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Sonochemical degradation of Rhodamine B in aqueous phase: Effects of additives

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ABSTRACT

The effects of various additives such as iron (elemental, bivalent and trivalent), carbon tetrachloride, hydrogen peroxide, tert-btyl alcohol, salt (Na_2SO_4), sucrose and glucose on the sonochemical destruction of cationic dye, Rhodamine B (RhB), in aqueous phase were studied. Additionally, sonolytic degradation of RhB was investigated at varying initial dye concentration, power, pH and temperature. RhB can be readily eliminated by the ultrasound process, but even after long ultrasound irradiation times (240 min), more than 40% of chemical oxygen demand (COD) remained in the solution. Sonochemical degradation of RhB was strongly affected by initial substrate concentration, ultrasonic power, temperature and pH. The ultrasonic degradation of dye was enhanced by iron addition. The acceleration effect of iron on the destruction rate displayed the following order: $Fe(II) > Fe(III) > Fe^0$. It was found that the degradation of the dye was accelerated with increased concentrations of CCl_4 via the formation of oxidant chlorine species. It was observed that there was an optimum concentration of H_2O_2 and Na_2SO_4 for enhancing the degradation degree of RhB. In the presence of tert-butyl alcohol at low concentration, unexpectedly, the rate of dye degradation was accelerated. Very slow RhB degradation occurs if the sonolysis is carried out in the presence of high tert-butyl alcohol concentration. The slight decrease in the degree of RhB removal in the presence of high concentrations of sucrose and glucose is a clear indication that ultrasonic irradiation is a promising process for the removal of RhB from alimentary liquids containing sucrose and glucose.

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1. Introduction

Rhodamine B (RhB), Basic Violet 10, is a highly water soluble, non-volatile, basic dye of the xanthene class. The color of the dye is bright reddish violet. It is widely used in industrial purposes as a colorant in textile, leather, jute and food industries, and is also a well-known water tracer fluorescent [1]. This dye is used for dying cotton, silk paper, bamboo, weed, leather, etc., preparing carbon paper, ball pen, stamp pad inks, paints, etc. It is harmful if swallowed by human beings and animals, and causes irritation to the skin, eyes, gastrointestinal tract and respiratory tract [2]. It also causes phototoxic and photoallergic reactions. The carcinogenicity, reproductive and developmental toxicity, neurotoxicity and chronic toxicity towards humans and animals have been experimentally proven [3].

Various industries are responsible for contributing such chemicals into the environment. These discharged effluents are colored due to the residual dyes and when they are disposed to the natural water sources, they pollute water. Colored effluents are known to cause high oxygen demand, fluctuating pH, large solid load and resistance to biological oxidation. Even a very small amount of dye in water is visible and it impedes light penetration and thus reduces photosynthesis in aquatic plants, affects their growth and decreases gas solubility, interfering with the natural purification process [4].

Use of dyes has led to pollution load increase, and the industries have been required to use certain techniques to decolorize the effluents before disposal into the surface water or to the land. Many physical and chemical methods, such as coagulation, floatation, chemical oxidation, solvent extraction, hyperfiltration, etc., have been tried in order to remove color from wastewater, but they have not been very successful since dyes are stable to light and oxidizing agents, and they involve high operational cost and aerobic digestion. Alternate technologies popularly known as Advanced Oxidation Processes (AOPs) have been extensively explored for effective degradation of these compounds for the past few decades. The AOPs are characterized by production of OH (hydroxyl) radical as primary oxidant. The OH radicals are extremely reactive species and are powerful oxidizing agent.

Sonochemical oxidation has been investigated as a viable AOP for the destruction of various pollutants in water. In this technique, the free radicals are generated through transient collapse of cavita-

tion bubbles driven by an ultrasound wave. Ultrasonic irradiation induces the production of cavitation bubbles in the liquid through which it is transmitted. These microbubbles grow during the subsequent compression–rarefaction cycles until they reach a critical size. Further compression leads to the collapse of the bubbles, with the concomitant release of heat and production of chemically active species during the last phase of the bubble collapse [5–7]. The chemical effects are a direct result of the very high temperatures, on the order of 5000 K, and pressures, in the range of hundreds of bars, which are reached in the gaseous cavities when the cavities size is reduced many orders of magnitude within a few microseconds [8]. The extremely high temperatures and pressures formed in collapsing cavitation bubbles in aqueous solutions lead to the thermal dissociation of water vapor into reactive hydroxyl radicals and hydrogen atoms [9,10]. The radical species produced can recombine, react with other gaseous species present in the cavity, or diffuse out of the bubble into the bulk fluid medium where they are able to react with solute molecules.

The two major pathways or mechanisms for the sonolytic degradation of organic compounds in dilute aqueous solution are thermal decomposition of the volatile pollutant molecules entrapped inside the bubble [11], and secondly, the reaction of OH radicals with the solute adsorbed at the bubble interface, in the bulk, and to some extent within the bubbles [12]. The extent of degradation in bulk liquid is limited by the quantity of hydroxyl radicals diffused into the water [13].

The aim of this work was to investigate the influence of various additives such as iron (elemental, bivalent and trivalent), carbon tetrachloride, hydrogen peroxide, tert-butyl alcohol, salt (Na_2SO_4), sucrose and glucose on the sonolytic degradation of RhB. Additionally, the effects of some experimental parameters such as initial dye concentration, ultrasonic power, pH and temperature on the sonochemical degradation of dye was studied.

2. Materials and methods

2.1. Reactor

Sonolysis experiments were performed in a cylindrical water-jacketed glass reactor operating at 300 kHz (Fig. 1). Ultrasonic waves introduced from the bottom of the solution through a plate Pyrex surface (diameter 5 cm) holding the piezoelectric disk (Saint-Gobain Quartz, France) with a diameter of 4 cm. The temperature of the solution was monitored using a thermocouple immersed in the reacting medium. The temperature inside the reactor was kept
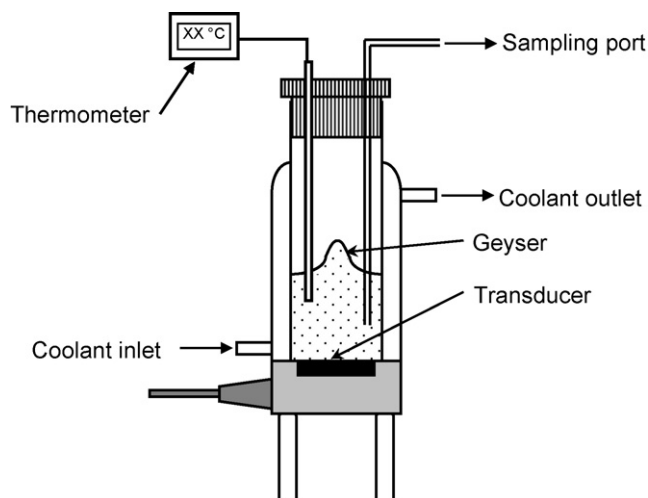

Fig. 1. Scheme of the sonochemical reactor used for RhB degradation.
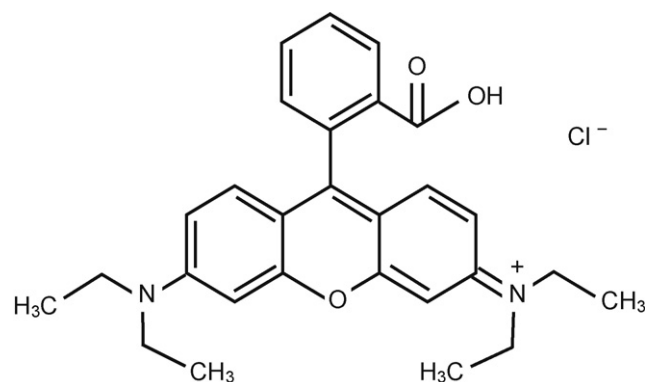

Fig. 2. Chemical structure of Rhodamine B (Basic Violet 10).

constant by circulating cooling water within the jacket surrounding the cell. Energy dissipated in the reactor was measured by the calorimetric method [14,15].

2.2. Materials

Rhodamine B (abbreviation: RhB; C.I. Basic Violet 10; C.I. number: 45170; chemical class: xanthene; molecular formula: $C_{28}H_{31}N_2O_3Cl$) was procured from Sigma–Aldrich. Rhodamine B (molecular weight: 479.01 g mol^{-1}); IUPAC Name N-[9-(ortho-carboxyphenyl)-6-(diethylamino)-3H-xanthen-3-ylidene] diethyl ammonium chloride, which is a highly water soluble, was used as a model solute. The molecular structure of RhB was shown in Fig. 2.

Elemental iron, ferrous sulfate, ferric sulfate, carbon tetrachloride, hydrogen peroxide, tert-butyl alcohol, sodium sulfate, sucrose and glucose were commercial products of the purest grade available (analytical grade). All solutions were prepared with distilled water.

2.3. Procedures

The initial concentration of RhB solution was 5 mg L^{-1} for all experiments, except for those carried out to examine the effect of initial dye concentration. Various aqueous solutions of RhB (5 mg L^{-1}) containing different additives were prepared by adding the required amount of these agents and stirring using a magnetic bar.

Sonolytic degradation of RhB was carried out at 300 kHz under different conditions using constant solution volume of 300 mL. Ultrasonic power was adjusted at 60 W, excluding runs conducted to investigate the influence of power. The temperature of the solution was maintained constant at the required value with circulating water. Aqueous samples were taken from the solution and the concentrations of dye were determined using a UV–vis spectrophotometer (Jenway 6405).

Experiments were performed at pH 5.3, which resulted from dissolution of RhB in distilled water without further adjustment, except for those conducted to examine the effect of solution pH. When the effect of pH was investigated, the solution pH was adjusted using 0.1N H_2SO_4 or NaOH aqueous solutions.

2.4. Analysis

A well-known procedure for determining RhB concentrations, based on Beer's law calibration plots, was applied using a UV–visible spectrophotometer (Jenway 6405). The wavelength resolution and the bandwidth were, respectively, 1 and 0.5 nm. The length of the optical path in glass cell was 1 cm. The maximum absorption wavelength was determined as equal to 553 nm at pH
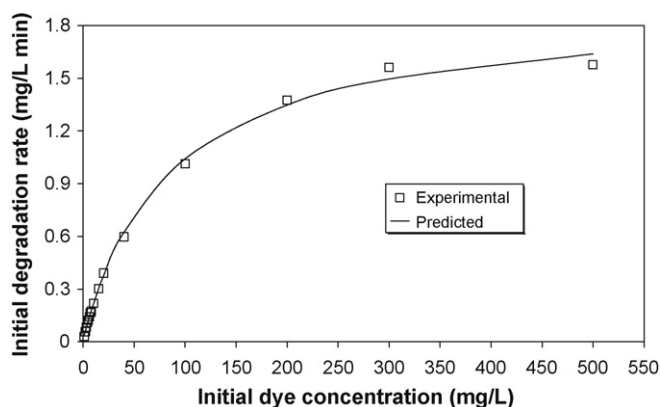
Fig. 3. Experimental and predicted initial RhB degradation rates for various dye concentrations (conditions: volume: 300 mL; initial dye concentration: 1–500 mg L^{-1}; temperature: 25 °C; pH: 5.3; frequency: 300 kHz; power: 60 W).

1–2, 552 nm at pH 3 and 551 nm at pH 4–13. Then, the calibration plot was constructed. The calibration was repeated five times during the period of measurements. The linearization of this plot usually provided determination coefficient close to 99.99%.

2.5. COD measurement

Chemical oxygen demand (COD) was measured according to the method presented by Thomas and Mazas [16], using a dichromate solution (Aldrich) as the oxidizer in a strong acid medium. Test solution (2 mL) was transferred into the dichromate reagent and digested at 150 °C for 2 h. The optical density for the color change of dichromate solution was determined with a UV–vis spectrophotometer (Jenway 6405). In order to avoid the interference of the residual hydrogen peroxide, samples were neutralized with sodium hydroxide and treated with catalase (supplied by Merck) previous to COD analysis.

3. Results and discussion

3.1. Effect of operational parameters

3.1.1. Effect of initial dye concentration

Application of 300 kHz and 60 W ultrasound irradiation to 300 mL of RhB solutions in the concentration range of 1–500 mg L^{-1} caused an exponential decrease of the dye concentration with time. Fig. 3 depicts the initial degradation rate (computed as $\Delta C/\Delta t$ over the first minutes of sonication from the results showing the evolution of RhB concentration as a function of sonication time) versus initial dye concentration. It is clear that degradation does not follow a first order kinetic as generally reported in the literature. During this study, different runs were compared using the initial degradation rate (mg L^{-1} min^{-1}) rather than the pseudo-first-order kinetic constant. From Fig. 3, it can also be noticed that the initial degradation rate increased with an increase in the initial concentration up to 300 mg L^{-1}, followed by almost constant sonolytic degradation rate for higher concentrations. The fact that the degradation rate increases proportionally with concentration despite the increased competition for hydroxyl radicals in the bulk solution shows that at higher concentrations decomposition occurs not only in the bulk liquid but also at the bubble-liquid interface. However, a linear relationship was not observed, as expected, for a first order kinetic law.

The initial degradation rate can be expected to be dependent on the concentration of OH radicals produced and the concentration of the dye molecules at the interface of the cavitation bubble. At the surface of the collapsed bubble, the OH radical concentration

is remarkably high [17]. At lower dye concentrations, a considerable part of these OH radicals will recombine yielding H$_2$O$_2$ and the degradation is carried out in the bulk of the solution where there is a lower concentration of OH radicals because only about 10% of the OH radicals generated in the bubble can diffuse into the bulk solution [18], which conduct to lower degradation rates. On an increase in the dye concentration, the probability of OH radical attack on RhB molecules increases, thus leading to an increase in the degradation rate. However, if the dye molecules at higher concentration reach a saturation limit at the bubble surface during the persistence time of the bubble, an almost constant degradation rate at higher solute concentrations is reached. At higher dye concentration, an increasing proportion of the OH radicals will be scavenged and the H$_2$O$_2$ yield progressively reduced and because RhB is a non-volatile compound, the sonochemical reaction with the hydroxyl radical is expected to take place at the cavitation bubble interface where the hydroxyl radical concentration attains an upper limit. In this work, H$_2$O$_2$ analysis [19] could not be carried out because of the colored solution of the dye.

In order to explain the local reaction zone in the interfacial region of cavitation bubbles, where RhB was degraded by high concentration of OH radicals, a heterogeneous kinetics model based on a Langmuir type mechanism was applied [20]. This model is given by the following equation [20]:

$$r = K_b + \frac{kKC_0}{1 + KC_0} \tag{1}$$

where K_b is a constant representing the rate of decomposition in the bulk liquid (mg L^{-1} min^{-1}), r is the initial degradation rate (mg L^{-1} min^{-1}), k is the pseudo-rate constant (mg L^{-1} min^{-1}), K is the equilibrium constant (L mg^{-1}) and C_0 (mg L^{-1}) is RhB initial concentration.

Expression (1) indicates that the rate of disappearance of the pollutant follows a concentration independent path and a concentration-dependent course [20]. In this model, the overall rate of solute decomposition r is the sum of the rates in the bulk solution and the interfacial layer and can be estimated by the observed concentration reduction within short time intervals.

The sonolytic degradation data was analyzed by non-linear curve fitting analysis method, using Microcal^{TM} Origin$^®$ software, to fit the kinetic model. The value of the model parameters are 11.76×10^{-3} L mg^{-1}, 1.899 mg L^{-1} min^{-1} and 15.42×10^{-3} mg L^{-1} min^{-1} for the equilibrium constant (K), the pseudo-rate constant (k) and rate of decomposition in the bulk liquid (K_b), respectively. A perfect description of the sonolytic destruction of RhB was obtained by the used model as shown in Fig. 3. These results indicate that the degradation of the dye most takes place at the bubble/solution interface by hydroxyl radical attack, whereas some radical reactions also occurred in the bulk of the solution.

3.1.2. Effect of power

In order to investigate the influence of ultrasonic power on the sonolytic degradation of RhB, experiments were conducted by varying ultrasonic power from 20 to 60 W and using 300 mL of 5 mg L^{-1} RhB aqueous solution. Fig. 4 shows the effect of ultrasonic power on sonochemical degradation of RhB. The obtained results clearly demonstrate that an increase in ultrasonic power results in an increase in sonochemical reactivity. The increase in dye degradation with an increase in ultrasonic power may be explained by the increase in the number of active cavitation bubbles. So because of the increasing acoustic amplitudes, degradation of dye increased. When power is increased, transmittance of ultrasonic energy into the reactor increases. Due to this energy, the pulsation and collapse of bubble occur more rapidly, the number of cavitation bubbles increase and realizing a higher concentration of OH radicals into
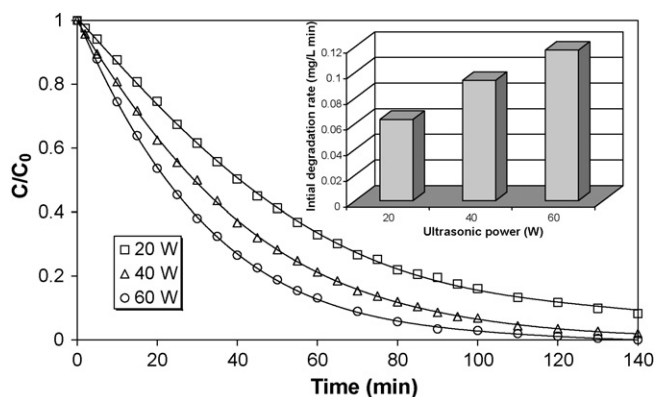
Fig. 4. Effect of ultrasonic power on sonochemical degradation of RhB (conditions: volume: 300 mL; initial dye concentration: 5 mg L^{-1}; temperature: 25 °C; pH: 5.3; frequency: 300 kHz).

Fig. 7. Effect of temperature on sonochemical degradation of RhB (conditions: volume: 300 mL; initial dye concentration: 5 mg L^{-1}; pH: 5.3; frequency: 300 kHz; power: 60 W).
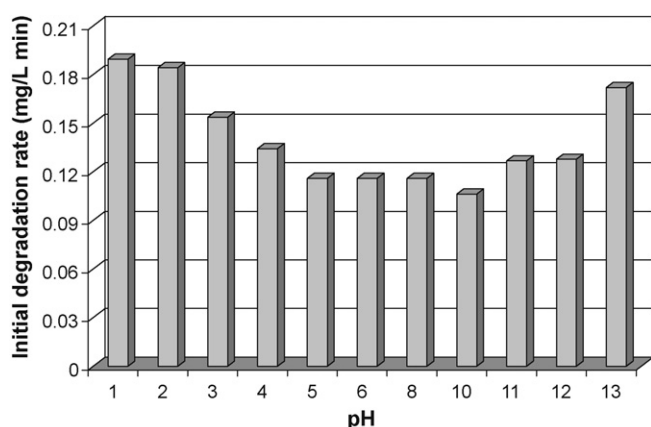

Fig. 5. Effect of pH on sonochemical degradation of RhB (conditions: volume: 300 mL; initial dye concentration: 5 mg L^{-1}; temperature: 25 °C; frequency: 300 kHz; power: 60 W).

the dye solution. Thus, an increase in ultrasonic power results in an increase in acoustic amplitude, which favors more violent cavitation bubble collapse because the bubble collapse time, the transient temperature, and the internal pressure in the cavitation bubble during collapse are all dependent on the acoustic amplitude [21]. That is, high enough ultrasonic power results in transient cavitation. Hence, the results of an increase in the sound power are greater sonochemical effects, resulting in higher degradation rates.

3.1.3. Effect of pH

The effect of pH was investigated by sonication of 5 mg L^{-1} RhB at different pH in the range 1–13. Fig. 5 shows the effect of pH on
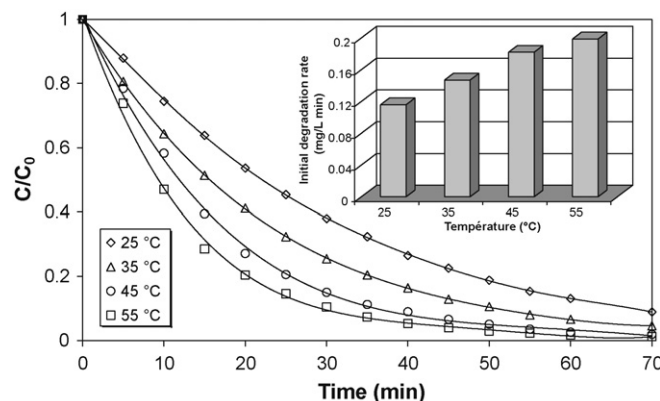
sonochemical degradation of RhB. The results indicated that the ultrasonic degradation rates in strong acidic water (pH 1–3) are higher than those obtained in higher pH aqueous solutions (pH 4–10). Degradation rates decrease from pH 1 to 5, and there is almost no change in the pH range 5–8. The lower degradation is observed at pH 10. Higher initial degradation rates are obtained in strong basic water (pH 11–13). It was observed that λ_{max} for the dye changed very little in the pH range 1–13. The obtained λ_{max} for RhB were 553 nm at pH 1–2, 552 nm at pH 3 and 551 at pH 4–13. In polar solvents, RhB is known to exist in two principal forms, viz., in cationic (RhB$^+$) or in zwitterionic form (RhB$^\pm$), as indicated in Fig. 6. At pH values higher than pKa of RhB (3.7 [20]), the carboxyl group of cationic form (RhB$^+$) is deprotonated and the dye is transformed into zwitterionic form (RhB$^\pm$) [22,23]. These two forms have nearly the same absorption spectrum. The hydrophylic character of RhB is lowest at very low pH conditions where the compound is in its cationic form, and the degradation rate of RhB is highest at the low pH. High pH solutions undergo sonolytic degradation at a much slower rate. In higher pH solutions, RhB is present in its zwitterioned form and does not readily accumulate at the bubble interface. In strong acidic pH, RhB exists in higher concentrations at the bubble interface and thus, is more readily subjected to the OH radical attack. The enhancement of degradation rate in strong basic conditions (pH 11–13) may be caused by the change of hydrophobic property of the dye.

3.1.4. Effect of temperature

The effect of temperature on the sonolytic degradation of RhB was investigated and the results are shown in Fig. 7. It can be observed that the degradation of RhB increases with the increase in temperature. The raise in temperature from 25 to 55 °C results in a 1.7-fold increase in the initial rate of RhB degradation. The increase
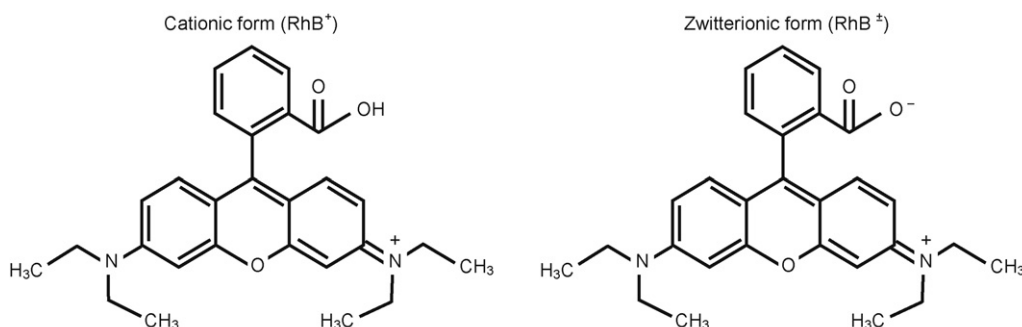

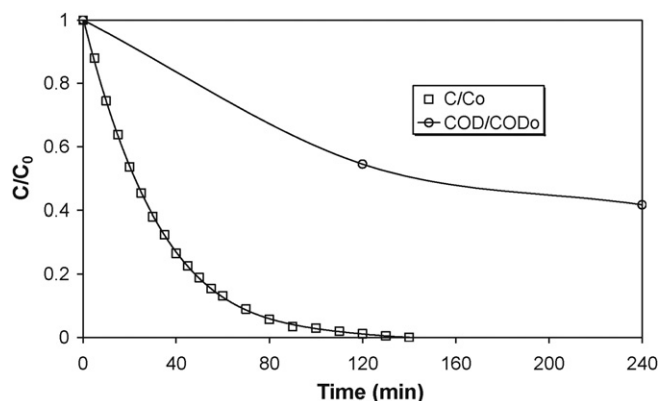**Fig. 6.** Forms of Rhodamine B in water.

Fig. 8. RhB and COD removal during ultrasonic treatment of RhB solution (conditions: volume: 300 mL; initial dye concentration: 5 mg L^{-1}; temperature: 25 °C; pH: 5.3; frequency: 300 kHz; power: 60 W).

of aqueous temperature certainly increases the number of cavitation bubbles on sonolysis and thus the rate of production of radicals though results in a lowering of the cavitation threshold due to the rise in vapor pressure associated with heating of the liquid [24].
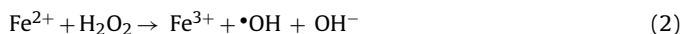
3.1.5. COD removal

Evolution of the initial compound concentration and chemical oxygen demand (COD) of a 5 mg L^{-1} RhB solution were determined to evaluate the pollutant elimination and COD removal respectively (Fig. 8). It can be observed from this figure that the RhB aqueous solution was decolorized after 140 min of irradiation but the oxidation is a relatively slow process with COD decrease being as low as about 45 and 58% after 120 and 240 min of sonication respectively. COD was not completely removed under the ultrasonic action even with a long treatment period (240 min). These results underline the fact that degradation products of RhB are recalcitrant toward sonochemical treatment. This is due to the fact that the intermediate products have very low probabilities of making contact with OH radicals, which react mainly at the interface of the bubble. Thus, the sonochemical action that gives rise to products bearing more hydroxyl (or carboxylic) groups is of low efficiency toward COD abatement.

3.2. Effect of various additives

3.2.1. Effect of iron addition

The influence of elemental, bivalent and trivalent iron on the sonolytic degradation of RhB was studied. The initial degradation rate for the sonolytic degradation of RhB as a function of the concentration of Fe^0, Fe(II) and Fe(III) are illustrated in Fig. 9. In these systems, the ultrasonic degradation of RhB was enhanced by iron addition. The acceleration effect of iron on the degradation rate displayed the following order: Fe(II) > Fe(III) > Fe^0. Enhancement of degradation by Fe(II) or Fe(III) addition in a catalytic amount was due to H$_2$O$_2$ decomposition and OH radical generation in the Fenton (Fe(II)/H$_2$O$_2$) and Fenton-like (Fe(III)/H$_2$O$_2$) processes (reactions (2)–(6)).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^\bullet OH + OH^- \qquad (2)$$

$$Fe^{2+} + {}^\bullet OH \rightarrow Fe^{3+} + OH^- \qquad (3)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe-OOH^{2+} + H^+ \qquad (4)$$

$$Fe-OOH^{2+} \rightarrow Fe^{2+} + HOO^\bullet \qquad (5)$$

$$Fe^{3+} + HOO^\bullet \rightarrow Fe^{2+} + O_2 + H^+ \qquad (6)$$

The rate enhancements in the presence of Fe^0 in the sonication process could be attributed to the iron solid effect and Fe(II)-
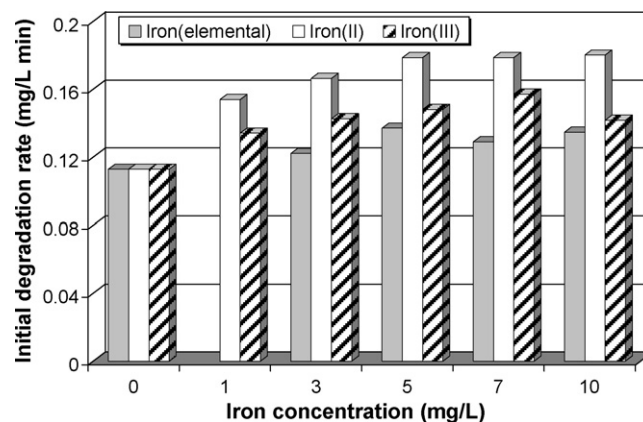

Fig. 9. Effect of iron addition (elemental, bivalent and trivalent) on sonochemical degradation of RhB (conditions: volume: 300 mL; initial dye concentration: 5 mg L^{-1}; temperature: 25 °C; pH: 3; frequency: 300 kHz; power: 60 W).

catalytic with promoting the production of OH radicals, as shown in reactions (7) and (8), resulting in the increase in the degradation efficiency of RhB. Furthermore, ultrasound increased the adsorption of RhB on iron particles by the enhancement of mass transfer by high-speed microjets, high-pressure shock waves and acoustic vortex microstreaming [25–27].

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \qquad (7)$$

$$2Fe^0 + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 2H_2 + 4OH^- \qquad (8)$$
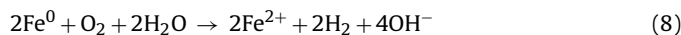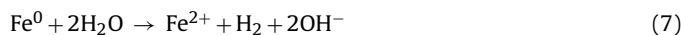
In the presence of Fe(II), the degradation rate increased with the increase of Fe(II) concentration up to a maximum at 5 mg L^{-1} Fe(II). No further enhancement of the sonolytic degradation was observed at concentrations over 5 mg L^{-1} Fe(II), because of the direct scavenging effect of the hydroxyl radical by the excessive quantity of Fe(II) (reaction (3)). In the presence of Fe(III), the maximum degradation rate was observed at a concentration of 7 mg L^{-1} Fe(III). It can be expected that Fe–OOH^{2+} as an intermediate produced from the reaction of Fe(III) with H$_2$O$_2$ may be partitioned as Fe(II) and HOO$^\bullet$ by the ultrasonic irradiation (reactions (4) and (5)). The regenerated Fe(II) also catalyzes the decomposition of H$_2$O$_2$. The concentration of Fe(II) would be held constant as a function of the Fe(III) concentration.

The acceleration effect of iron on the destruction rate displayed the following order: Fe(II) > Fe(III) > Fe^0. For Fe(II), because the beginning of the reaction between Fe(II) and H$_2$O$_2$ (Eq. (2)) during the initial step is faster, the degradation of RhB rapidly occurs. For Fe(III) and Fe^0, the overall degradation of dye is slower.

3.2.2. Effect of carbon tetrachloride addition

Ultrasonic degradation of RhB was investigated in the presence of different concentrations of carbon tetrachloride ranging from 50 to 200 mg L^{-1}. The obtained results were presented in Fig. 10. It was clear that the degradation of dye was appreciably enhanced by the addition of CCl$_4$. This improvement is due to the degradation of CCl$_4$ by pyrolytic cleavage in cavitation bubbles, which conducts to the release of oxidizing agents that can react with dye molecules. The sonolytic degradation of CCl$_4$ has been studied by several research groups [28–31]. The overall reaction mechanism can be written as [28–31]

$$CCl_4 \rightarrow {}^\bullet CCl_3 + {}^\bullet Cl \qquad (9)$$

$$CCl_4 \rightarrow {:}CCl_2 + Cl_2 \qquad (10)$$

$${}^\bullet CCl_3 \rightarrow {:}CCl_2 + {}^\bullet Cl \qquad (11)$$

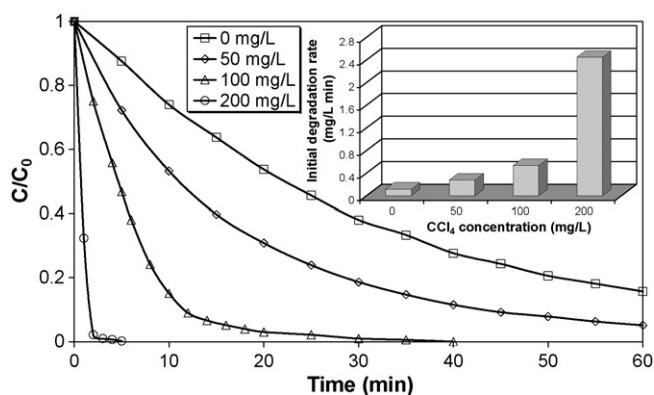$${}^\bullet CCl_3 + {}^\bullet CCl_3 \rightarrow CCl_4 + {:}CCl_2 \qquad (12)$$

Fig. 10. Effect of carbon tetrachloride addition on sonochemical degradation of RhB (conditions: volume: 300 mL; initial dye concentration: 5 mg L^{-1}; temperature: 25 °C; pH: 5.3; frequency: 300 kHz; power: 60 W).

$$\bullet CCl_3 + \bullet CCl_3 \rightarrow C_2Cl_6 \tag{13}$$

$$: CCl_2 + : CCl_2 \rightarrow C_2Cl_4 \tag{14}$$

$$\bullet Cl + \bullet Cl \rightarrow Cl_2 \tag{15}$$

$$Cl_2 + H_2O \rightarrow HClO + HCl \tag{16}$$

The sonolytic degradation of CCl$_4$ generates $\bullet$Cl radicals that will lead to a series of recombination reactions conducting to the formation of additional active species, such as HClO, Cl$_2$ and chlorine-containing radicals ($\bullet$Cl, $\bullet$CCl$_3$ and :CCl$_2$), having strong oxidizing property, which will markedly accelerate the degradation of RhB in aqueous solution.

From Fig. 10, it was clear that the destruction rate increased with increasing the concentration of CCl$_4$. It was also found that the initial degradation rate became 2.4 times larger by the addition of 50 mg L^{-1} of CCl$_4$ and 4.6 times larger by the addition of 100 mg L^{-1} of CCl$_4$ and 21 times larger by the addition of 200 mg L^{-1} of CCl$_4$, respectively. Further studies are needed to optimize the concentration of CCl$_4$ and in order to prevent residual amount of CCl$_4$ in the final discharge effluent stream.

3.2.3. Effect of hydrogen peroxide addition

In order to investigate the effect induced from the addition of H$_2$O$_2$, the sonolytic degradation of RhB at 5 mg L^{-1} in the presence of 50–1000 mg L^{-1} H$_2$O$_2$ was performed. These results are illustrated in Fig. 11. The rate of dye degradation was increased by the addition of H$_2$O$_2$ to the ultrasound system. This is due to the decomposition of hydrogen peroxide into hydroxyl radicals causing high
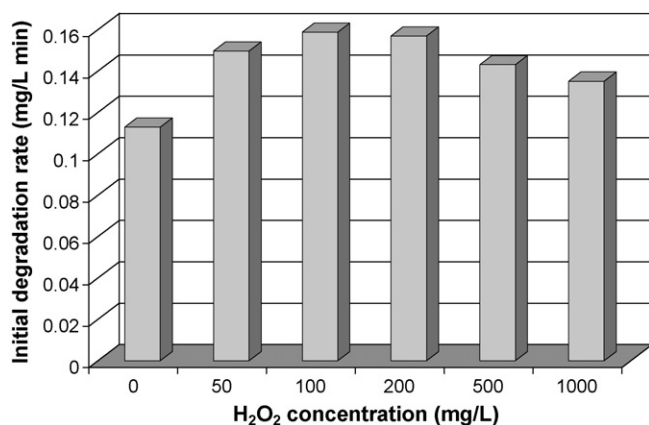
degradation rate [32,33]. The degradation rate increased with the increase of H$_2$O$_2$ concentration up to 100 mg L^{-1} and decreased afterward.

In order to evaluate the effect of H$_2$O$_2$ alone on the degradation of RhB, control experiments were carried out by adding H$_2$O$_2$ from an external source in a continuously stirred 300 mL solution containing 5 mg L^{-1} of RhB. The dosage of added hydrogen peroxide (50–1000 mg L^{-1}) was the same as the amounts used in the presence of ultrasound. The results indicate that a similar dosage of H$_2$O$_2$ in absence of ultrasound produce low degradation of RhB, even after long times (240 min). Thus, hydrogen peroxide alone has a very limited effect on the degradation rate of RhB.

As the addition of hydrogen peroxide in the presence of ultrasound enhances the degradation rate of RhB due to additional free radicals generation, it can be concluded that the controlling mechanism of RhB degradation is the free radical attack. The degradation rate was not appreciably increased by the addition of H$_2$O$_2$, although its concentration was much higher than that of RhB. The H$_2$O$_2$ may be mainly present not inside the cavitation bubbles but in the bulk solution due to the high water solubility and the low volatility. The lower intensification of degradation rate in the presence of high concentrations of H$_2$O$_2$ may be attributed to the increased level of OH radical scavenging by H$_2$O$_2$ itself (reaction (17)). As the concentration of H$_2$O$_2$ in the solution is increased from 200 to 1000 mg L^{-1}, its $\bullet$OH scavenging effect increased causing a decrease in the degradation of dye.

$$H_2O_2 + \bullet OH \rightarrow H_2O + HOO^\bullet \tag{17}$$
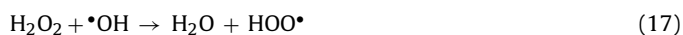
Similar results for the enhancement of sonolytic degradation of RhB in the presence of hydrogen peroxide were reported in literature [33,34].

3.2.4. Effect of tert-butyl alcohol addition

It is expected that the sonolytic degradation of RhB would mainly occur by hydroxyl radical attack. In order to investigate the dependence of the hydroxyl radical during the degradation of RhB by ultrasonic irradiation, the sonolytic degradation of RhB in the presence of tert-butyl alcohol, known as an effective hydroxyl radical scavenger, was performed. Extensive work on the sonochemistry of tert-butyl alcohol has been reported by Tauber et al. [35]. The tert-butyl alcohol is able to scavenge OH radicals in the bubble and prevent the accumulation of OH radicals at the interface of the bubble. The degradation results of RhB in the presence of tert-butyl alcohol are illustrated in Fig. 12. At low tert-butyl alcohol concentrations (7 and 20 mg L^{-1}), unexpectedly, the rate of dye degradation was accelerated. This enhancement may be attributed

Fig. 11. Effect of H$_2$O$_2$ addition on sonochemical degradation of RhB (conditions: volume: 300 mL; initial dye concentration: 5 mg L^{-1}; temperature: 25 °C; pH: 5.3; frequency: 300 kHz; power: 60 W).
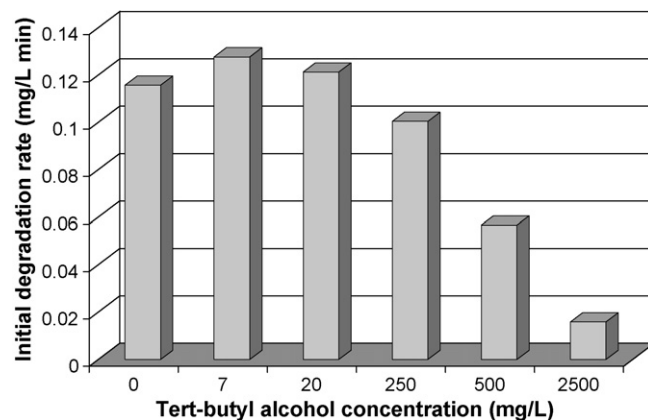

Fig. 12. Effect of tert-butyl alcohol addition on sonochemical degradation of RhB (conditions: volume: 300 mL; initial dye concentration: 5 mg L^{-1}; temperature: 25 °C; pH: 5.3; frequency: 300 kHz; power: 60 W).

to the relatively low dose of tert-butyl alcohol, at which competition for OH radical is unlikely and the rapid decomposition of the additive to produce reactive methyl radicals ($^\bullet CH_3$), which are the main products of high-temperature pyrolysis of the additive [36]. Additionally, tert-butyl alcohol, a surfactant substance, can reduce the surface tension of the liquid and thus reduce the cavitation threshold and facilitate the generation of bubbles and, therefore, the production of hydroxyl radicals. At high tert-butyl alcohol concentrations (250–2500 mg L^{-1}), the degradation was effectively quenched, but not completely, by the addition of tert-butyl alcohol, suggesting that the main mechanism of RhB destruction is chemical oxidation by hydroxyl radicals. The degradation efficiency of RhB decreased with the increase of concentration of tert-butyl alcohol in solution. Another factor that also affects the rate of RhB degradation is the formation of volatile products from the tert-butyl alcohol degradation that accumulate inside the bubble. Such volatile products decrease the temperature inside the bubble, which, in turn, slow the sonolytic reactions [35].

3.2.5. Effect of salt (Na₂SO₄) addition

Sonication experiments were conducted with RhB solutions including Na$_2$SO$_4$ to study the effect of salt addition on the degradation of dye at 5 mg L^{-1} and 25 °C. Fig. 13 presents the effect of Na$_2$SO$_4$ salt added on sonolytic degradation of RhB in aqueous solution. As it can be seen from Fig. 13, addition of Na$_2$SO$_4$ slightly enhanced the degradation of RhB up to 2 g L^{-1} when compared with the absence of Na$_2$SO$_4$ salt. The positive effect of Na$_2$SO$_4$ on the destruction of RhB decreased very slightly in the concentration range 2–5 g L^{-1}, but the initial degradation rate remained higher than that obtained without Na$_2$SO$_4$. So there may be an optimum amount of Na$_2$SO$_4$ to increase degradation rate. Addition of salt to dye aqueous solution pushes RhB molecules from the bulk aqueous phase to the bulk–bubble interface [37,38]. The presence of salt may increase the hydrophilicity, the surface tension and ionic strength of the aqueous phase and decrease the vapor pressure [37,38]. All these factors help in collapsing of the bubbles more violently, resulting in high degradation of dye. Excessive amount of Na$_2$SO$_4$ may interfere with the introduction of ultrasound into the liquid [39].

3.2.6. Effect of sucrose and glucose addition

The sonolytic degradation of RhB solutions was investigated in the presence of organic competitors such as sucrose (water solubility: 2.1×10^3 g L^{-1}, K_{ow}: 2×10^{-4}, Henry's law constant: 4.4×10^{-22} atm m^3 mol^{-1}) and glucose (water solubility: 0.661×10^3 g L^{-1}, K_{ow}: 1.5×10^{-3}, Henry's law constant:

Fig. 13. Effect of sodium sulfate addition on sonochemical degradation of RhB (conditions: volume: 300 mL; initial dye concentration: 5 mg L^{-1}; temperature: 25 °C; pH: 5.3; frequency: 300 kHz; power: 60 W).
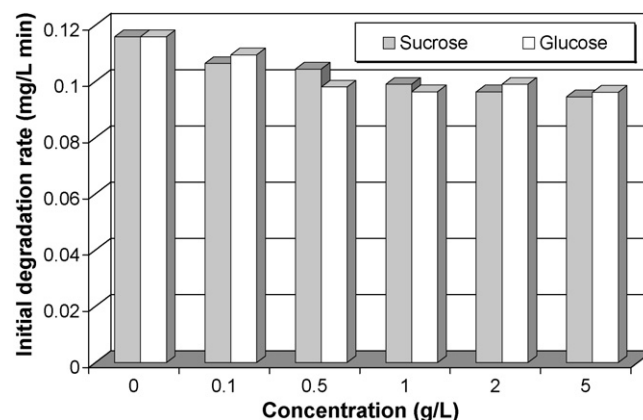

Fig. 14. Effect of sucrose and glucose addition on sonochemical degradation of RhB (conditions: volume: 300 mL; initial dye concentration: 5 mg L^{-1}; temperature: 25 °C; pH: 5.3; frequency: 300 kHz; power: 60 W).

4.28×10^{-20} atm m^3 mol^{-1}). The effect of sucrose and glucose addition (0.1–5 g L^{-1}) on the sonochemical degradation of RhB (5 mg L^{-1}) was shown in Fig. 14. It was observed that the sonolytic degradation of dye slightly decreased in the presence of sucrose and glucose. The slight decrease in the degree of RhB removal by an increase in the relative concentration of sucrose and glucose in the mixture is a clear indication of interfacial reactions of RhB with hydroxyl radical. The present study demonstrated that ultrasonic irradiation is a promising process for the removal of RhB from alimentary liquids containing sucrose and glucose.

4. Conclusion

The present work has shown that Rhodamine B (RhB) can be effectively removed from water by 300 kHz ultrasound irradiation. This study demonstrates that RhB sonochemical degradation occurs mainly through reactions with hydroxyl radicals. It was found that the initial degradation rate increased with an increase in the initial dye concentration up to a certain value (300 mg L^{-1}), followed by almost constant sonolytic degradation rate for higher concentrations. Reaction rates are strongly affected by ultrasonic power, temperature and pH. COD of RhB solutions was not completely removed under the ultrasonic action even with a long treatment period (240 min). The degradation of RhB was enhanced by iron addition. The acceleration effect of iron on the degradation rate displayed the following order: Fe(II) > Fe(III) > Fe^0. The sonolytic degradation of RhB was drastically improved by the addition of CCl$_4$ via the formation of HClO, Cl$_2$ and chlorine-containing radicals ($^\bullet$Cl, $^\bullet$CCl$_3$ and:CCl$_2$), having strong oxidizing property. The destruction rate increased with increasing the concentration of CCl$_4$. The rate of dye degradation was increased by the addition of H$_2$O$_2$ to the ultrasound system. The degradation increased with the increase of H$_2$O$_2$ concentration up to a definite value (100 mg L^{-1}) and decreased afterward. In the presence of tert-butyl alcohol at low concentrations, unexpectedly, the rate of dye degradation was accelerated. At high tert-butyl alcohol concentrations, the degradation was effectively quenched, but not completely, by the addition of tert-butyl alcohol. The sonolytic degradation of dye decreased in the presence of sucrose and glucose. The slight decrease in the degree of RhB removal in the presence of high concentrations of sucrose and glucose in the mixture is a clear indication that ultrasonic treatment is a promising process for the removal of RhB from alimentary liquids containing sucrose and glucose.
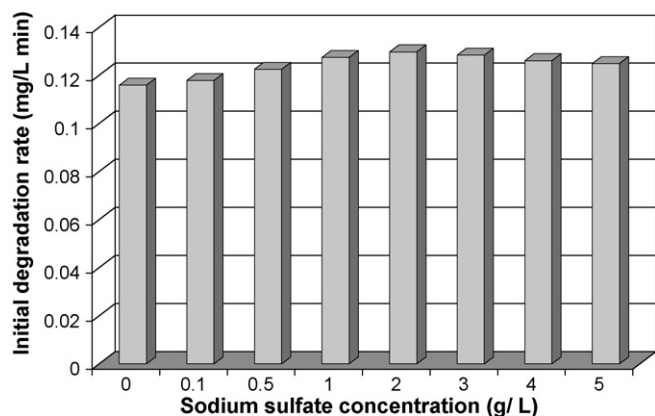
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References

[1] S.D. Richardson, C.S. Wilson, K.A. Rusch, Use of rhodamine water tracer in the marshland upwelling system, Ground Water 42 (2004) 678–688.
[2] J. Rochat, P. Demenge, J.C. Rerat, Toxicologic study of a fluorescent tracer: rhodamine b, Toxicol. Eur. Res. 1 (1978) 23–26.
[3] R. Jain, M. Mathur, S. Sikarwar, A. Mittal, Removal of the hazardous dye rhodamine B through photocatalytic and adsorption treatments, J. Environ. Manage. 85 (2007) 956–964.
[4] O. Hamdaoui, Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick, J. Hazard. Mater. B135 (2006) 264–273.
[5] A.J. Colussi, L.K. Weavers, M.R. Hoffmann, Chemical bubble dynamics and quantitative sonochemistry, J. Phys. Chem. A 102 (1998) 6927–6934.
[6] Y.G. Adewuyi, Sonochemistry: environmental science and engineering applications, Ind. Eng. Chem. Res. 40 (2001) 4681–4715.
[7] L.H. Thompson, L.K. Doraiswamy, Sonochemistry: science and engineering, Ind. Eng. Chem. Res. 38 (1999) 1215–1249.
[8] K.S. Suslick, The temperature of cavitation, Science 253 (1991) 1397–1399.
[9] E.J. Hart, A. Henglein, Free radical and free atom reactions in the sonolysis of aqueous iodide and formate solutions, J. Phys. Chem. 89 (1985) 4342–4347.
[10] E.J. Hart, A. Henglein, Sonochemistry of aqueous solutions: hydrogen–oxygen combustion in cavitation bubbles, J. Phys. Chem. 91 (1987) 3654–3656.
[11] L.K. Weavers, M.R. Hoffmann, Sonolytic decomposition of ozone in aqueous solution: mass transfer effects, Environ. Sci. Technol. 32 (1998) 3941–3947.
[12] M.R. Hoffmann, I. Hua, R. Höchemer, Application of ultrasonic irradiation for the degradation of chemical contaminants in water, Ultrason. Sonochem. 3 (1996) S163–S172.
[13] A. Henglein, Contributions to various aspects of cavitation chemistry, Adv. Sonochem. 3 (1993) 17–83.
[14] S. Koda, T. Kimura, T. Kondo, H. Mitome, A standard method to calibrate sonochemical efficiency of an individual reaction system, Ultrason. Sonochem. 10 (2003) 149–156.
[15] T.J. Mason, J.P. Lorimer, D.M. Bates, Quantifying sonochemistry: casting some light on a 'black art', Ultrasonics 30 (1992) 40–42.
[16] O. Thomas, N. Mazas, La mesure de la demande chimique en oxygène dans les milieux faiblement pollués, Analusis 14 (1986) 300–302.
[17] A. Tauber, H.-P. Schuchmann, C. von Sonntag, Sonolysis of aqueous 4-nitrophenol at low and high pH, Ultrason. Sonochem. 7 (2000) 45–52.
[18] M. Goel, H. Hongqiang, A.S. Mujumdar, M.B. Ray, Sonochemical decomposition of volatile and non–volatile organic compounds—a comparative study, Water Res. 38 (2004) 4247–4261.
[19] C. Kormann, D.W. Bahnemann, M.R. Hoffmann, Photocatalytic production of H_2O_2 and organic peroxides in aqueous suspensions of TiO_2, ZnO, and desert sand, Environ. Sci. Technol. 22 (1988) 798–806.
[20] N. Serpone, R. Terzian, H. Hidaka, E. Pelizzetti, Ultrasonic induced dehalogenation and oxidation of 2-, 3-, and 4-chlorophenol in air-equilibrated aqueous media. Similarities with irradiated semiconductor particulates, J. Phys. Chem. 98 (1994) 2634–2640.
[21] S.O. Owusu, Y.G. Adewuyi, Sonochemical removal of nitric oxide from flue gases, Ind. Eng. Chem. Res. 45 (2006) 4475–4485.
[22] S. Woislawski, The spectrophotometric determination of ionization constants of basic dyes, J. Am. Chem. Soc. 75 (1953) 5201–5203.
[23] R.W. Ramette, E.B. Sandell, Rhodamine B equilibria, J. Am. Chem. Soc. 78 (1956) 4872–4877.
[24] Y. Jiang, C. Pétrier, T.D. Waite, Sonolysis of 4-chlorophenol in aqueous solution: effects of substrate concentration, aqueous temperature and ultrasonic frequency, Ultrason. Sonochem. 13 (2006) 415–422.
[25] O. Hamdaoui, E. Naffrechoux, L. Tifouti, C. Pétrier, Effects of ultrasound on adsorption–desorption of p-chlorophenol on granular activated carbon, Ultrason. Sonochem. 10 (2003) 109–114.
[26] L. Nouri, O. Hamdaoui, Ultrasonication-assisted sorption of cadmium from aqueous phase by wheat bran, J. Phys. Chem. A 111 (2007) 8456–8463.
[27] O. Hamdaoui, Removal of cadmium from aqueous medium under ultrasound assistance using olive leaves as sorbent, Chem. Eng. Process. 48 (2009) 1157–1166.
[28] A. Bhatnagar, H.M. Cheung, Sonochemical destruction of chlorinated c1 and c2 volatile organic compounds in dilute aqueous solution, Environ. Sci. Technol. 28 (1994) 1481–1486.
[29] A. Francony, C. Pétrier, Sonochemical degradation of carbon tetrachloride in aqueous solution at two frequencies: 20 kHz and 500 kHz, Ultrason. Sonochem. 3 (1996) S77–S82.
[30] I. Hua, M.K. Hoffmann, Kinetics and mechanism of the sonolytic degradation of CCl_4: intermediates and byproducts, Environ. Sci. Technol. 30 (1996) 864–871.
[31] C. Pétrier, A. Francony, Ultrasonic waste-water treatment: incidence of ultrasonic frequency on the rate of phenol and carbon tetrachloride degradation, Ultrason. Sonochem. 4 (1997) 295–300.
[32] K.C. Teo, Y. Xu, C. Yang, Sonochemical degradation for toxic halogenated organic compounds, Ultrason. Sonochem. 8 (2001) 241–246.
[33] M.A. Behnajady, N. Modirshahla, S. Bavili Tabrizi, S. Molanee, Ultrasonic degradation of Rhodamine B in aqueous solution: influence of operational parameters, J. Hazard. Mater. 152 (2008) 381–386.
[34] A. Mehrdad, R. Hashemzadeh, Ultrasonic degradation of Rhodamine B in the presence of hydrogen peroxide and some metal oxide, Ultrason. Sonochem. 17 (2010) 168–172.
[35] A. Tauber, G. Mark, H.-P. Schuchmann, C. von Sonntag, Sonolysis of tert-butyl alcohol in aqueous solution, J. Chem. Soc., Perkin Trans. 2 (1999) 1129–1135.
[36] N.H. Ince, I. Gültekin, G. Tezcanli-Güyer, Sonochemical destruction of nonylphenol: effects of pH and hydroxyl radical scavengers, J. Hazard. Mater. 172 (2009) 739–743.
[37] J.D. Seymour, R.B. Gupta, Oxidation of aqueous pollutants using ultrasound: salt induced enhancement, Ind. Eng. Chem. Res. 36 (1997) 3453–3457.
[38] S. Findik, G. Gunduz, Sonolytic degradation of acetic acid in aqueous solutions, Ultrason. Sonochem. 14 (2007) 157–162.
[39] M. Dükkancı, G. Gündüz, Ultrasonic degradation of oxalic acid in aqueous solutions, Ultrason. Sonochem. 13 (2006) 517–522.