



## Photodegradation of C.I. Reactive Red 2 in UV/TiO<sub>2</sub>-based systems: Effects of ultrasound irradiation

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### ABSTRACT

This investigation elucidated the decolorization of C.I. Reactive Red 2 (RR2) in US/TiO<sub>2</sub>, UV/TiO<sub>2</sub> and UV/US/TiO<sub>2</sub> systems and evaluated the effect of ultrasound (US) irradiation in photocatalysis. The effects of RR2 concentration, temperature and the addition of NaCl, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and radical scavenger were determined. The decolorization reactions obeyed the pseudo-first-order kinetics in all tested systems. In US-related systems, the decolorization rate of RR2 declines as RR2 concentration increases. At pH 7, the decolorization rates followed the order UV/US/TiO<sub>2</sub> (0.94 h<sup>-1</sup>) > UV/TiO<sub>2</sub> (0.85 h<sup>-1</sup>) > US/TiO<sub>2</sub> (0.25 h<sup>-1</sup>). The promotion efficiencies of adding NaCl in US/TiO<sub>2</sub>, UV/TiO<sub>2</sub> and UV/US/TiO<sub>2</sub> systems were 16%, 18% and 29%, respectively. The decolorization rate increased with the temperature; additionally, the decolorization rate in UV/US/TiO<sub>2</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> exceeded that in UV/US/TiO<sub>2</sub>. The inhibition of RR2 decolorization by adding 1-butanol reveals that the primary decolorization pathway involves hydroxyl radicals, and that direct oxidation by photogenerated holes is probably important in the UV/TiO<sub>2</sub>-based system. After 120 min of the reaction, the TOC degradation efficiencies of UV/TiO<sub>2</sub> and UV/US/TiO<sub>2</sub> systems were 47% and 63%, respectively.

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### 1. Introduction

The textile industry consumes large volumes of water in different wet processes; therefore, very large amounts of textile wastewater, which is heavily charged with unconsumed dyes and other chemicals, are produced. Azo dyes are well-known carcinogenic organic substances. Reductive enzymes in the liver can catalyze the reductive cleavage of the azo linkage to produce aromatic amines and can even lead to intestinal cancer [1,2]. Thus, the efficient removal of such a dye is the prime aim of this research. Accordingly, C.I. Reactive Red 2 (RR2), the azo dye with the most commonly used anchor—the dichlorotriazine group, was selected as the parent compound herein. Treatments of dye-containing wastewater by conventional methods such as coagulation and flocculation are quite ineffective because dyes are highly water-soluble. Furthermore, these approaches merely transfer the dyes from the wastewater to the solid phase, generating sludge and causing problems of disposal. Advanced oxidation processes are alternative methods for decolorizing and reducing recalcitrant wastewater loads that are produced by textile companies. Most investigations of the photo-assisted decomposition of dyes use TiO<sub>2</sub> as a model photocatalyst due to its chemical and biological stability, large

availability, cheapness, non-toxicity and high photocatalytic reactivity. Hence, this study employs TiO<sub>2</sub> as the model photocatalyst in evaluating the effects of the operational parameters on decolorization.

In UV/TiO<sub>2</sub>, photogenerated holes are generated when TiO<sub>2</sub> particles are irradiated with UV light. Hydroxyl radicals are formed mainly in the oxidation of OH<sup>-</sup> or H<sub>2</sub>O by these photogenerated holes, and are principally responsible for the destruction of organic species. Oxygen acts primarily as an efficient electron trap, preventing the recombination of electrons and photogenerated holes. If oxygen is limited, rapid recombination of photoproduced electrons and holes in TiO<sub>2</sub> significantly reduces the efficiency of photocatalytic reactions; consequently, such a system has limited practical application.

In recent years, attention has focused on the application of ultrasonic energy to solve problems associated with wastewater treatment. Ultrasound (US) irradiation causes acoustic cavitation, and bubble collapse causes intense local heating, high pressures, and very short lifetimes of bubbles; these transient, localized hot spots drive high-energy chemical reactions [3]. Any solute or solvent in contact with or inside these cavities in the vapor phase undergoes fragmentation, yielding free radicals, and can be used to degrade toxic compounds. The enhanced mass transfer and phase transfer properties around solid surfaces caused by US could accelerate the oxidation. The combination of US with other techniques such as UV [4], S<sub>2</sub>O<sub>8</sub><sup>2-</sup> [5], TiO<sub>2</sub> [6,7], O<sub>3</sub> [8,9], H<sub>2</sub>O<sub>2</sub>

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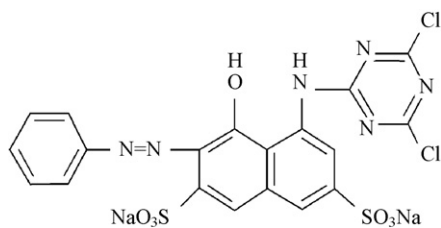


Fig. 1. Structure of RR2.

[10–12],  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  [10,13], UV/US/ $\text{TiO}_2$  [14–17], UV/US/ $\text{ZnO}$  [4] and UV/US/ $\text{O}_3$  [9] increases the efficiency of the decomposition and removal of pollutant. However, for some compounds, conflicting results exist concerning the effects of such process parameters as pH, US frequency, temperature and additional oxidants on the rate of sonochemical degradation. Further research must be performed to improve understanding of the effects of the operational conditions. Hence, this work conducts a systematic study of the photocatalytic and the sonophotocatalytic degradation for RR2. This investigation attempts (i) to assess the influences of RR2 concentration in UV/ $\text{TiO}_2$  and UV/US/ $\text{TiO}_2$  systems; (ii) to elucidate the impact of NaCl addition in US/ $\text{TiO}_2$ , UV/ $\text{TiO}_2$  and UV/US/ $\text{TiO}_2$  systems; (iii) to determine the effects of  $\text{Na}_2\text{S}_2\text{O}_8$  addition in UV/US/ $\text{TiO}_2$  system; (iv) to measure the effects of temperature in UV/US/ $\text{TiO}_2$  and UV/US/ $\text{TiO}_2/\text{Na}_2\text{S}_2\text{O}_8$  systems, and (v) to evaluate the effects of radical scavenger addition in UV/ $\text{TiO}_2$ , UV/US/ $\text{TiO}_2$  and UV/US/ $\text{TiO}_2/\text{Na}_2\text{S}_2\text{O}_8$  systems.

## 2. Materials and methods

### 2.1. Materials

$\text{TiO}_2$  (crystalline structure: anatase) was obtained from Riedel-Haen Co. (Sleeze, Germany). The diameter, specific surface area and band gap energy of  $\text{TiO}_2$  were 100–500 nm,  $8.85 \text{ m}^2/\text{g}$  and 3.13 eV (UV absorption threshold = 396 nm), respectively [18]. The parent compound, RR2, obtained from Aldrich Chemical Company, was used without further purification. The formula, molecular weight and maximum light absorption wavelength ( $\lambda_{\text{max}}$ ) of RR2 were  $\text{C}_{19}\text{H}_{10}\text{Cl}_2\text{N}_6\text{Na}_2\text{O}_7\text{S}_2$ , 615 g/mol and 538 nm, respectively. Fig. 1 displays the structure of RR2. The  $\lambda_{\text{max}}$  of RR2 did not vary with pH (data not shown for lack of space). 1-Butanol ( $\text{C}_4\text{H}_9\text{OH}$ ) was used as the hydroxyl radical scavenger. NaCl and  $\text{Na}_2\text{S}_2\text{O}_8$  were selected to evaluate the enhancement of decolorization.  $\text{HNO}_3$ ,  $\text{Na}_2\text{S}_2\text{O}_8$  and NaOH were obtained from Merck. NaCl and 1-butanol were obtained from Katayama. The pH of the solution was controlled by adding  $\text{HNO}_3$  and NaOH via an automatic titrator. All reagents were of analytical grade and used as-purchased.

### 2.2. Decolorization experiments

Fig. 2 presents the equipment scheme. Decolorization experiments were conducted in a 3 l, hollow cylindrical glass reactor. A 15 W UVC lamp (254 nm,  $10 \text{ mW}/\text{cm}^2$ , 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 maintained at 2 cm. All of the experimental procedures were similar to those adopted by Wu [4]. Aliquots (15 ml) were withdrawn from the photoreactor at pre-specified intervals. The suspended  $\text{TiO}_2$  particles were separated by filtering them through a  $0.22 \mu\text{m}$  filter (Millipore). The RR2 concentration was measured using a spectrophotometer (Hitachi U-2001) at 538 nm. Ionic chromatography (IC, Dionex DX-120) was utilized to determine the concentrations of

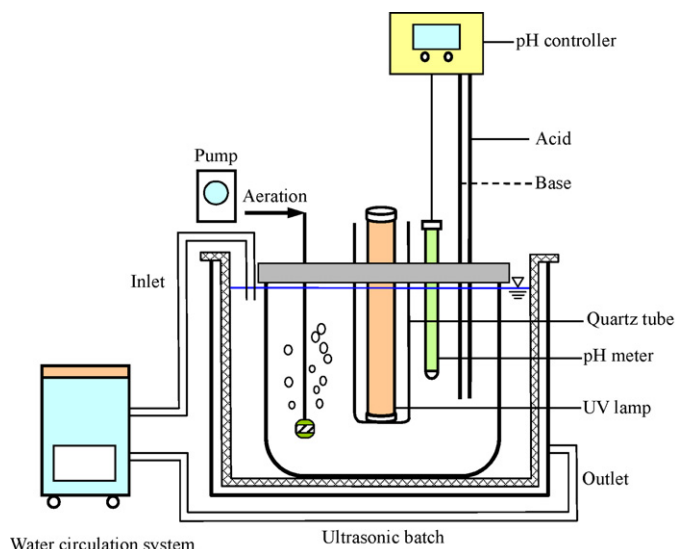


Fig. 2. Scheme of equipment.

sulfate and chloride anions during decolorization. The mineralization of RR2 was identified by the reduction of total organic carbon (TOC), as measured using an O.I. 1010 TOC analyzer.

## 3. Results and discussion

### 3.1. Effects of RR2 concentration in UV/ $\text{TiO}_2$ and UV/US/ $\text{TiO}_2$ systems

No significant reduction more than 5% after 120 min reaction occurred during vaporization, adsorption or direct photolysis; hence, the degradation of RR2 may have been attributable to UV/ $\text{TiO}_2$  and UV/US/ $\text{TiO}_2$  reaction (data not presented). The effect of initial dye concentration on the rate of RR2 decolorization was determined by varying initial concentrations of RR2 at 10, 20, 40, 60 and 80 mg/l at pH 7 in UV/ $\text{TiO}_2$  and UV/US/ $\text{TiO}_2$  systems (Fig. 3). The decolorization rates fit a pseudo-first-order reaction model, and various studies have shown that the dye photodegradation rates generally can be approximated by pseudo-first-order kinetics [4,6,8,19]. The  $k$  values fell as the dye concentration increased (Table 1). Several investigations have yielded similar experimental findings for UV/ $\text{TiO}_2$ -based systems [8,10,13,16,17]. This phenomenon has three possible explanations. First, as the initial concentration of dye increased, the  $\text{TiO}_2$  surfaces adsorbed additional dye molecules: (i) inhibiting direct contact between dye molecules and photogenerated holes [16] and (ii) suppressing the generation of hydroxyl radicals on  $\text{TiO}_2$  surfaces as dye molecules cover active sites [20]. Second, a significant quantity of UV light may be absorbed by the highly concentrated dye molecules rather than by the  $\text{TiO}_2$  particles, reducing decolorization efficiency; the dye thus has a UV-screening effect. As the dye concentration increases,

Table 1

Pseudo-first-order decolorization rate constants of UV/ $\text{TiO}_2$  and UV/US/ $\text{TiO}_2$  systems at various RR2 concentrations ( $\text{TiO}_2 = 2 \text{ g/l}$ , pH 7 and  $30^\circ\text{C}$ ).

RR2 concentration (mg/l)	UV/ $\text{TiO}_2$		UV/US/ $\text{TiO}_2$	
	$k$ ( $\text{h}^{-1}$ )	$r^2$	$k$ ( $\text{h}^{-1}$ )	$r^2$
10	1.78	0.996	2.03	0.988
20	0.85	0.996	0.94	0.988
40	0.58	0.994	0.60	0.992
60	0.29	0.998	0.49	0.982
80	0.24	0.996	0.31	0.996

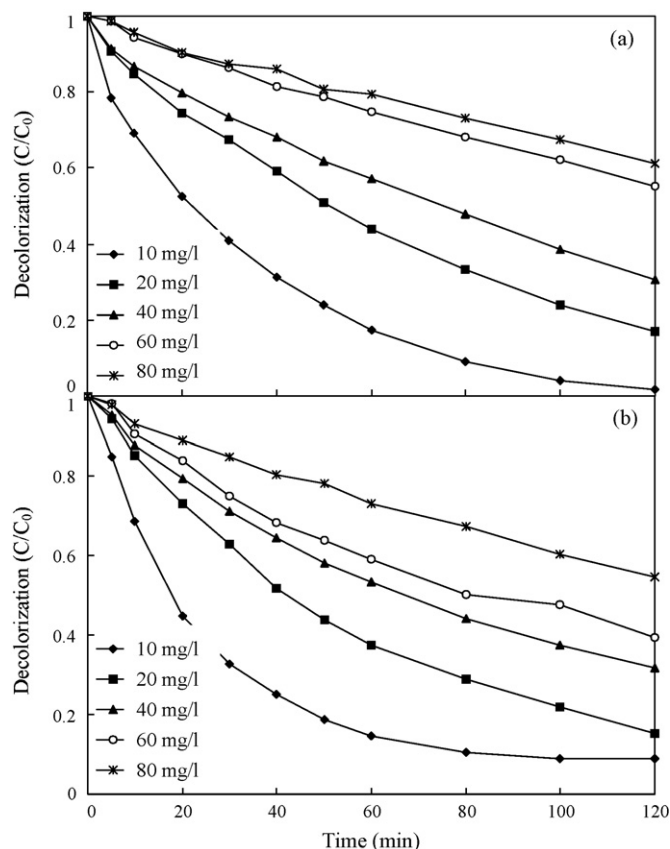


Fig. 3. Effects of RR2 concentration in UV/TiO<sub>2</sub> and UV/US/TiO<sub>2</sub> systems (a) UV/TiO<sub>2</sub> and (b) UV/US/TiO<sub>2</sub> (TiO<sub>2</sub> = 2 g/l, pH 7 and 30 °C).

few photons reach the TiO<sub>2</sub> surface, slowing the formation of hydroxyl radicals. Third, increased amounts of dyes and reaction intermediates compete with hydroxyl radicals and active reaction sites of TiO<sub>2</sub> as the initial dye concentration increases. Since the amount of TiO<sub>2</sub> remained constant, the rate of formation of hydroxyl radicals on TiO<sub>2</sub> surfaces was also constant. Therefore, the fraction of hydroxyl radicals that attack dye molecules and its reaction intermediates declines as the initial dye concentration increases. Simultaneous sonolysis did not alter this trend, suggesting that reaction system exhibits the same dependence on the amount of dye, which determines the water–semiconductor interface phenomena under photocatalytic and sonophotocatalytic conditions [15]. The linear correlation between decolorization rate and RR2 concentration in UV/TiO<sub>2</sub> and UV/US/TiO<sub>2</sub> was  $k = 0.2668[\text{RR2}]^{-0.9535}$  ( $r^2 = 0.980$ ) and  $k = 0.2203[\text{RR2}]^{-0.8404}$  ( $r^2 = 0.978$ ), respectively. This result implies that the RR2 concentration affected the decolorization rate more in UV/TiO<sub>2</sub> than in UV/US/TiO<sub>2</sub>.

### 3.2. Effects of NaCl addition in US/TiO<sub>2</sub>, UV/TiO<sub>2</sub> and UV/US/TiO<sub>2</sub> systems

#### 3.2.1. Effects of NaCl addition

The effects of NaCl addition were evaluated in US/TiO<sub>2</sub>, UV/TiO<sub>2</sub> and UV/US/TiO<sub>2</sub> systems at pH 7 (Fig. 4). Under 5 g/l NaCl addition, the decolorization rates of US/TiO<sub>2</sub>, UV/TiO<sub>2</sub> and UV/US/TiO<sub>2</sub> systems were 0.29, 1.00 and 1.21 h<sup>-1</sup>, respectively. The promotion efficiency of NaCl addition in US/TiO<sub>2</sub>, UV/TiO<sub>2</sub> and UV/US/TiO<sub>2</sub> systems was 16%, 18% and 29%, respectively. Adding NaCl increases the ionic strength of the aqueous phase, driving the organic compounds to the bulk–bubble interface in US-related systems [21]. Other properties of the solution, such as viscosity, vapor pressure

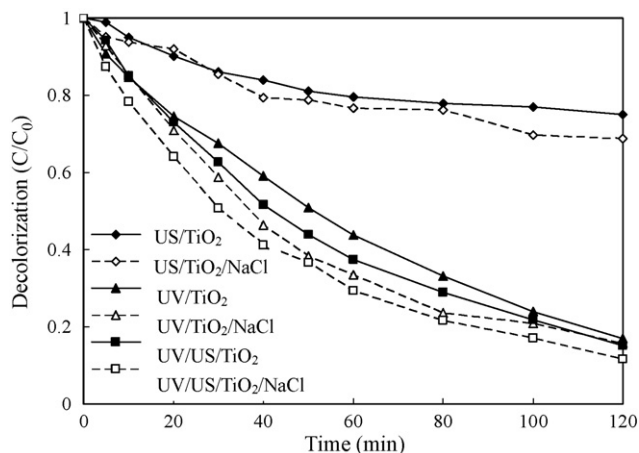
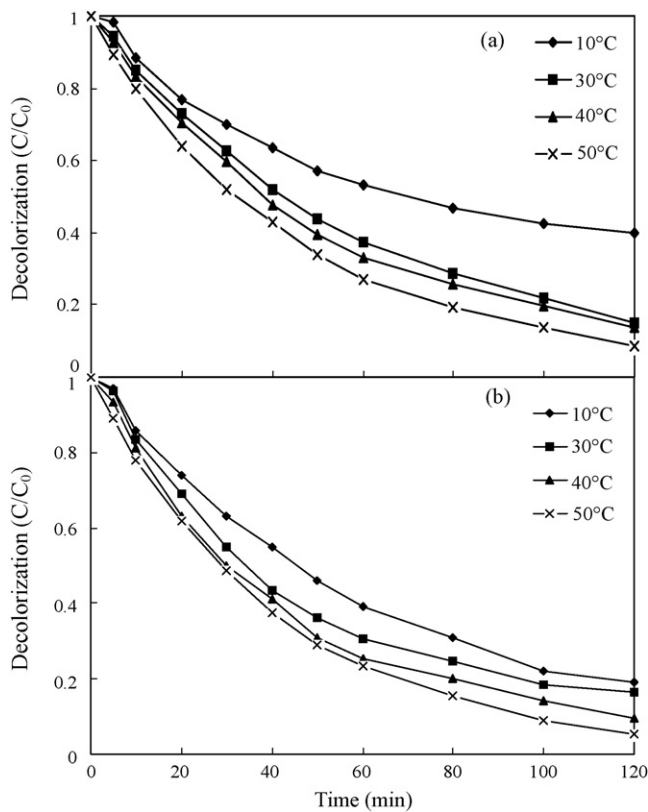


Fig. 4. Effects of NaCl addition in US/TiO<sub>2</sub>, UV/TiO<sub>2</sub> and UV/US/TiO<sub>2</sub> systems (RR2 = 20 mg/l, NaCl = 5 g/l, TiO<sub>2</sub> = 2 g/l, pH 7 and 30 °C).

and heat capacity change accordingly. The enhancement of the presence of NaCl can be attributed to the increase in partitioning of the pollutant species upon cavitation implosion in US-related system. Beyond the partitioning enhancement, the presence of salt reduces vapor pressure and increases surface tension [11]. All of these factors help to collapse the bubbles more violently, causing high pollutant degradation. Previous studies have yielded similar results concerning the degradation of organics in the presence of NaCl in US-based systems [4,11,21]. Wang et al. [22] indicated that the 0.01 M NaCl addition did not affect the reaction of UV/TiO<sub>2</sub>; however, adding 0.01 M Na<sub>2</sub>SO<sub>4</sub> promoted the reaction. Clearly, higher ionic strength was responsible for greater promotion in the UV/TiO<sub>2</sub> system. In UV/TiO<sub>2</sub>, the addition of NaCl pushed RR2 from the bulk aqueous phase toward the TiO<sub>2</sub> surface; therefore, the adsorption of RR2 increased. Hence, the decolorization rate was accelerated.

#### 3.2.2. Comparisons of US/TiO<sub>2</sub>, UV/TiO<sub>2</sub> and UV/US/TiO<sub>2</sub> systems

Both sonolysis and photocatalysis produced hydroxyl radicals in water, which may attack RR2, initiating its degradation. At pH 7, the decolorization rates followed the order UV/US/TiO<sub>2</sub> (0.94 h<sup>-1</sup>) > UV/TiO<sub>2</sub> (0.85 h<sup>-1</sup>) > US/TiO<sub>2</sub> (0.25 h<sup>-1</sup>). Under US irradiation, water is pyrolyzed, in which process hydrogen radicals (\*H), hydroxyl radicals (\*OH), oxygen radicals (\*O) and hydroperoxyl radicals (\*O<sub>2</sub>H) are formed and then react with RR2 in the bulk solution or at the interface between the bubbles and the liquid phase [23,24]. Under aqueous US irradiation, hydroxyl radicals form during the thermolytic reactions of water and self-recombine to form H<sub>2</sub>O<sub>2</sub> [23]. Additionally, ozone is generated in the presence of oxygen under US irradiation [24]. Combining ozone with UV promotes RR2 degradation via the direct and indirect production of hydroxyl radicals. Hence, the decolorization rate of UV/US/TiO<sub>2</sub> exceeded that of US/TiO<sub>2</sub> and UV/TiO<sub>2</sub>. The following explanations are suggested for US/TiO<sub>2</sub> and UV/US/TiO<sub>2</sub> systems: (i) US acted as a deaggregator by microstreaming and causing microbubble collapse, which induced surface cleaning of the TiO<sub>2</sub> 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 TiO<sub>2</sub> surface. Wang et al. [6,7] proposed that US irradiation can produce US-induced luminescence at a wavelength of below 375 nm; can excite the TiO<sub>2</sub> particle as a photocatalyst, and generate highly oxidative hydroxyl radicals on the surface of the TiO<sub>2</sub> particles. However, the intensity of US-induced luminescence was lower than that of UV herein; hence, the decolorization rates obeyed UV/TiO<sub>2</sub> > US/TiO<sub>2</sub>. Numerous studies have



**Fig. 5.** Effects of temperature in UV/US/TiO<sub>2</sub> and UV/US/TiO<sub>2</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> systems: (a) UV/US/TiO<sub>2</sub> and (b) UV/US/TiO<sub>2</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (RR2 = 20 mg/l, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> = 238 mg/l, TiO<sub>2</sub> = 2 g/l and pH 7).

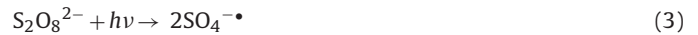
also demonstrated that the degradation rates of organics follow the order UV/US/TiO<sub>2</sub> > UV/TiO<sub>2</sub> > US/TiO<sub>2</sub> [14,16].

### 3.3. Effects of temperature in UV/US/TiO<sub>2</sub> and UV/US/TiO<sub>2</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> systems

#### 3.3.1. Influences of Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> addition

The effects of temperature were evaluated in UV/US/TiO<sub>2</sub> and UV/US/TiO<sub>2</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> systems at 10, 30, 40 and 50 °C (Fig. 5). The experimental results indicated that the decolorization rate of UV/US/TiO<sub>2</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> exceeded that of UV/US/TiO<sub>2</sub> at 10–50 °C (Table 2). Persulfate ions trap photogenerated electrons, preventing their recombination with positive holes, while simultaneously generating sulfate free radicals (Eq. (1)). Sulfate-free radicals react with water molecules to form hydroxyl radicals (Eq. (2)) [25]. Ivanov et al. [26] found that persulfate ions undergo photolysis under light irradiation, producing sulfate free radicals (Eq. (3)). According to Eqs. (1)–(3), persulfate ions generate additional sulfate free radicals and hydroxyl radicals, such that the decolorization rate of

UV/US/TiO<sub>2</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> exceeded that of UV/US/TiO<sub>2</sub>:



The mechanism of thermal decomposition is believed to involve the sulfate radical, which can abstract a hydrogen from water to yield hydroxyl radicals (Eqs. (4) and (5)) [27]:



Price and Clifton [28] stated that the first-order kinetics constants of the thermal and sonochemical decomposition of persulfate both increased with temperature. Moreover, US can accelerate significantly the decomposition of persulfate [5]. Therefore, the decolorization rate increased with the temperature; additionally, the decolorization rate in UV/US/TiO<sub>2</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was higher than that in UV/US/TiO<sub>2</sub> (Table 2).

#### 3.3.2. Temperature effects

The temperature of the bulk phase influences the viscosity, gas solubility, surface tension and vapor pressure. For the most of chemical reactions, the higher the temperature in reaction system is, the quicker the reaction becomes. A high temperature typically has a positive effect on cavitation; conversely, a high temperature reduces implosion in US-related systems [29]. All of the above factors make the effects of temperature on sonochemical degradation rate complex. Accordingly, no consistent results are available on the impact of temperature on the decomposition of organics. An increase in temperature does not favor most sonochemical reactions because it reduces the amount of dissolved gas and increases vapor pressure [23]. Manousaki et al. [13] and Wang et al. [6,7] found that increasing the temperature in US-related systems inhibited the degradation of organics. However, Svitselka et al. [30] and Wang et al. [31] revealed that the degradation rate increased with the temperature in the US-based systems and this study was similar to those. The rate constants of the pseudo-first-order model were adopted to calculate the activation energy of decolorization using the Arrhenius equation (Eq. (6)):

$$\ln(k) = \ln(A) - \frac{E_a}{RT} \quad (6)$$

where  $k_B$ ,  $A$ ,  $E_a$ ,  $R$  and  $T$  are the rate constant of the pseudo-first-order model ( $\text{h}^{-1}$ ), the Arrhenius coefficient, the activation energy (kJ/mol), the gas constant (8.314 J/(mol K)) and the temperature (K), respectively. The activation energy was determined from the slope of the plot of  $\ln(k)$  versus  $1/T$ . The activation energy of RR2 decolorization in UV/US/TiO<sub>2</sub> and UV/US/TiO<sub>2</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was calculated to be 11.62 kJ/mol ( $r^2 = 0.999$ ) and 9.26 kJ/mol ( $r^2 = 0.994$ ) at pH 7, respectively.

#### 3.4. Effects of 1-butanol addition in UV/TiO<sub>2</sub>, UV/US/TiO<sub>2</sub> and UV/US/TiO<sub>2</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> systems

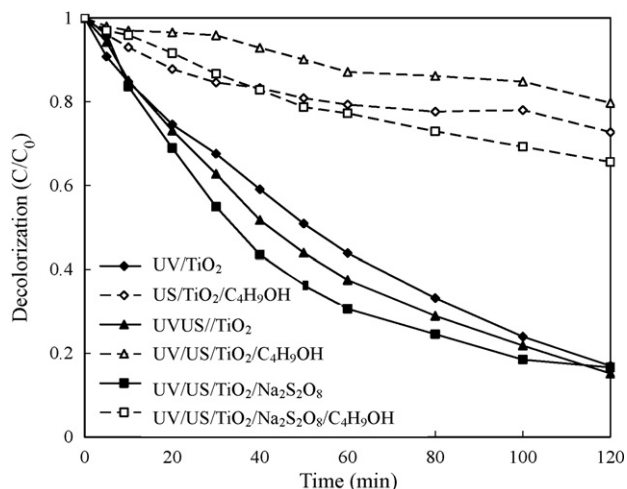
Aqueous sonication occurs in three important regions. The first region is the interior of the collapsing cavitation bubbles; the second region is the interfacial boundary between the gaseous and liquid phases, and the third is the solution bulk [32]. Since the RR2 utilized herein is a non-volatile compound, the solutes do not pyrolyze in the cavitation bubbles. To verify the reaction pathway, the effects of the radical scavenger, 1-butanol, on the rate of RR2 decolorization in UV/TiO<sub>2</sub>, UV/US/TiO<sub>2</sub> and UV/US/TiO<sub>2</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> systems at pH 7 was examined. Adding 1-butanol to UV/TiO<sub>2</sub>,

**Table 2**

Pseudo-first-order decolorization rate constants of UV/US/TiO<sub>2</sub> and UV/US/TiO<sub>2</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> at different temperatures (RR2 = 20 mg/l, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> = 238 mg/l, TiO<sub>2</sub> = 2 g/l and pH 7).

Temperature (°C)	UV/US/TiO <sub>2</sub>		UV/US/TiO <sub>2</sub> /Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	
	$k$ (h <sup>-1</sup> )	$r^2$	$k$ (h <sup>-1</sup> )	$r^2$
10	0.67	0.986	0.88	0.994
30	0.94	0.988	1.14	0.986
40	1.07	0.995	1.25	0.984
50	1.24	0.997	1.45	0.999

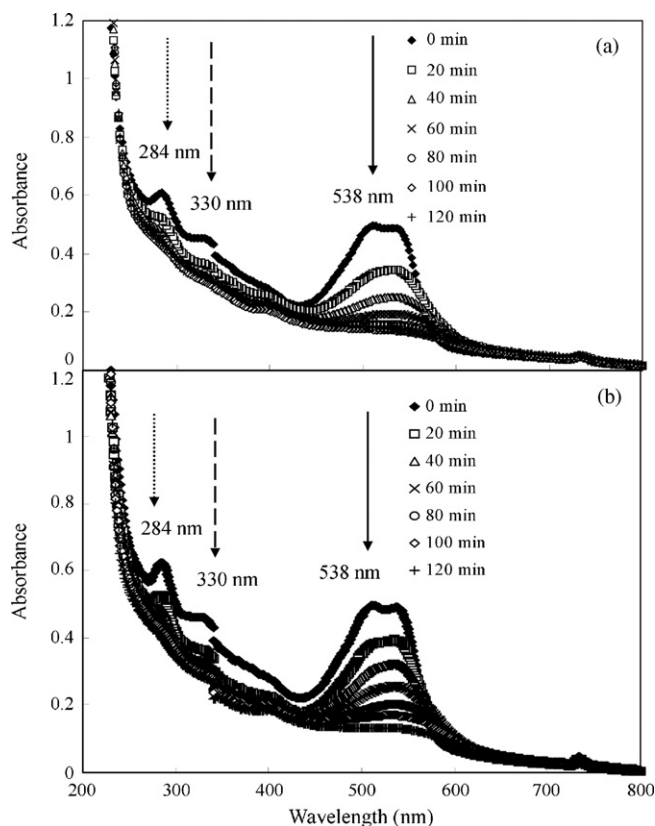




**Fig. 6.** Effects of  $C_4H_9OH$  addition in UV/ $TiO_2$ , UV/US/ $TiO_2$  and UV/US/ $TiO_2/Na_2S_2O_8$  systems (RR2 = 20 mg/l,  $Na_2S_2O_8$  = 238 mg/l,  $C_4H_9OH$  = 1200 mg/l,  $TiO_2$  = 2 g/l, pH 7 and 30 °C).

UV/US/ $TiO_2$  and UV/US/ $TiO_2/Na_2S_2O_8$  systems reduced the decolorization rate (Fig. 6). The  $k$  values of UV/ $TiO_2$ , UV/US/ $TiO_2$  and UV/US/ $TiO_2/Na_2S_2O_8$  systems without added 1-butanol were 0.85, 0.94 and 1.14  $h^{-1}$ , respectively, while those with 1200 mg/l added 1-butanol were 0.26, 0.11 and 0.28  $h^{-1}$ , respectively. Previous works have demonstrated that butanol quenches hydroxyl radicals, reducing the photodegradation rate [13,33]. Experimental findings imply that the hydroxyl radicals significantly influence the rate of RR2 decolorization. However, adding 1200 mg/l 1-butanol does not completely prevent decolorization. This experimental result suggests that decolorization involves another reactive species that does not react with 1-butanol. This species is most likely the photo-generated holes that are formed upon the irradiation of  $TiO_2$ . The inhibition by adding 1-butanol shows that the primary decolorization pathway involves hydroxyl radicals, and that direct oxidation by photogenerated holes is probably significant in the UV/ $TiO_2$ -based system. Several studies have yielded similar results [4,34,35]. Since RR2 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/ $TiO_2$  system. Accordingly, the main pathway for the destruction of RR2 is chemical oxidation by hydroxyl radicals in the bulk liquid and/or the interface region of the cavitation bubbles in the US-based system [4,17]. Furthermore, the effects of sulfate radicals cannot be ignored in the UV/US/ $TiO_2/Na_2S_2O_8$  system.

Fig. 7 displays the UV–vis spectra changes of RR2 at pH 7 in UV/ $TiO_2$  and UV/US/ $TiO_2$  systems. Before treatment, the UV–vis spectra of RR2 have three main absorption bands—two in the UV region (284 and 330 nm) and one in the visible region (538 nm). The UV band is characteristic of two adjacent rings, whereas the visible band is associated with a long conjugated  $\pi$  system that is internally linked by two azo groups [36]. The intensity of absorption at 538 nm declines extremely rapidly; however, the UV bands at 284 and 330 nm vanished more slowly than did the visible band. In the UV/ $TiO_2$  system, the rate of disappearance of 284, 330 and 538 nm was 0.25, 0.29 and 0.85  $h^{-1}$ , respectively; in the UV/US/ $TiO_2$  system, the rate of disappearance of 284, 330 and 538 nm was 0.25, 0.30 and 0.94  $h^{-1}$ , respectively. The rates of disappearance of UV bands in the UV/ $TiO_2$  and UV/US/ $TiO_2$  systems were almost the same. The significantly higher rate of decay of the visible band is attributable to the priority of hydroxylation of the azo-links in the oxidation process, which causes the rapid disappearance of chromophores in the dye structure [8]. The hydroxyl radicals initially attack azo groups and open the N=N bonds; the N=N bonds are more easily



**Fig. 7.** UV–vis spectra variations in UV/ $TiO_2$  and UV/US/ $TiO_2$  systems: (a) UV/ $TiO_2$  and (b) UV/US/ $TiO_2$  (RR2 = 20 mg/l,  $TiO_2$  = 2 g/l, pH 7 and 30 °C).

destroyed than the aromatic structures. The experimental results were similar to those presented in previous studies [4,8,9,37] of azo dye decolorization.

RR2 decolorization converts organic carbon to  $CO_2$  and its intermediates, while nitrogen, sulfur and chloride heteroatoms are mineralized into inorganic ions. This study detected the formation of inorganic ions during the photocatalytic and sonophotocatalytic reactions. Table 3 presents the concentrations of  $Cl^-$ ,  $SO_4^{2-}$  and TOC in UV/ $TiO_2$  and UV/US/ $TiO_2$  systems after 120 min of reaction. The concentration of dissociated chloride and sulfate in the UV/US/ $TiO_2$  system markedly exceeded that in the UV/ $TiO_2$  system. Despite the fact that RR2 is completely decolorized after it has reacted for 120 min in the UV/ $TiO_2$  and UV/US/ $TiO_2$  systems at pH 7, the concentrations of dissociated chloride and sulfate in UV/ $TiO_2$  and UV/US/ $TiO_2$  systems were below their respective theoretical values. This finding is explained by the following two factors: (i) dissociated chloride and sulfate were adsorbed onto  $TiO_2$  surfaces and (ii) Cl and S atoms were incorporated into intermediates. Accordingly, this investigation suggests that the sulfur and chloride heteroatoms of RR2 may bind with intermediates and form sulfur-containing or chloro-containing compounds in both UV/ $TiO_2$  and UV/US/ $TiO_2$  systems. In this study, after 120 min of a reaction, the TOC degradation efficiency in the UV/ $TiO_2$  and UV/US/ $TiO_2$  systems was 47% and 63%, respectively. The experimental results revealed

**Table 3**

Analyses of IC and TOC in UV/ $TiO_2$  and UV/US/ $TiO_2$  systems (RR2 = 20 mg/l,  $TiO_2$  = 2 g/l, reaction time = 120 min, pH 7 and 30 °C).

Unit (mg/l)	Theoretical value	UV/ $TiO_2$	UV/US/ $TiO_2$
$Cl^-$	2.31	1.53	2.18
$SO_4^{2-}$	6.24	4.15	5.02
TOC	7.41	3.96	2.71

that the UV/US/TiO<sub>2</sub> system not only completely decolorized RR2 but also effectively mineralized RR2.

#### 4. Conclusion

This investigation determined the promotion of RR2 decolorization by US irradiation in a UV/TiO<sub>2</sub> system. This study observed that the linear correlation between decolorization rate and RR2 concentration in UV/TiO<sub>2</sub> and UV/US/TiO<sub>2</sub> was  $k = 0.2668[\text{RR2}]^{-0.9535}$  and  $k = 0.2203[\text{RR2}]^{-0.8404}$ , respectively. NaCl addition increases the ionic strength of the aqueous phase, driving RR2 to the bulk–bubble interface in the US-related systems, increasing the RR2 decolorization rate. The experimental results indicated that the decolorization rate of UV/US/TiO<sub>2</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> exceeded that of UV/US/TiO<sub>2</sub> at 10–50 °C; additionally, the decolorization rate constants increase with temperature increasing in both systems. The main route for the destruction of RR2 is chemical oxidation by hydroxyl radicals in the bulk liquid and/or the interface region of the cavitation bubbles in the UV/US/TiO<sub>2</sub> system. Results of this study suggest that the UV/US/TiO<sub>2</sub> system not only completely decolorized RR2 but also effectively mineralized RR2.

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