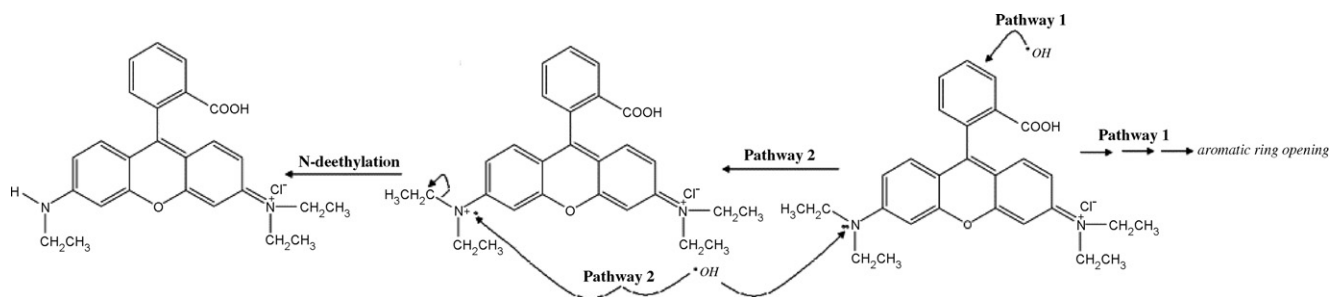


Fig. 9. Pseudo-first-order degradation rate constant of RB as a function of NaCl concentration. $[RB]_0 = 5 \text{ mg l}^{-1}$, $T = 25 \pm 2^\circ \text{C}$, $V = 500 \text{ cm}^3$.

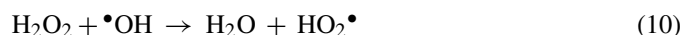


Scheme 1. The degradation mechanism of RB with hydroxyl radicals via two competitive processes: *N*-deethylation and destruction of the aromatic rings.

centration until 0.625 g l^{-1} , above this amount the k_{ap} decreased with increasing NaCl concentration. So there may be an optimum amount of NaCl to increase removal rate. Adding salt in sonicated reaction mixture results in reduced vapor pressure and increased surface tension thus promoting a more violent collapse of the cavitating bubble. But the oxidation reactions occur in the bubble–bulk interface area. Addition of NaCl may change the physical properties of the interfacial film and diffusion of RB toward the interface becomes more and more difficult [17].

3.6. The effect of H_2O_2 addition

Under temperature of 5000 K and pressure of 1000 atm in the ultrasonic cavitation, hydrogen peroxide readily decomposes into hydroxyl radicals causing high removal rate. Fig. 10 shows the effect of hydrogen peroxide concentration in the removal rate of RB with ultrasonic waves. The results show that the removal rate increases with increasing H_2O_2 concentration up to 10 mg l^{-1} . This is as a result of formation of more hydroxyl radicals from hydrogen peroxide decomposition. Above 10 mg l^{-1} the reaction rate decreases with increasing hydrogen peroxide concentration. This is reasonable, since when H_2O_2 concentration reaches above a critical value, $\bullet\text{OH}$ and $\bullet\text{H}$ generated by the thermolysis of water in the solution medium efficiently reacts with H_2O_2 , which is a $\bullet\text{OH}$ scavenger as follows [4]:



The enhancement in $\bullet\text{OH}$ produced in the presence of H_2O_2 , can be proved with *N,N*-dimethyl-*p*-nitroso-anilin (RNO). This compound has absorption peak at $\lambda_{\text{max}} = 440 \text{ nm}$, which reacts selectively with hydroxyl radical but not with perhydroxyl and superoxide radicals [20]. As shown in Fig. 11, the absorbance

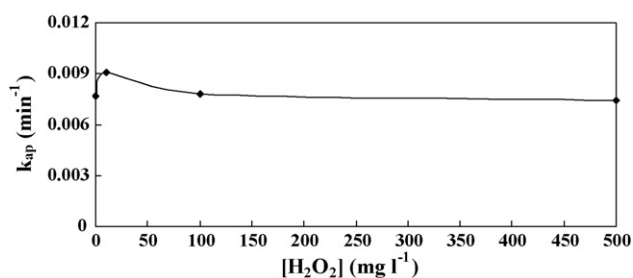


Fig. 10. Pseudo-first-order degradation rate constant of RB as a function of H_2O_2 concentration. $[\text{RB}]_0 = 5 \text{ mg l}^{-1}$, $T = 25 \pm 2 \text{ }^\circ\text{C}$, $V = 500 \text{ cm}^3$.

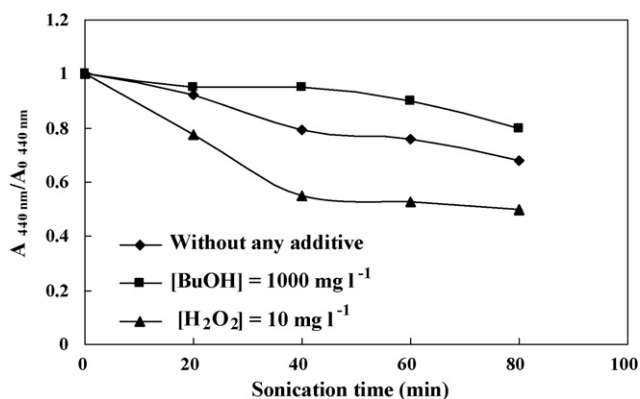


Fig. 11. Changes of RNO absorbance at 440 nm with ultrasonic irradiation. $[\text{RNO}]_0 = 10^{-5} \text{ M}$.

of RNO at 440 nm decreased faster in the presence of 10 mg l^{-1} H_2O_2 . This result shows that in the presence of H_2O_2 high amount of $\bullet\text{OH}$ radicals are produced, therefore the absorption peak of RNO at $\lambda_{\text{max}} = 440 \text{ nm}$ decreased very faster in the presence of H_2O_2 .

3.7. The effect of BuOH as an electron scavenger

An evidence for the role of hydroxyl radicals as the primary oxidant can be established by carrying out the sonolysis in aqueous solution in the presence of alcohols such as BuOH. Alcohols are commonly used to quench the hydroxyl radicals. Fig. 12 shows that addition of BuOH inhibits the sonochemical degradation of RB. The retarding effect of BuOH can be explained

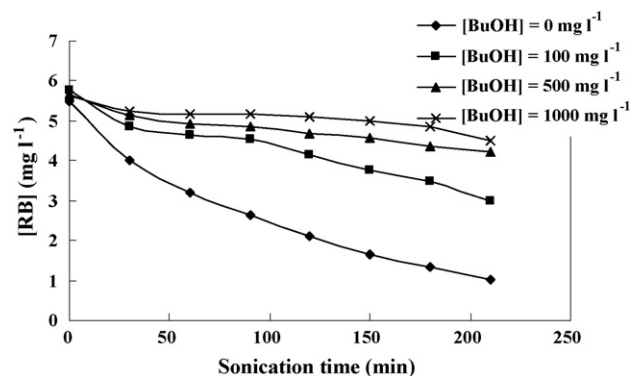


Fig. 12. Effect of BuOH concentration on RB sonochemical degradation. $[\text{RB}]_0 = 5 \text{ mg l}^{-1}$, $T = 25 \pm 2 \text{ }^\circ\text{C}$, $V = 500 \text{ cm}^3$.

by $\bullet\text{OH}$ competitive reactions with RB and BuOH [8]. This result shows that hydroxyl radicals play a major role in the sonochemical degradation of RB. The competitive reaction of $\bullet\text{OH}$ with alcohols and MG can be proved with *N,N*-dimethyl-*p*-nitroso-anilin (RNO). As shown in Fig. 11, the absorption peak of RNO at $\lambda_{\text{max}} = 440 \text{ nm}$ decreased much slower in the presence of 1000 mg l^{-1} BuOH, which shows $\bullet\text{OH}$ is consumed by BuOH molecules therefore the decrease of RNO absorption peak at 440 nm in the presence of BuOH is very slow.

4. Conclusions

In this study, ultrasonic degradation of RB, as a basic red fluorescent dye structurally related to xanthene dyes, was studied using sonication by using an ultrasonic bath. The effects of operational parameters such as initial RB concentration, power density, pH, H_2O_2 and NaCl concentrations were investigated on the removal rate of RB. The removal rate of RB follows pseudo-first-order kinetic with respect to the RB concentration. The removal rate decreases with increasing initial concentration of RB, but it increases with increasing power density as follows:

$$k_{\text{ap}} = 0.058 \left(\frac{P}{V} \right)^{0.94}$$

Decreasing of pH, enhances the removal rate and H_2O_2 , NaCl concentrations have critical effect in the removal of RB. Results show that both *N*-deethylation and degradation of RB chromophore structure take place under sonolysis, which decomposition of aromatic structure is predominate.

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