

Effects of sonication on decolorization of C.I. Reactive Red 198 in UV/ZnO system

Chung-Hsin Wu*

Department of Environmental Engineering, Da-Yeh University, 112, Shan-Jiau Road, Da-Tsuen, Chang-Hua, Taiwan, ROC

Received 21 June 2007; received in revised form 21 September 2007; accepted 21 September 2007

Available online 29 September 2007

Abstract

This study discusses the effects of ultrasound (US) irradiation on the decolorization of C.I. Reactive Red 198 (RR198) in UV/ZnO system. The influences of ZnO dosage, pH and the addition of NaCl or a radical scavenger were evaluated. The decolorization rate of RR198 increased with the ZnO dosage in 0.1–1 g/l and with pH in the UV/ZnO system. US accelerated the decolorization of RR198 in the UV-based system. The enhancement in the presence of NaCl can be attributed to an increase in the partitioning of RR198 upon cavitation implosion in US/ZnO system. At pH 7, the decolorization rate constants of UV/US/ZnO, UV/ZnO, US/ZnO, UV/US and US were 0.0739, 0.0534, 0.0022, 0.0020 and 0.0013 min⁻¹, respectively. The decolorization rate was effectively inhibited by adding 1-butanol to UV/ZnO and UV/US/ZnO systems, suggesting that the main mechanism of RR198 destruction is chemical oxidation by hydroxyl radicals in the bulk liquid. The experimental results revealed that the UV/US/ZnO system cannot only completely decolorize RR198 but can effectively mineralize RR198.

© 2007 Elsevier B.V. All rights reserved.

Keywords: UV; Sonication; Azo dye; ZnO; Radical scavenger

1. Introduction

Azo dyes constitute the largest group of industrial colorants. Textile dyeing wastewater usually contains high concentrations of coloring material. Removing color from wastewater is more important than treating other colorless organics because small amounts of dye are clearly visible and detrimental to the water environment. Hence, C.I. Reactive Red 198 (RR198), a dye that contains two of the most commonly used anchors – monochlorotriazine and vinyl sulfone groups – was employed as the parent compound. The treatment of dye-containing wastewater to decolorize it by such conventional methods as flocculation and coagulation is relatively ineffective, because dyes are highly soluble in water [1]. Advanced oxidation processes (AOPs) are alternative approaches for decolorizing and reducing the recalcitrant wastewater loads that are generated by textile companies. Most AOPs use ultraviolet (UV) irradiation to catalyze catalysts that involve the generation of an extremely powerful and non-selective oxidizing agent, the hydroxyl radical ($\bullet\text{OH}$), to

destroy hazardous pollutants. However, the utilization efficiency of UV is low because of the UV-screening effect of catalysts. This disadvantage can be overcome by utilizing ultrasound (US) irradiation. The US can effectively catalyze the same chemical reactions as the UV [2]. Additionally, the joint application of US and other AOPs have motivated some interesting studies that have improved degradation rates [3–9].

The application of ultrasonic energy has received increasing attention in recent years, particularly in the removal of toxic and hazardous organic compounds from contaminated water [6–9]. Ultrasonic irradiation causes acoustic cavitation, and bubble collapse produces intense local heating, high pressures, and very short lifetimes; these transient, localized hot spots drive high-energy chemical reactions [10]. Any solute or solvent in contact with or inside these cavities in the vapor form undergoes fragmentation, generating free radicals, and can be used to degrade toxic compounds. Ultrasonic cavitation in liquid–solid systems also has high-energy physical effects, including (i) the improvement of mass transfer, (ii) the fragmentation of friable solids, and (iii) the generation of surface damage at liquid–solid interfaces [10]. Three important regions exist for aqueous sonication. The first region is the interior of the collapsing cavitation bubbles; the second region is the interfacial boundary between the

* Fax: +886 5 5334958.

E-mail address: chunghsinwu@yahoo.com.tw.

gaseous and liquid phases, and the third region is the solution bulk [11]. Toxic compound degradation is typically achieved via a combination of pyrolytic reactions that occur inside or near the bubble and radical reactions in the liquid bulk [2,12].

Sonication is a relatively innovative AOP. The combination of US with other techniques such as UV [13], Fe^{2+} [12,14–17], Fe^{3+} [15], Fe^0 [17,18], TiO_2 [19,20], O_3 [7,21], H_2O_2 [22,23] and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ [16,22] can increase the decomposition efficiency of pollutant removal. Relatively few reports have used US in combination with photocatalytic degradation, with the exception of UV/US/ TiO_2 [3–6,8,9] and UV/US/ O_3 [7]. To date, no ready-made mechanism or satisfactory explanation exists for the sonocatalytic degradation of dyes in combination with a UV/ZnO system. This work evaluates the decolorization efficiency of UV/US/ZnO to improve our understanding of the degradation process and the corresponding reaction mechanisms. Although the degradation rate of C.I. Acid Red 91 is higher in a probe system than in an ultrasonic bath, the latter offers greater energy efficiency [24]. Moreover, the ultrasonic cleaning bath is the most widely used and economical source of US in the laboratory. An ultrasonic cleaning bath thus was selected as the US source in this study. This investigation has the following objectives: (i) to determine the effects of ZnO dosage in the UV/ZnO system; (ii) to elucidate the impact of pH in UV-based and US-based systems; (iii) to evaluate the effects of US in the UV/ZnO system; (iv) to investigate the effects of NaCl addition in the US/ZnO system and (v) to measure the effects of radical scavenger addition in UV/ZnO and UV/US/ZnO systems.

2. Materials and methods

2.1. Materials

The ZnO catalyst was sourced from Fluka. The diameter, specific surface area and band gap energy of ZnO were 27 nm, $4.6 \text{ m}^2/\text{g}$ and 2.92 eV (UV absorption threshold = 425 nm), respectively [25]. The parent compound, RR198, was obtained from Everlight Industrial Chemical Company. Table 1 presents the chemical structure and properties of RR198. The λ_{max} of

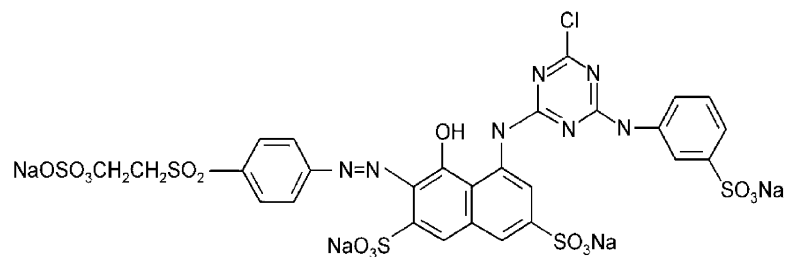
RR198 did not vary with pH [26]. 1-butanol was used as the hydroxyl radical scavenger. NaCl was selected to determine the enhancement of decolorization in the US/ZnO system. $\text{Ti}(\text{SO}_4)_2$ and H_2SO_4 were used to prepare the titanium complexing solution to determine the concentration of H_2O_2 . HNO_3 , H_2SO_4 and NaOH were obtained from Merck. NaCl, $\text{Ti}(\text{SO}_4)_2$ and 1-butanol were obtained from Katayama. Solution pH was controlled using HNO_3 and NaOH via an automatic titrator. All reagents were of analytical grade and used as purchased.

2.2. Decolorization experiments

The RR198 concentration was 20 mg/l in all experiments. Decolorization experiments were performed in a 31, hollow cylindrical glass reactor. A 15 W UVC lamp (254 nm, Philips) was placed inside the quartz tube as an irradiation source. The ultrasonic bath operated at 40 kHz and a US power of 400 W (Delta, DC 400H). The distance between the bottom of the reactor and the ultrasonic bath was fixed at 2 cm. ZnO doses of 0.1, 0.2, 0.5 and 1 g/l were utilized to determine the effect of ZnO dosage in the UV/ZnO system. The ZnO dose was 1 g/l in all US/ZnO-based systems. At pH 7, NaCl concentrations of 1 and 5 g/l were added to assess the influence of NaCl addition in the US/ZnO system; 1-butanol (300 and 1200 mg/l) was adopted to determine the effect of adding a radical scavenger in UV/ZnO and UV/US/ZnO systems. All systems were stirred at 260 rpm and aerated continuously; the temperature was controlled at 30°C using a water circulation system. Aliquots (15 ml) were withdrawn from the photoreactor at pre-specified intervals. The suspended ZnO particles were separated by filtering them through a $0.22 \mu\text{m}$ filter (Millipore). The RR198 concentration was measured using a spectrophotometer (Hitachi U-2001) at 520 nm. The H_2O_2 concentration generated in UV/ZnO and UV/US/ZnO systems was determined via the titanium complexing method that was proposed by Manousaki et al. [16]. Ionic chromatography (Dionex DX-120) was employed to determine the concentrations of sulfate and chloride anions during decolorization. Mineralization of RR198 was identified by the reduction in total organic carbon (TOC), as measured using an O.I. 1010 TOC analyzer.

Table 1
Structure and characteristics of RR198

Chemical structure



Formula
Molecular weight
 λ_{max}

$\text{C}_{27}\text{H}_{18}\text{ClN}_7\text{Na}_4\text{O}_{15}\text{S}_5$
967.5 g/mol
520 nm

3. Results and discussion

3.1. Decolorization in UV/ZnO system

3.1.1. Effects of ZnO dosage

The adsorption of ZnO and direct photolysis of RR198 were assessed at pH 7 and the experimental results revealed no significant disappearance of RR198 (data did not shown). Subsequent decolorization in UV-based systems was thus primarily attributable to photocatalytic reactions.

Fig. 1 plots the effects of ZnO dosage in the UV/ZnO system. Fig. 1(c) displays the UV-vis spectral changes of RR198 in a UV/ZnO system under various ZnO doses after 30 min reaction. Before treatment, the UV-vis spectra of RR198 exhibit three main absorption bands – two in the UV region (220 and 280 nm) and one in the visible region (520 nm). The UV band is characterized by two adjacent rings, and the visible band is associated with a long conjugated π system that is linked by two azo groups [27]. The decolorization of RR198 was simultaneously monitored at 220 and 520 nm in the UV/ZnO system. The removal percentage of RR198 increased with ZnO dosage; the visible band disappeared faster than the UV band. Plotting $\ln(C_0/C)$ as a function of time yields the decolorization rate constant (k). The k values of RR198 in a UV/ZnO system are consistent with first-order kinetics, and various studies have demonstrated that dye decolorization rates can generally be approximated as first-order kinetics [7,21,26,28,29]. The decolorization rate of RR198

Table 2

Effects of ZnO dosage in UV/ZnO system (RR198 = 20 mg/l and pH = 7)

Systems	k (min^{-1})	r^2
220 nm		
UV/ZnO (0.1 g/l)	0.0028	0.9711
UV/ZnO (0.2 g/l)	0.0044	0.9535
UV/ZnO (0.5 g/l)	0.0059	0.9774
UV/ZnO (1 g/l)	0.0112	0.9901
520 nm		
UV/ZnO (0.1 g/l)	0.0133	0.9356
UV/ZnO (0.2 g/l)	0.0211	0.9209
UV/ZnO (0.5 g/l)	0.0265	0.9264
UV/ZnO (1 g/l)	0.0534	0.9475

increased with ZnO dosage in the range 0.1–1 g/l (Table 2). Photogenerated holes and hydroxyl radicals are produced and the yield of holes and radicals increases with ZnO dosage. Hence, the proportion of hydroxyl radicals that attack RR198 and the reaction intermediates increases with ZnO dosage. However, adding a large amount of ZnO may reduce UV penetration and have a UV-screening effect, inhibiting photodegradation. This study found that the UV-screening effect of 1 g/l ZnO addition was negligible and was associated with the highest decolorization rate. Accordingly, 1 g/l ZnO was added in the following experiments.

For all of the systems tested herein, the absorption intensity at 520 nm declines extremely rapid; however, the UV bands at

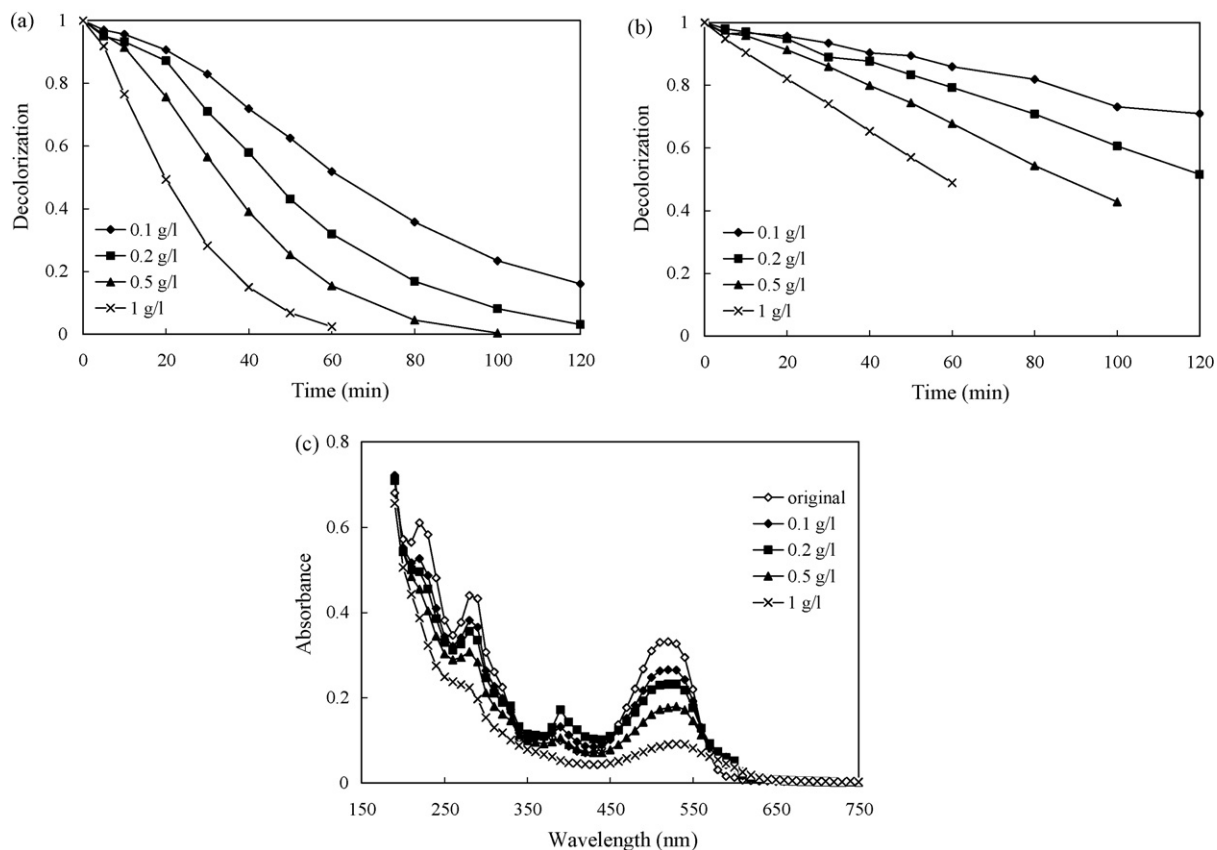


Fig. 1. Effects of ZnO dosage in UV/ZnO system (a) monitored by absorption at 520 nm, (b) monitored by absorption at 220 nm and (c) UV-vis spectra variations (RR198 = 20 mg/l and pH = 7).

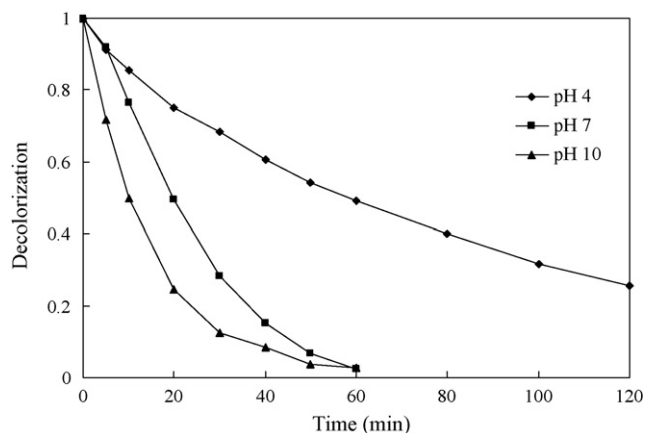


Fig. 2. Effects of pH in UV/ZnO system (RR198 = 20 mg/l and ZnO = 1 g/l).

220 nm and 280 nm disappeared more slowly than the visible band. The disappearance rate of the visible band is approximately five times that of the UV band (Table 2). The substantially high rate of decay of the visible band is attributed to the fact that hydroxyl radicals most effectively attack the azo-links in the photodegradation process. The decay of the absorbance at the UV band is considered to indicate aromatic fragment degradation in the dye molecule and its intermediates [21]. The hydroxyl radicals initially attack azo groups and open the N=N bonds, which are more easily destroyed than are aromatic structures. The experimental results were similar to those of previous studies [7,21,26,28] on azo dye decolorization.

3.1.2. Effects of pH

The decolorization efficiency of UV/ZnO system was determined at pH 4, 7 and 10 (Fig. 2). The k values for the UV/ZnO system increased with pH (Table 3). pH affects ZnO surface properties, dye dissociation and hydroxyl radical formation. Therefore, interpreting the effects of pH on degradation efficiency is extremely difficult. Since various mechanisms govern dye degradation, including hydroxyl radical attack, direct oxidation by positive holes, and direct reduction by electrons, the

Table 3

Reaction rate constants and correlation coefficients of various UV-based and US-based systems (RR198 = 20 mg/l and ZnO = 1 g/l)

Systems	k (min ⁻¹)	r^2
US (pH 4)	0.0007	0.9843
US (pH 7)	0.0013	0.9568
US (pH 10)	0.0036	0.7852
UV/US (pH 4)	0.0016 (0.56) ^a	0.9911
UV/US (pH 7)	0.0020 (0.35) ^a	0.9895
UV/US (pH 10)	0.0042 (0.14) ^a	0.8269
UV/ZnO (pH 4)	0.0116	0.9947
UV/ZnO (pH 7)	0.0534	0.9475
UV/ZnO (pH 10)	0.0637	0.9934
US/ZnO (pH 7)	0.0022 (0.41) ^a	0.9128
UV/US/ZnO (pH 7)	0.0739 (0.26) ^a	0.9659
UV/US/ZnO (pH 10)	0.0944 (0.29) ^a	0.9968

^a () presents the synergistic coefficient and synergistic coefficient = $\frac{k_{(\text{system A}+\text{system B}+\text{system C})} - k_{(\text{system A}+\text{system B})} - k_{(\text{system A}+\text{system C})}}{k_{(\text{system A}+\text{system B}+\text{system C})}}$.

effect of pH on degradation efficiency differs from that of photocatalysts and model substrates. Hydroxyl anions in alkaline solution typically act as scavenger of holes on the surface of ZnO particles and become hydroxyl radicals with strong oxidation ability after they lose one electron. Consequently, the probability of generating hydroxyl radicals increases with pH [19,20], explaining why the degradation rate of RR198 increases with pH in the UV/ZnO system. Notably, the k value of UV/ZnO system at pH 4 was markedly lower than that at pH 7 or 10. ZnO is a poor photocatalyst in the oxidative degradation at pH 4 because it corrodes in aqueous acidic media, a finding that was consistent with earlier investigations [30,31]. Therefore, the following ZnO-based experiments were performed only at pH 7 and 10.

3.2. Decolorization in US-based systems

Fig. 3 plots the decolorization of RR198 in US and UV/US systems. The k values of US and UV/US systems both increased with pH. Furthermore, UV increases the decolorization rate in a US system (Table 3). The following chain reactions occur in the sonication of pure water [2]:



Eqs. (5)–(10) describe additional reactions in the presence of oxygen [32].

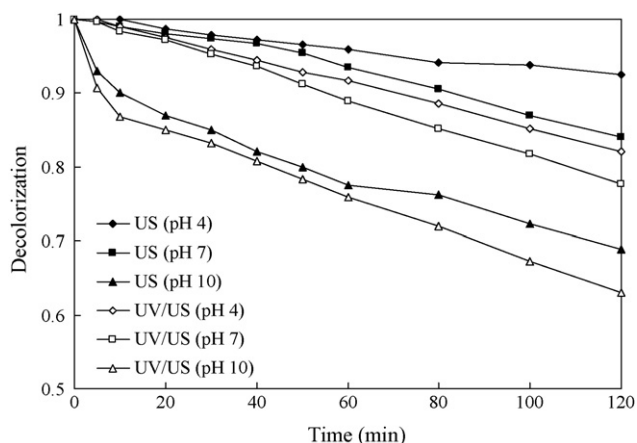
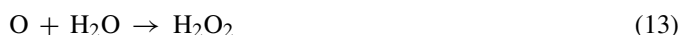


Fig. 3. Effects of pH in US and UV/US systems (RR198 = 20 mg/l).

Under US irradiation, water is pyrolyzed, in which process hydrogen radicals ($\bullet\text{H}$), hydroxyl radicals ($\bullet\text{OH}$), oxygen radicals ($\bullet\text{O}$) and hydroperoxyl radicals ($\bullet\text{O}_2\text{H}$) are produced and then react with RR198 in the bulk solution or at the interface between the bubbles and the liquid phase. During aqueous US irradiation, hydroxyl radicals form during the thermolytic reactions of water and self-recombine to form H_2O_2 (Eq. (3)). Additionally, ozone is produced in the presence of oxygen under US irradiation (Eq. (6)). Combining ozone with UV promotes RR198 degradation via the direct and indirect production of hydroxyl radicals (Eqs. (11)–(14)) [33]:



Hence, UV accelerated the decolorization of RR198 in the US system. Naffrechoux et al. [13] proposed that combining UV and US yields synergies and could be explained by the concurrent action of three oxidation mechanisms – (i) photodegradation, (ii) sonodegradation and (iii) ozone oxidation. Ma et al. [34] investigated synergies associated with the combination of visible light and US irradiation.

The effects of NaCl addition were evaluated in US/ZnO at pH 7 (Fig. 4). As presented in Fig. 4, the decolorization degree of RR198 increases with concentration of NaCl. NaCl addition increases the ionic strength of the aqueous phase, driving the organic compounds to the bulk-bubble interface [24]. The enhancement of the presence of NaCl can be attributed to the increase in partitioning of the pollutant species upon cavitation implosion. Beyond the partitioning enhancement, the presence of salt reduces vapor pressure and increases surface tension [23,35]. All of these factors help to collapse the bubbles more violently, causing high pollutant degradation. Previous studies yielded similar results for organ-

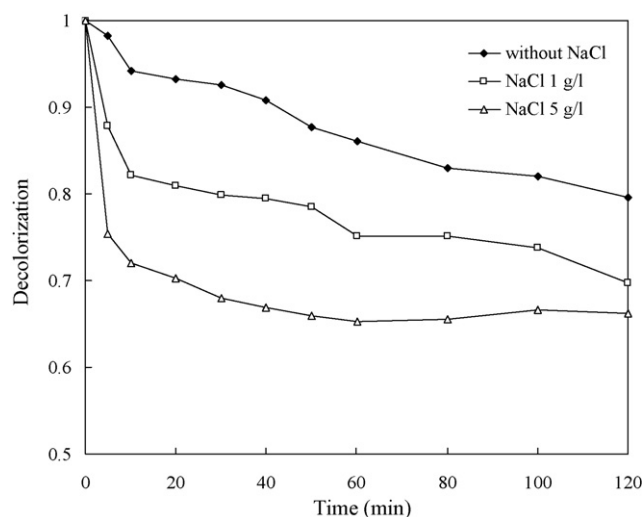


Fig. 4. Effects of NaCl addition in US/ZnO system (RR198 = 20 mg/l, ZnO = 1 g/l and pH = 7).

ics degradation in the presence of NaCl in US-based systems [23,24,35].

The k value of US/ZnO (0.0022 min^{-1}) exceeded that of US (0.0013 min^{-1}) (Table 3). The following explanations are suggested for US/ZnO system: (i) US acted as a deaggregator by microstreaming and causing microbubble collapse, which induced surface cleaning of the ZnO particles; (ii) the presence of an additional liquid–solid interface in the liquid bulk promotes cavitation, and (iii) US-accelerated mass transfer occurs between the solution phase and the ZnO surface. Accordingly, the decolorization rate obtained using US/ZnO exceeded that obtained using US. Keck et al. [36] reported that particle addition increases the reaction rate to double that without particles. Wang et al. [19,20] proposed that US irradiation can cause the formation of US-induced luminescence at a wavelength of below 375 nm, can excite the ZnO particle as a photocatalyst and produce hydroxyl radicals with high oxidative activity on the surface of the ZnO particles.

Fig. 5 plots the effect of pH on the decolorization rate of RR198 in UV/US/ZnO. The effect of pH on the k values in the UV/ZnO system was identical to that in the UV/US/ZnO system. At pH 7, the k values followed the order UV/US/ZnO > UV/ZnO > US/UV > US; the order was the same at pH 10 (Table 3). The experimental results clearly indicate that US irradiation accelerated RR198 decolorization in the UV/ZnO system. Sonication may increase the photocatalytic reaction rate in a nonspecific manner by increasing the catalytic activity of the catalyst. This phenomenon occurs by reducing the size of the photocatalyst particles following particle deaggregation, increasing the surface area and therefore the catalytic performance [3,4,6]. Additionally, the synergistic effect of UV/US/ZnO can also be attributed to (i) the increased production of hydroxyl radicals by US, (ii) the enhanced mass transfer of organics between the liquid phase and the catalyst surface and (iii) the excitation of the catalyst by US-induced luminescence (<375 nm) [6,9], as was explained for the US/ZnO system. Numerous studies have demonstrated that combining the action of US irradiation and UV-assisted photocatalysis yielded synergistic effects [4–6,8,9].

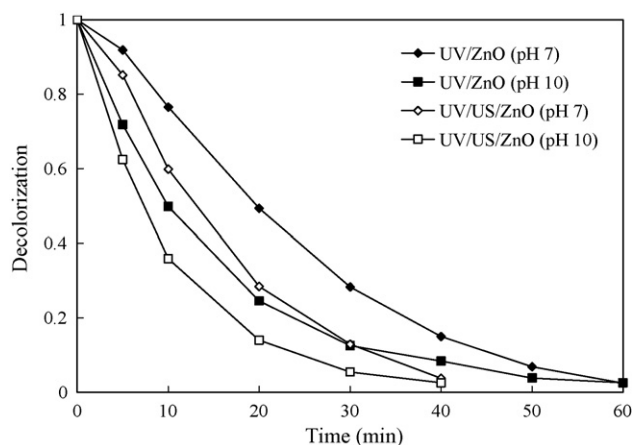


Fig. 5. Comparisons of decolorization efficiency in UV/ZnO and UV/US/ZnO systems (RR198 = 20 mg/l and ZnO = 1 g/l).

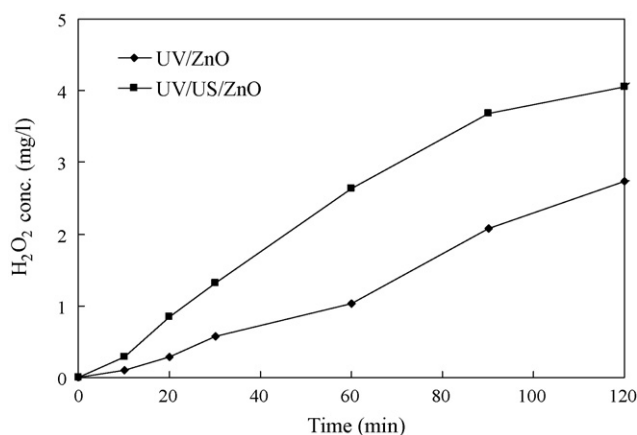


Fig. 6. H_2O_2 generated concentration in UV/ZnO and UV/US/ZnO systems (RR198 = 20 mg/l ZnO = 1 g/l and pH = 7).

Fig. 6 plots the H_2O_2 concentration that is generated in UV/ZnO and UV/US/ZnO systems. The concentration of H_2O_2 clearly increased linearly with the reaction time in both systems. After 120 min of reaction, the H_2O_2 concentrations in the UV/ZnO and UV/US/ZnO systems were 2.7 and 4.1 mg/l, respectively. Under UV irradiation, the generated H_2O_2 can decompose to hydroxyl radicals (Eq. (14)). Therefore, the radical concentration in UV/US/ZnO exceeded that of UV/ZnO, causing the decolorization rate of RR198 in UV/US/ZnO to exceed that of UV/ZnO. Jiang et al. [37] indicated that the rates of 4-chlorophenol degradation increased with H_2O_2 formation rate in the US system.

Fig. 7 presents the effects of adding radical scavengers in the UV/ZnO and UV/US/ZnO systems. Adding 1-butanol in UV/ZnO and UV/US/ZnO systems reduced the decolorization rate (Fig. 7). The k values of UV/ZnO upon adding 300 and 1200 mg/l 1-butanol were 0.0121 and 0.0083 min^{-1} , respectively, while those of UV/US/ZnO were 0.0195 and 0.0063 min^{-1} , respectively. Previous investigations have demonstrated that butanol quenches hydroxyl radicals, reducing photodegradation rate [14,16,18]. Small quantities of 1-butanol suppress RR198 decolorization. Experimental findings imply that hydroxyl radicals significantly affect the rate of RR198 decolorization. However, decolorization is not completely prevented by adding 1200 mg/l 1-butanol. This experimental result suggests that decolorization involves another reactive species that does not react with 1-butanol. This species is most likely the photogenerated holes that are produced on irradiated ZnO. The inhibition by adding 1-butanol indicates that the primary decolorization pathway involves hydroxyl radicals, and that direct oxidation by photogenerated holes is probably significant in the UV/ZnO-based system. Several studies have presented similar results [38,39]. Since RR198 is highly soluble in water, and thus hydrophilic, its partitioning into the gas phase is unlikely and direct pyrolysis should be a very minor reaction path in a UV/US/ZnO system. Hence, the main route for the destruction of azo dyes is chemical oxidation by hydroxyl radicals in the bulk liquid and/or the interface region of the cavitation bubbles [9,28].

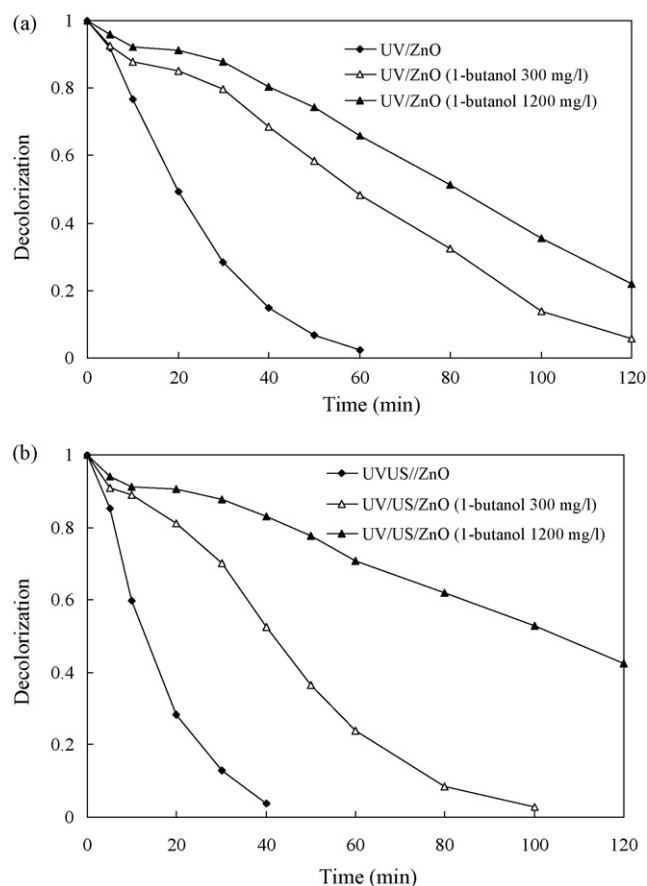


Fig. 7. Effects of radical scavenger addition in UV/ZnO and UV/US/ZnO systems (a) UV/ZnO and (b) UV/US/ZnO (RR198 = 20 mg/l, ZnO = 1 g/l and pH = 7).

Table 4 presents the concentrations of Cl^- , SO_4^{2-} and TOC in UV/ZnO and UV/US/ZnO systems after 240 min reaction. The concentration of dissociated sulfate in the UV/US/ZnO system markedly exceeded that in the UV/ZnO system. Despite the fact that RR198 is completely decolorized after it has reacted for 120 min in the UV/ZnO and UV/US/ZnO systems at pH 7, the dissociated concentrations of Cl^- and SO_4^{2-} in UV/ZnO and UV/US/ZnO systems were below their respective theoretical values. Mahmoodi et al. [40], who determined that the dissociated concentrations of Cl^- and SO_4^{2-} of 50 mg/l RR198 in a UV/ TiO_2 / H_2O_2 system after irradiation of 240 min were 2.5 and 9.5 mg/l, respectively, obtained experimental results that were also less than the theoretical values. This finding may be explained by the following two factors: (i) dissociated Cl^- and SO_4^{2-} were adsorbed onto catalyst surfaces and (ii) Cl and S atoms were incorporated into intermediates. Mahmoodi

Table 4
Analyses of IC and TOC in UV/ZnO and UV/US/ZnO systems (RR198 = 20 mg/l, ZnO = 1 g/l, reaction time = 120 min and pH 7)

Unit (mg/l)	Theoretical value	UV/ZnO	UV/US/ZnO
Cl^-	0.73	0.27	0.30
SO_4^{2-}	9.92	2.05	4.35
TOC	6.70	3.75	1.48

et al. [40] further demonstrated that the primary intermediates of RR198 in the advanced oxidation process were formate and oxalate anions, which were further oxidized slowly to CO₂. In this study, after 120 min of a reaction, the TOC degradation efficiency exceeded 75% in UV/US/ZnO system (Table 4). The experimental results indicated that the UV/US/ZnO system not only decolorizes RR198 totally but also mineralizes RR198 effectively.

4. Conclusion

This study investigated the sonocatalytic degradation of RR198 and evaluated the decolorization efficiency of US, UV/US, UV/ZnO, US/ZnO and UV/US/ZnO systems. The removal percentage of RR198 increased with ZnO dosage; the disappearance of the visible band exceeded that of the UV band. The *k* values of US, UV/US, UV/ZnO and UV/US/ZnO systems all increased with pH. At pH 7, the *k* values followed the order UV/US/ZnO > UV/ZnO > US/ZnO > US/UV > US. Adding NaCl increased decolorization in the US/ZnO system; conversely, adding 1-butanol inhibited decolorization of RR198 in UV/ZnO and UV/US/ZnO systems. The experimental results revealed that the primary decolorization pathway involves hydroxyl radicals, and that direct oxidation by photogenerated holes is probably significant in the UV/ZnO-based system. This work indicated that the combination of US irradiation with the UV/ZnO system effectively decolorizes and mineralizes RR198.

Acknowledgements

The author would like to thank the National Science Council of the Republic of China for financially supporting this research under Contract No. NSC 95-2221-E-212-022. Mr. Yu-Hsiang Peng of Da-Yeh University is appreciated for performing some of the experiments.

References

- [1] T. An, H. Gu, Y. Xiong, W. Chen, X. Zhu, G. Sheng, J. Fu, Decolorization and COD removal from reactive dye-containing wastewater using sonophotocatalytic technology, *J. Chem. Technol. Biotechnol.* 78 (2003) 1142–1148.
- [2] N.H. Ince, G. Tezcanli-Guyer, R.K. Belen, I.G. Apikyan, Ultrasound as a catalyzer of aqueous reaction systems: the state of the art and environmental applications, *Appl. Catal. B: Environ.* 29 (2001) 167–176.
- [3] I. Shirgaonkar, A.B. Pandit, Sonophotocatalytic destruction of aqueous solution of 2,4,6-trichlorophenol, *Ultrason. Sonochem.* 5 (1998) 53–61.
- [4] L. Davydov, E.P. Reddy, P. France, P.G. Smirniotis, Sonophotocatalytic destruction of organic contaminants in aqueous systems on TiO₂ powders, *Appl. Catal. B: Environ.* 32 (2001) 95–105.
- [5] V. Ragaini, E. Selli, C.L. Bianchi, C. Pirola, Sono-photocatalytic degradation of 2-chlorophenol in water: kinetic and energetic comparison with other techniques, *Ultrason. Sonochem.* 8 (2001) 251–258.
- [6] M. Mrowetz, C. Pirola, E. Selli, Degradation of organic water pollutants through sonophotocatalysis in the presence of TiO₂, *Ultrason. Sonochem.* 10 (2003) 247–254.
- [7] G. Tezcanli-Guyer, N.H. Ince, Individual and combined effects of ultrasound, ozone and UV irradiation: a case study with textile dyes, *Ultrasonics* 42 (2004) 603–609.
- [8] E. Selli, C.L. Bianchi, C. Pirola, M. Bertelli, Degradation of methyl *tert*-butyl ether in water: effects of the combined use of sonolysis and photocatalysis, *Ultrason. Sonochem.* 12 (2005) 395–400.
- [9] D.E. Kritikos, N.P. Xekoukoulotakis, E. Psillakis, D. Mantzavinos, Photocatalytic degradation of Reactive Black 5 in aqueous solutions: Effect of operating conditions and coupling with ultrasound irradiation, *Water Res.* 41 (2007) 2236–2246.
- [10] K.S. Suslick, *Ultrasound: Its Chemical, Physical and Biological Effects*, VCH, New York, 1988.
- [11] A. De Visscher, P. Van Eenoo, D. Drijvers, H.V. Langenhove, Kinetic model for the sonochemical degradation of monocyclic aromatic compounds in aqueous solution, *J. Phys. Chem.* 100 (1996) 11636–11642.
- [12] M. Papadaki, R.J. Emery, M.A. Abu-Hassan, A. Diaz-Bustos, I.S. Metcalfe, D. Mantzavinos, Sonocatalytic oxidation processes for the removal of contaminants containing aromatic rings from aqueous effluents, *Sep. Purif. Technol.* 34 (2004) 35–42.
- [13] E. Naffrechoux, S. Chanoux, C. Petrier, J. Suptil, Sonochemical and photochemical oxidation of organic matter, *Ultrason. Sonochem.* 7 (2000) 255–259.
- [14] Y. Nagata, M. Nakagawa, H. Okuno, Y. Mizukoshi, B. Yim, Y. Maeda, Sonochemical degradation of chlorophenols in water, *Ultrason. Sonochem.* 7 (2000) 115–120.
- [15] B. Yim, Y. Yoo, Y. Maeda, Sonolysis of alkylphenols in aqueous solution with Fe(II) and Fe(III), *Chemosphere* 50 (2003) 1015–1023.
- [16] E. Manousaki, E. Psillakis, N. Kalogerakis, D. Mantzavinos, Degradation of sodium dodecylbenzene sulfonate in water by ultrasonic irradiation, *Water Res.* 38 (2004) 3751–3759.
- [17] H.S. Son, S.B. Choi, E. Khan, K.D. Zoh, Removal of 1,4-dioxane from water using sonication: effect of adding oxidants on the degradation kinetics, *Water Res.* 40 (2006) 692–698.
- [18] Y. Dai, F. Li, F. Ge, F. Zhu, L. Wu, X. Yang, Mechanism of the enhanced degradation of pentachlorophenol by ultrasound in the presence of elemental iron, *J. Hazard. Mater.* 137 (2006) 1424–1429.
- [19] J. Wang, T. Ma, Z. Zhang, X. Zhang, Y. Jiang, D. Dong, P. Zhang, Y. Li, Investigation on the sonocatalytic degradation of parathion in the presence of nanometer rutile titanium dioxide (TiO₂) catalyst, *J. Hazard. Mater.* 137 (2006) 972–980.
- [20] J. Wang, Z. Pan, Z. Zhang, X. Zhang, F. Wen, T. Ma, Y. Jiang, L. Wang, L. Xu, P. Kang, Sonocatalytic degradation of methyl parathion in the presence of nanometer and ordinary anatase titanium dioxide catalysts and comparison of their sonocatalytic abilities, *Ultrason. Sonochem.* 13 (2006) 493–500.
- [21] N.H. Ince, G. Tezcanli, Reactive dyestuff degradation by combined sonolysis and ozonation, *Dyes Pigm.* 49 (2001) 145–153.
- [22] S. Chitra, K. Paramasivan, P.K. Sinha, K.B. Lal, Ultrasonic treatment of liquid waste containing EDTA, *J. Cleaner Prod.* 12 (2004) 429–435.
- [23] M. Dukkanci, G. Gunduz, Ultrasonic degradation of oxalic acid in aqueous solutions, *Ultrason. Sonochem.* 13 (2006) 517–522.
- [24] 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.
- [25] C.H. Wu, G.P. Chang-Chien, W.S. Lee, Photodegradation of polychlorinated dibenzo-*p*-dioxins: comparison of photocatalysts, *J. Hazard. Mater.* 114 (2004) 191–197.
- [26] C.H. Wu, Effects of operational parameters on the decolorization of C.I. Reactive Red 198 in UV/TiO₂-based systems, *Dyes Pigm.* 11 (2008) 31–38.
- [27] R.M.C. Silverstein, G.C. Basdler, G.C. Morrill, *Spectrophotometric identification of organic compounds*, Wiley, New York, 1991.
- [28] N.H. Ince, G. Tezcanli-Guyer, Impacts of pH and molecular structure on ultrasonic degradation of azo dyes, *Ultrasonics* 42 (2004) 591–596.
- [29] C.H. Wu, C.L. Chang, Decolorization of Procion Red MX-5B by advanced oxidation processes: Comparative studies of the homogeneous and heterogeneous systems, *J. Hazard. Mater.* 128 (2006) 265–272.
- [30] A.A. Khodja, T. Sehili, J.F. Pilichowski, P. Boule, Photocatalytic degradation of 2-phenylphenol on TiO₂ and ZnO in aqueous suspensions, *J. Photochem. Photobiol. A: Chem.* 141 (2001) 231–239.

- [31] X.H. Ou, S.L. Lo, C.H. Wu, Exploring the interparticle electron transfer process in the photocatalytic oxidation of 4-chlorophenol, *J. Hazard. Mater.* 137 (2006) 1362–1370.
- [32] M.A. Beckett, I. Hua, Elucidation of the 1,4-dioxane decomposition pathway at discrete ultrasonic frequencies, *Environ. Sci. Technol.* 34 (2000) 3944–3953.
- [33] G.R. Peyton, W.H. Glaze, The mechanism of photolytic ozonation, *Abstr. Papers Am. Chem. Soc.* 189 (1985) 5.
- [34] C.Y. Ma, J.Y. Xu, X.J. Liu, Decomposition of an azo dye in aqueous solution by combination of ultrasound and visible light, *Ultrasonics* 44 (2006) 375–378.
- [35] P.R. Gogate, S. Mujumdar, J. Thampi, A.M. Wilhelm, A.B. Pandit, Destruction of phenol using sonochemical reactors: scale up aspects and comparison of novel configuration with conventional reactors, *Sep. Purif. Technol.* 34 (2004) 25–34.
- [36] A. Keck, E. Gilbert, R. Koster, Influence of particles on sonochemical reactions in aqueous solutions, *Ultrasonics* 40 (2002) 661–665.
- [37] Y. Jiang, C. Petrier, 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.
- [38] N. Daneshvar, D. Salari, A.R. Khataee, Photocatalytic degradation of azo dye acid red 14 in water: investigation of the effect of operational parameters, *J. Photochem. Photobiol. A: Chem.* 157 (2003) 111–116.
- [39] N. Daneshvar, D. Salari, A.R. Khataee, Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO₂, *J. Photochem. Photobiol. A: Chem.* 162 (2004) 317–322.
- [40] N.M. Mahmoodi, M. Arami, N.Y. Limaee, Photocatalytic degradation of triazinic ring-containing azo dye (Reactive Red 198) by using immobilized TiO₂ photoreactor: Bench scale study, *J. Hazard. Mater.* 133 (2006) 113–118.