Mechanistic Investigations on Sonophotocatalytic Degradation of Textile Dyes with Surface Active Solutes

4 AUTHORS, INCLUDING:

Balaji Chilukoti

Indian Institute of Technology Guwahati

1 PUBLICATION   **16** CITATIONS

SEE PROFILE

Aniruddha Pandit

Institute of Chemical Technology, Mumbai

320 PUBLICATIONS   **9,162** CITATIONS

SEE PROFILE

Mechanistic Investigations on Sonophotocatalytic Degradation of Textile Dyes with Surface Active Solutes

Chilukoti Balaji,[†] Vijayanand S. Moholkar,[*,†] Aniruddha B. Pandit,[‡] and Muthupandian Ashokkumar[§]

[†]Department of Chemical Engineering, Indian Institute of Technology, Guwahati 781 039, Assam, India

[‡]Chemical Engineering Department, Institute of Chemical Technology, Nathalal Parekh Marg, Matunga, Mumbai 400 019, Maharashtra, India

[§]Particulate Fluids Processing Centre, School of Chemistry, University of Melbourne, Victoria 3010, Australia

ABSTRACT: In recent years, two advanced oxidation processes, namely, photocatalysis and sonolysis have been extensively investigated for the degradation of recalcitrant organic pollutants. Simultaneous application of these two techniques, known as sonophotocatalysis has been found to give synergistic enhancement in degradation under specific experimental conditions. The present study attempts to establish the physical mechanism of sonophotocatalytic process by finding the synergy between two techniques that gives enhancement in degradation. Transient collapse of cavitation bubbles gives rise to light emission (known as *sonoluminescence*), which could provide activation of the photocatalyst. To test this hypothesis, we have conducted experiments on the basis of known effects of surface active solutes on sonoluminescence. Three different textile dyes have been chosen as model pollutants. Experiments have been conducted in the presence of three different surface active solutes, namely, SDS, 2-propanol, and 1-butanol. The rate of degradation reduces drastically with the addition of surface active solutes. The reduction in the degradation process ranges from 5-fold (for Acid Red B) to ~20% (for Direct Blue 6) for SDS, while for alcohols much higher (~ 10-fold) reduction is seen for all three dyes. It is revealed that the interaction between photocatalyst and sonolysis is merely of physical nature. The sonoluminescence light from cavitation bubbles is not able to activate the photocatalyst. The role of TiO_2 is revealed to be only that of an adsorbent for the dyes. The degradation is caused mostly due to the radicals generated by the cavitation bubble, with negligible role of the radical generation from photocatalyst.

1. INTRODUCTION

With rapid industrialization of developing countries, such as India, the civilian and commercial sector in these countries are facing daunting environmental problems related to the remediation of hazardous waste, contaminated groundwater, and toxic air contaminants. A number of large and medium sized industries do not have adequate effluent treatment facilities, as they cannot afford enormous investments in pollution control equipment. Many of the toxic pollutants contained in wastewater discharge from these industries are recalcitrant and not amenable to conventional aerobic biological treatment. Examples of such pollutants are the dyes in the wastewater discharge from textile mills. Effective degradation of these dyes requires advanced oxidation processes (AOPs), which have been a subject of intense research activity worldwide.[1] The most widely investigated AOPs are[2] (1) H_2O_2/Fe^+ (Fenton), (2) $H_2O_2/Fe^{2+}(Fe^{3+})/UV$ (photo-Fenton), (3) H_2O_2/Fe^{3+}-oxalate, (4) $Mn^{2+}/oxalic$ acid/ozone, (5) photocatalysis $TiO_2/h\nu/O_2$, (6) ozone/H_2O_2, (7) ozone/UV, and (8) H_2O_2/UV. Although above techniques make use of different reaction systems, the principle underlying all techniques is production of $^\bullet OH$ radicals, which are extraordinary oxidizing species with an oxidation potential of 2.5 eV. The $^\bullet OH$ radicals attack organic molecules with an astounding rate constant,[2] of the order of $10^6-10^9 M^{-1} s^{-1}$. Another merit of $^\bullet OH$ radicals is that they do not have any specificity of attack. Therefore, practically all kinds of pollutants (aliphatic, aromatic, polycyclic etc.) are amenable to oxidation with $^\bullet OH$ radicals.

A new AOP that has emerged in the recent past is sonolysis, in which the $^\bullet OH$ radicals are generated from transient collapse of cavitation bubbles driven by ultrasound. Transient collapse of cavitation bubbles results in generation of extreme conditions of temperature and pressure (~5000 K and 500 bar) inside the bubble.[3] At these conditions, the solvent (usually water) vapor molecules entrapped in the bubble undergo thermal dissociation to generate radical species.[4−9] At these conditions, the bubbles also emit light, which is a phenomenon known as sonoluminescence. The spectrum of this emission extends the UV to well beyond the red end of the visible wavelength range. The principal merit of sonolysis is that it does not require addition of any external chemical. In the recent past, numerous researchers have combined the techniques of sonolysis and photocatalysis for a hybrid treatment known as sonophotocatalysis.[10−27] The combination of sonolysis and photocatalysis is reported to give greater degradation of the pollutants than the individual techniques. We would like to specifically state that more than 100 papers have been published in the past 15 years in area of sonophotocatalytic degradation of large variety of pollutants. A detailed review of this literature is beyond the scope of the present paper. Cited above are the few representative contributions in this area, especially for degradation of textile dyes. Despite this voluminous

contribution, the exact mechanism of interaction between sonolysis and photocatalysis that leads to the observed enhancement in degradation of pollutants is not established yet. In this paper, we have addressed this important issue. One obvious conjecture for the synergism between the two techniques (which have completely different individual mechanisms) could be that the sonoluminescence emissions from the cavitation bubbles help activate the photocatalyst to produce additional $^\bullet$OH radicals (than produced by transient bubble collapse during sonolysis) to give enhanced degradation of pollutants. Our approach is based on use of surface active solutes that alter the sonoluminescing behavior of cavitation bubbles in the medium. With comparison of the degradation of model textile dyes in presence of surface active solutes and that in the pure solution, we have attempted to form a link between physics of cavitation bubbles and photocatalysis.

2. EFFECT OF SURFACE ACTIVE SOLUTES ON SONOLUMINESCENCE

The phenomenon of sonoluminescence (SL) in case of either a single bubble (SBSL) or multibubble field (MBSL) is influenced by surface active solutes. This subject has been extensively investigated in the past two decades, and we present herewith a brief summary of the important contributions in the area of effect of surface active solutes on MBSL. We refer the readers to the review by Ashokkumar and Grieser.[28] Ashokkumar et al.[29] have studied the sonoluminescence generated in water with pulsed 515 kHz ultrasound in presence of different chain length (C_1-C_5) aliphatic alcohols and an anionic (SDS), cationic (DTAC) and zwitterionic (DAPS) surfactant. The intensity of the sonoluminescence was reduced as concentration of aliphatic alcohols increased. Greater quenching of sonoluminescence was seen for longer chain alcohols, which are less volatile. For the surfactants, the sonoluminescence intensity increased with SDS and DTAC until concentration 1 mM, and thereafter reduced. With addition of NaCl to the solution, this variation was not seen. The explanation for these trends was given on the basis of adsorption of surfactant molecules on the bubble surface, because of which the surface gets charged either positively or negatively, depending on the headgroup. As a result, the neighboring bubbles repel each other leading to "declustering" effect. This causes greater exposure of the bubbles to the acoustic field as the shielding provided by the neighboring bubbles is reduced. The bubbles undergo more intense collapse resulting in SL emission of greater intensity. Addition of an electrolyte like NaCl to such a system causes electrostatic screening and reclustering of the bubbles. The reduction in SL by alcohols was directly proportional to the surface excess (and not bulk) concentration, which is higher for longer chain alcohols. The volatility of the alcohols (for which is higher for smaller chain alcohols) was rather irrelevant. Unlike surfactants, for the alcohols continuous reduction in SL intensity was seen with concentration. For the same surface excess concentration as for the surfactants, alcohols are able to quench SL completely. Alcohols evaporated into the bubble during radial motion could not be responsible for this, as greater quenching was seen for less volatile (or long chain) alcohols. The quenching effect of alcohols was explained on the basis that interfacially adsorbed molecules are able to evaporate into the bubble core during collapse, and quench the precursor species of sonoluminescence such as H$^\bullet$ and $^\bullet$OH radicals. Tronson et al.[30] have extended the work of Ashokkumar et al.[29] using a lower 20 kHz frequency, and have found a similar, yet less marked (or sensitive) trends in

Scheme 1. Molecular Structure of Acid Red B
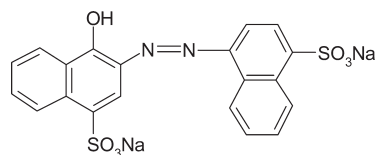
SL with different surface active solutes. The relative insensitivity of SL to surface active solutes at 20 kHz frequency, as compared to 515 kHz frequency used by Ashokkumar et al.,[29] was explained in terms of transient nature and short−life of bubble motion at 20 kHz frequency than high energy repetitive (or high energy stable) nature at 515 kHz. The short life of the bubble is rather insufficient to have complete (or saturation) adsorption of the surface active solutes on bubble surface. Similar approach as that of Ashokkumar et al.[29] and Tronson et al.[30] has been adapted by Segebarth et al.[31] and Sunartio et al.[32,33] with interesting results.

2.1. Approach of Present Study. Experimental protocol and analysis of results in the present study was based on the effect of surface active solutes discussed above. The main aim of this study was to deduce the exact mechanism of sonophotocatalysis, i.e. to deduce as how the mechanism of sonolysis and photocatalysis interact. To achieve this goal, we have conducted experiments to vary the sonoluminescence intensity in the medium by using same surface active solutes, that is , surfactant and alcohol, as in previous studies. The variation in the degradation of the model textile dyes obtained in the presence of the surface active solutes should be able to give hints toward the exact role played by TiO$_2$. The experiments would give an idea as whether sonoluminescence emissions from cavitation bubbles present in the medium are able to activate the photocatalyst to generate additional $^\bullet$OH radicals (than generated by the cavitation bubbles) that would give enhanced degradation. Otherwise, the role of TiO$_2$ is merely that of an adsorbent, which causes localized concentration of dye molecules in a relatively dilute solution, which would enable their faster degradation through radical generated from cavitation bubbles. The surface active solutes in the present study also adsorb on TiO$_2$, in addition to the bubble bulk interface. Reduction in the adsorption of dye in presence of these solutes, coupled with trends in degradation in presence or absence of TiO$_2$ would lead us to the answer sought in this study. We would like to make a mention of a previous paper by Rahal et al.,[34] in which similar approach has been adopted of having a synergy between anthraquinone-2-carboxylic acid (AQ-COOH) and TiO$_2$ for betterment of cotton fabrics under visible light. This synergy has been achieved in presence of visible light during which reactive oxygen species, such as singlet oxygen or superoxide radical-anion are produced.

3. MATERIALS AND METHODS

3.1. Materials. The three model compounds Acid Red B, Reactive Red 2, and Direct Blue 6 are obtained from Sigma Aldrich Chemical Co., without further purification. Anatase TiO$_2$ (99% pure, median of particle size distribution = 0.7 μm), an anionic surfactant Sodium dodecyl sulfate (SDS), 2-propanol, and 1-butanol are obtained from Merck. The molecular structures of these dyes are shown in Schemes 1−3.

3.2. Experimental Setup. A schematic diagram of the experimental setup used in the present study is shown in Figure 1, along with the actual photograph. The experiments were done in a 100 mL glass beaker with internal diameter of 5 cm. For sonication of the

Scheme 2. Molecular Structure of Reactive Red 2


Scheme 3. Molecular Structure of Direct Blue 6
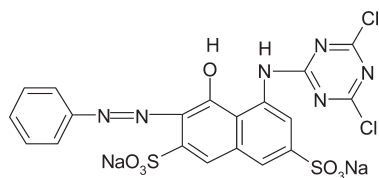
reaction mixture, a programmable and microprocessor based sonic processor (Sonics & Materials, Model: VCX 500) was used. The ultrasonic probe of the processor was fabricated from high grade titanium alloy and had a tip diameter of 13 mm. The ultrasound frequency generated by this probe was 20 kHz with maximum power output of 500 W. The processor had facility of power output control. The power control knob was set at 20% during sonication resulting in net consumption of 100 W. This power value corresponds to theoretical (or maximum) ultrasound intensity. The actual value of the ultrasound intensity in the medium is much different, and was determined to be 1.39 W using calorimetric technique.[35] In addition, the ultrasonic processor used in this study had facilities of automatic frequency tuning and amplitude compensation, which ensures constant power delivery to the reaction system during sonication (irrespective of the changes occurring in the medium, such as the sonochemical reactions). The tip of the ultrasound probe was dipped approximately 2 cm below surface of dye solution. Per calorimetric measurements, for an actual power consumption of 1.39 W with ultrasound probe of 13 mm diameter, the pressure amplitude of the ultrasound waves generated was calculated as 1.5 bar (for greater details we refer the reader to Sivasankar et al.[35]).

3.3. Experimental Procedure. *3.3.1. Calibration.* A scan of the absorbance of the aqueous solutions (10 ppm) of the three dyes was obtained using UV−vis spectrophotometer (Thermo Scientific, Model UV 2300). The peak of the absorbance spectrum for Acid Red B, Reactive Red 2, and Direct Blue 6 occurs at 514, 538 and 579 nm respectively. Following this, sample dye solutions were prepared in the concentration range of 0−15 ppm and calibration charts were prepared.

3.3.2. Degradation Experiments. For the experiments on degradation of dyes, 10 ppm solutions of each all three dyes were prepared using water (Millipore, Model Elix 3). 100 mL dye solution was used for sonication in each experiment. The initial temperature of solution was 25 °C. Total sonication time was 90 min in pulses of 15 min each with a power input of 100 W (by setting the power control knob at 20%). Within 15 min of sonication, the temperature of the solution increased by ~3 °C. Sufficient time gap (~ 10 min) was allowed between the pulses so as to reduce the temperature of dye solution to the initial (25 °C) condition. All experiments were carried out in dark so as to avoid interference of external light on the photocatalyst used (explained in next paragraph).

The experimental were carried out in 6 categories with different additives in the dye solution: (1) sonication alone (without any additive in the medium), (2) sonication with addition of TiO$_2$ (either 25 or 50 mg), (3) sonication with addition of SDS alone (concentration 1 mM, without TiO$_2$), (4) sonication with addition of 25 mg TiO$_2$ and varying concentration of SDS (0.5, 1, and 2 mM), (5) sonication with addition of 50 mg TiO$_2$ and varying concentration of SDS (0.5, 1, and 2 mM), and (6) sonication with addition of aliphatic alcohols (2-propanol and 1-butanol in concentration of 0.02 M). The
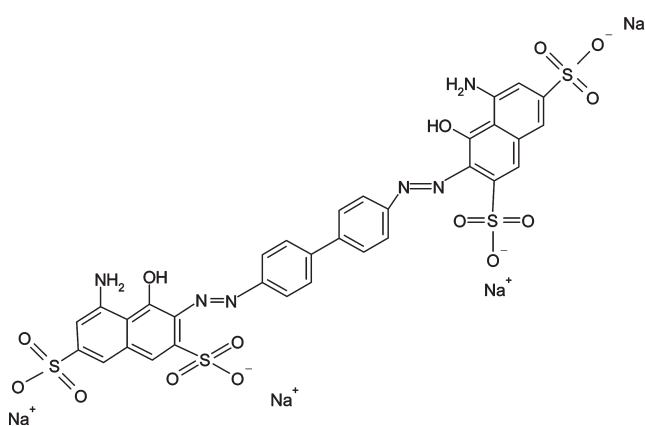
rationale underlying these categories will be explained subsequently. The presence of solid particles in the medium causes scattering and attenuation of ultrasound. However, in the present situation the amount of TiO$_2$ particles added to the medium was quite small, and this attenuation effect is likely to be negligible.

In all of the experimental categories, to monitor the degradation rate, samples of the reaction solution (5 mL) were withdrawn every 15 min for UV analysis. It should be noted some dye adsorbs on the TiO$_2$ particles, and this is wrongly accounted for as degraded dye in all samples withdrawn during sonication. This error was avoided by drawing the last sample twice: first after completion of sonication and next after adjusting the pH of the solution to alkaline (~9), which would desorb all the dye. The difference of dye concentration in these two samples would give the adsorbed quantity of dye. This quantity was added to all the earlier samples withdrawn from the solution. The residual dye concentration in samples of Acid Red B, Reactive Red 2, and Direct Blue 6 was monitored on UV−vis spectrophotometer (Thermo Scientific, Model UV 2300). To assess the reproducibility of experimental results, each experiment in the 6 categories was conducted twice, and the average value of dye concentration was considered for analysis.

3.3.3. Adsorption Experiments. To assess the change in the adsorption of dye on TiO$_2$ in presence of SDS, experiments were conducted as follows: 10 ppm of all three dye solutions were prepared in water (Millipore, Model Elix 3). In the first step, 25 mg TiO$_2$ was added to 100 mL solution, and the mixture was mildly stirred for 1 h so as to attain equilibrium. Thereafter, the solution was filtered using Whatmann filter paper no. 1 to remove the TiO$_2$ particles, and the absorbance of the solution was measured at the characteristic wavelengths to assess the residual concentration of dye in the solution. In the second step, same procedure as in first step was followed except that 1 mM SDS was added to the dye solution along with 25 mg TiO$_2$. After 1 h of mild stirring, the residual concentration of dye in the solution was measured.

4. RESULTS AND DISCUSSION

The source of •OH radicals in case of sonolysis is thermal dissociation of solvent vapor (usually water) at the extreme conditions reached at the transient collapse of cavitation bubbles. In addition, light emission from the excited state species produced at transient collapse, and the reaction
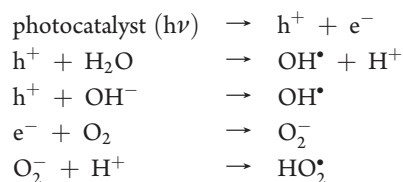
$$H^\bullet + {}^\bullet OH + M \rightarrow H_2O + M + h\nu$$
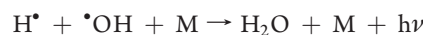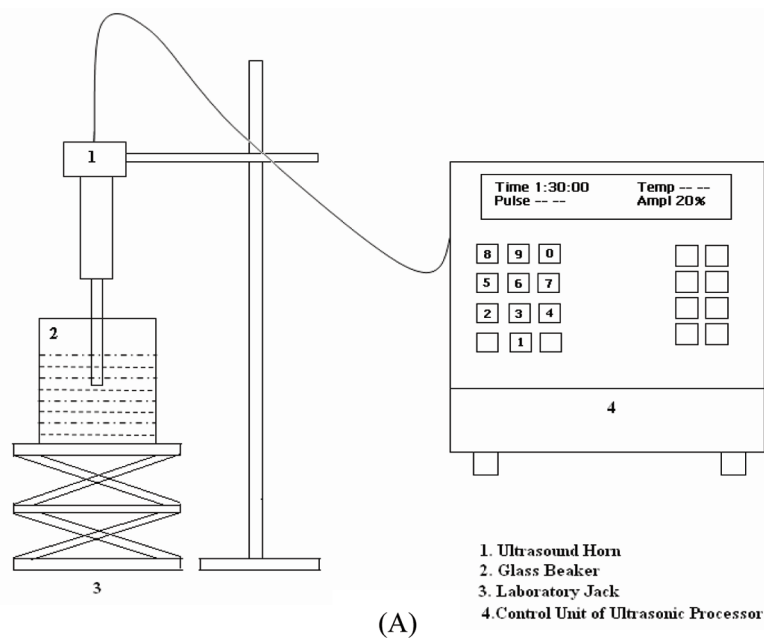
Figure 1. (A) Schematic of the experimental setup. (B) Picture of the experimental setup.

(where M is a third body collision partner), are responsible for sonoluminescence, that is, emission of light. A photocatalyst on the other hand, absorbs UV radiation (from any available light source) to produce pairs of electrons and holes. The positive hole of TiO_2 breaks apart water molecule (which is adsorbed on TiO_2) to form hydrogen gas and $OH^\bullet$ radicals. The electron reacts with oxygen molecules to form superoxide anion. A simplified mechanism for this process is given as follows:[2]

$$\text{photocatalyst } (h\nu) \quad \rightarrow \quad h^+ + e^-$$
$$h^+ + H_2O \quad \rightarrow \quad OH^\bullet + H^+$$
$$h^+ + OH^- \quad \rightarrow \quad OH^\bullet$$
$$e^- + O_2 \quad \rightarrow \quad O_2^-$$
$$O_2^- + H^+ \quad \rightarrow \quad HO_2^\bullet$$

In the next section, we explain the rationale underlying experimental protocol and also present a theoretical—contemplation as

how the results of these experiments would lead us to the answer we are seeking for.

4.1. Ultrasound, Cavitation, and Photocatalysis. Given that the spectrum of multibubble sonoluminescence, as observed in bulk solution, is a quite broad (ranging from UV to infrared), the best conjecture one can make regarding the synergy between sonolysis and photocatalysis is that the UV radiation for the excitation of photocatalyst should originate from multibubble sonoluminescence. If so, the photocatalyst would generate additional $^\bullet OH$ radicals that would give enhancement in degradation. Notably, an external source of UV light for the photocatalyst would not be required, if such synergy indeed exists.

Another possible mechanism through which the photocatalyst can enhance the degradation of dye (in a secondary role) is adsorption. Since the dye solutions used in the present study are quite dilute, the rate of degradation by sonolysis is also influenced by the probability of interaction between the dye
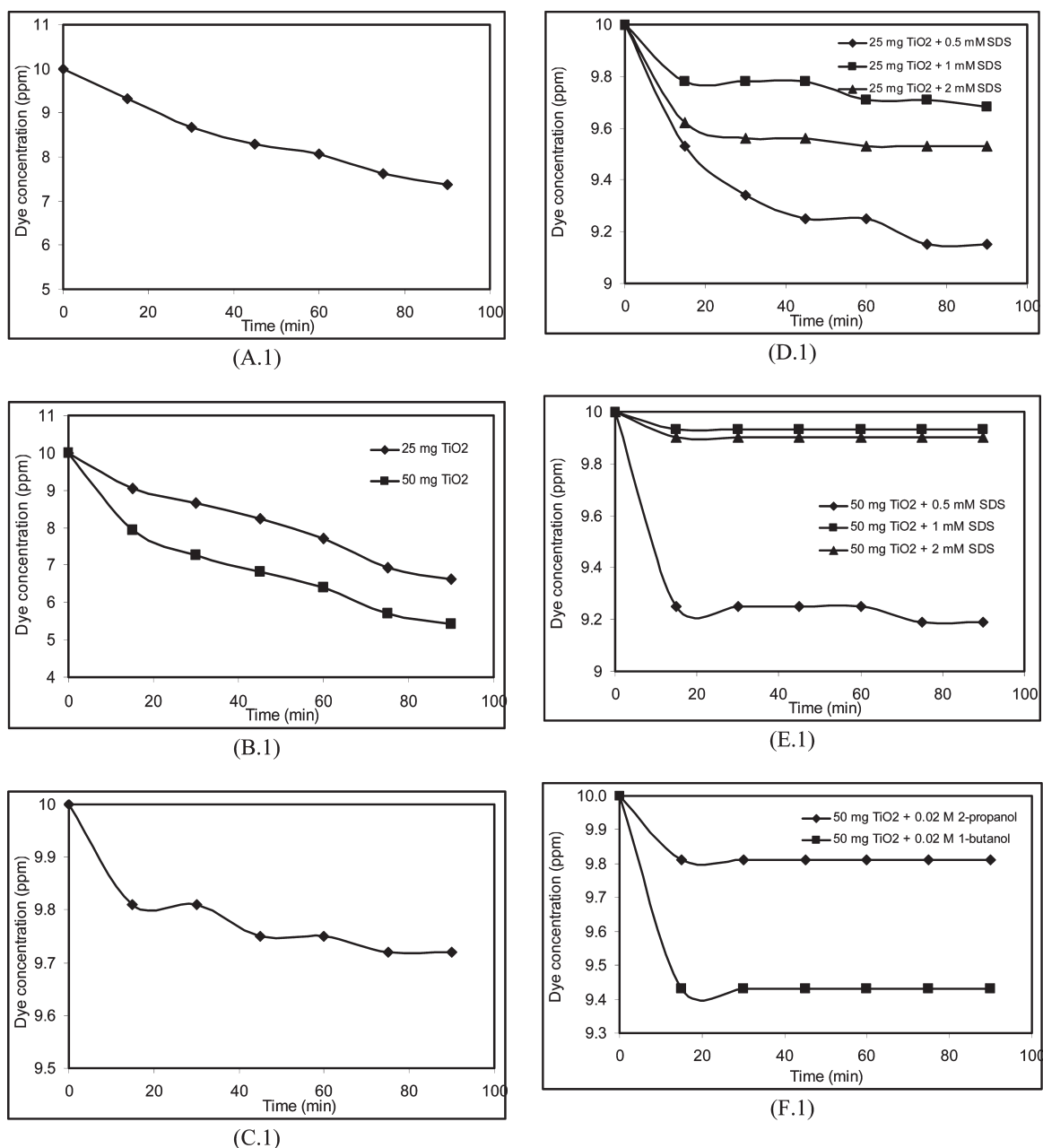
Figure 2. Trends on degradation of Acid Red B in different experimental categories (refer to Table 2A for greater details in experimental conditions). (A.1) Category 1, (B.1) category 2, (C.1) category 3, (D.1) category 4, (E.1) category 5, and (F.1) category 6.

molecule and the radicals generated from cavitation bubbles.[36] The radicals are highly energetic and unstable entities. After releasing into the medium with fragmentation of bubble collapse, these do not penetrate or diffuse into medium. Thus, the reaction between $^{\bullet}$OH radical and dye molecule will occur only if dye molecules are present in (sufficiently large concentration) at the site of bubble collapse. In case this condition is not met, the radicals would simply recombine to yield H_2O_2 or H_2O, which is clear loss of oxidation potential of cavitation bubbles. The probability of dye—radical interaction in a dilute solution is low, leading to small rates of degradation. This probability can be enhanced, if an adsorbent is present in the medium that causes an increase in local concentration of the dye molecules. The adsorbent, being a solid particle, can also provide nuclei for

cavitation.[37] The net consequence of this is an enhancement in the degradation of dye.

In the present study, we have conducted experiments with several parameters such as sonolysis alone, sonolysis with TiO_2 addition (25 and 50 mg), sonolysis with addition of TiO_2 and surfactant SDS (in 3 different concentrations), and sonolysis with addition of TiO_2 and aliphatic alcohols (2-propanol and 1-butanol). Addition of SDS to the reaction system would result in enhancement of the sonoluminescence, which is likely to enhance production of radicals through TiO_2. On the other hand, SDS itself is a good scavenger of the radicals, and thus, SDS molecules adsorbed at the bubble interface (or bubble wall) are likely to consume major fraction of radicals, before these can attack dye molecules and degraded them. SDS would also compete with the
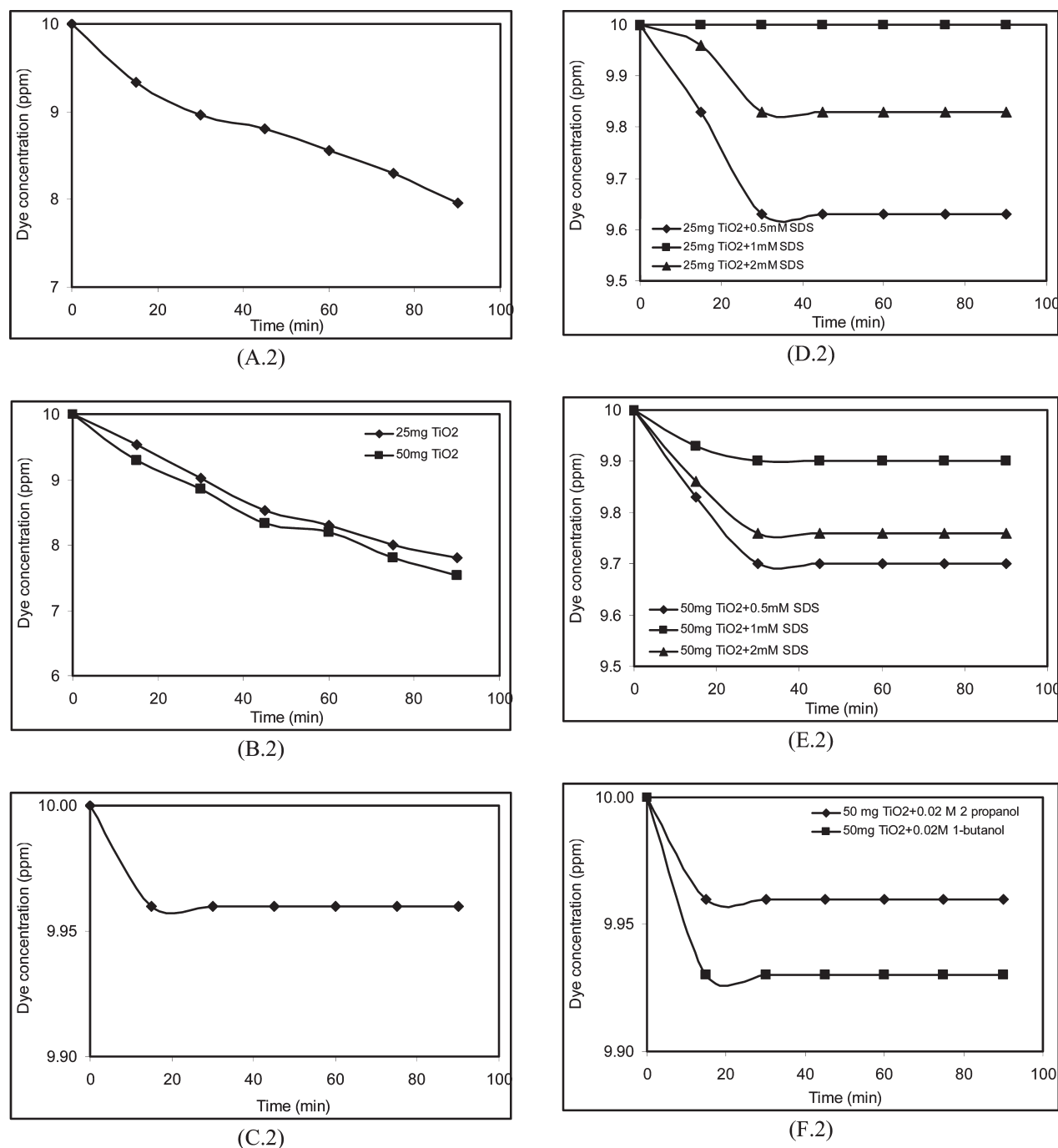
Figure 3. Trends on degradation of Reactive Red 2 in different experimental categories (refer to Table 2A for greater details in experimental conditions). (A.2) Category 1, (B.2) category 2, (C.2) category 3, (D.2) category 4, (E.2) category 5, (F.2) category 6.

dye molecules for adsorption onto TiO_2. Thus, results of experiments will provide an answer as what is the likely role played by the radicals generated from cavitation bubbles and the photocatalyst in overall degradation of dye.

Aliphatic alcohols are not likely to change the sonoluminescence intensity of cavitation bubbles. However, they are excellent scavengers of the $H^{\bullet}$ and $^{\bullet}OH$ radicals. Thus, like SDS, the alcohol molecules adsorbed on the interface as well as present in the bulk medium are likely to consume the radicals generated from cavitation bubbles, before they can attack and degrade the dye. Moreover, the alcohol can also compete with dye for adsorption onto the

TiO_2, causing reduction in the dye concentration on TiO_2. It should be noted that the holes and electrons generated on TiO_2 are extremely unstable. Therefore, the generation of the $^{\bullet}OH$ radical from these entities depends on extent of adsorption of water on TiO_2 surface. Moreover, the reaction of the $^{\bullet}OH$ radical so generated would be proportional to extent of dye adsorption on TiO_2. Some other physical mechanisms are also associated with UV-TiO_2 system. Rico et al.[38] have reported increase in hydrophilicity of the TiO_2 particles in presence of UV light, which can possibly contribute to greater adsorption of water on to the surface of these particles. This in turn could increase the
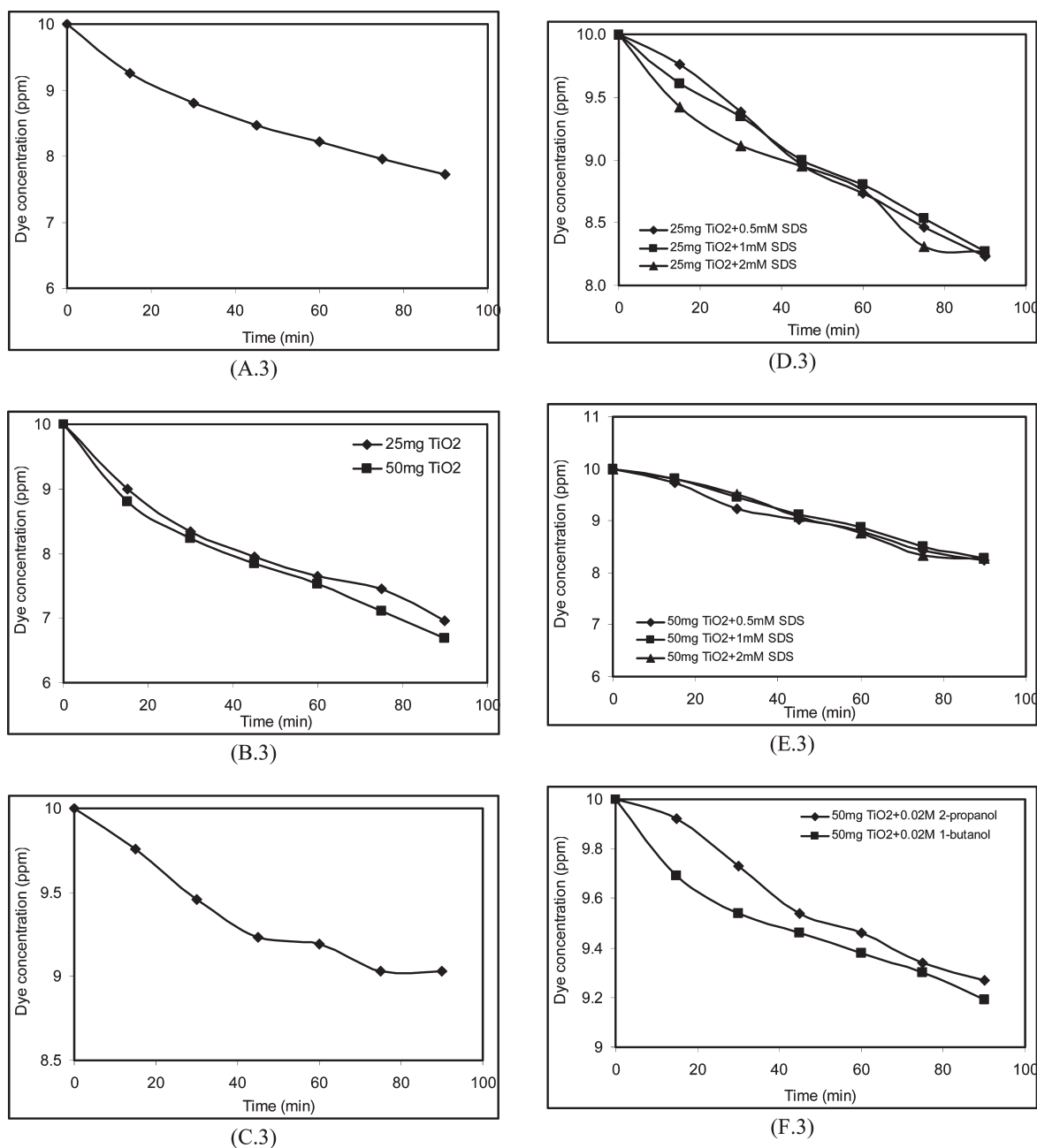
Figure 4. Trends on degradation of Direct Blue 6 in different experimental categories (refer to Table 2A for greater details in experimental conditions). (A.3) Category 1, (B.3) category 2, (C.3) category 3, (D.3) category 4, (E.3) category 5, and (F.3) category 6.

interaction between holes generated by photons and the water molecules and lead to formation of more radicals. Greater adsorption of water on particles may also reduce adsorption of dye molecules. However, we believe that these effects are more pronounced when an external UV light source is used in experiments.

With this preamble, we present the results of the experiments on sonochemical degradation of dyes with addition of photocatalyst, as well as surface active solutes, and try to deduce the role of the photocatalyst in the process.

4.2. Experimental Results. The experiments were done in 6 categories, namely, (1) sonolysis alone, (2) sonolysis with addition of TiO2 (25 and 50 mg), (3) sonolysis with addition of 1 mM SDS, (4) sonolysis with addition of 25 mg TiO2 and 3 concentrations of SDS

(0.5, 1, and 2 mM), (5) sonolysis with addition of 50 mg TiO2 and 3 concentrations of SDS (0.5, 1, and 2 mM), and (6) sonolysis with addition of 50 mg TiO2 and 0.02 M of aliphatic alcohols (2-propanol and 1-butanol). The results of these experiments, that is, percentage degradations in 90 min along with residual concentration of dye in the solution, are summarized in Table 2. Figures 2—4 depict the time history of degradation of Acid Red B, Reactive Red 2 and Direct Blue 6 dyes, respectively in 90 min of sonication. Table 3 gives the result of studies on dye adsorption on 25 mg TiO2 in pure solution and the solution with addition of 1 mM SDS.

From the results presented in Figures 2—4 and Tables 1 and 2, we can identify following trends in the degradation under different experimental conditions:

11491

dx.doi.org/10.1021/ie201127v |*Ind. Eng. Chem. Res.* 2011, 50, 11485–11494

Table 1. Physical Properties of Dyes

properties	Acid Red B	Reactive Red 2	Direct Blue 6
formula	$C_{20}H_{12}N_2Na_2O_7S_2$	$C_{19}H_{10}Cl_2N_6Na_2O_7S_2$	$C_{32}H_{20}N_6Na_4O_{14}S_4$
molecular weight	502.44 g/mol	615 g/mol	932.74 g/mol
peak absorption wavelength, λ_{max}	514 nm	538 nm	579 nm

Table 2. Experimental Results[a]

(A) summary of results on degradation of model dyes under different experimental conditions					
	Acid Red B		Reactive Red 2		Direct Blue 6	
category no. and experimental conditions	η (%)	C_R (ppm)	η (%)	C_R (ppm)	η (%)	C_R (ppm)
1. Sonication alone	26.3	7.37	20.4	7.96	22.8	7.72
2a. Sonication with 25 mg TiO_2	33.8	6.62	22	7.78	30.4	6.96
2b. Sonication with 50 mg TiO_2	45.7	5.43	24.7	7.53	33.1	6.69
3. Sonication with 1 mM SDS	2.8	9.72	0.4	9.96	9.7	9.03
4a. Sonication with 25 mg TiO_2 and 0.5 mM SDS	8.5	9.15	3.7	9.63	17.7	8.23
4b. Sonication with 25 mg TiO_2 and 1 mM SDS	3.2	9.68	0	10.0	17.3	8.27
4c. Sonication with 25 mg TiO_2 and 2 mM SDS	4.7	9.53	1.7	9.83	17.3	8.23
5a. Sonication with 50 mg TiO_2 and 0.5 mM SDS	8.1	9.19	3	9.7	17.7	8.23
5b. Sonication with 50 mg TiO_2 and 1 mM SDS	0.7	9.93	1.0	9.9	17.3	8.27
5c. Sonication with 50 mg TiO_2 and 2 mM SDS	1	9.9	2.4	9.76	17.3	8.27
6a. Sonication with 50 mg TiO_2 and 0.02 M 2−propanol	1.9	9.81	0.4	9.96	7.3	9.27
6b. Sonication with 50 mg TiO_2 and 0.02 M 1−butanol	5.7	9.43	0.7	9.93	8.1	9.19

(B) results on adsorption of various dyes on TiO_2 in presence of 1 mM SDS					
	Acid Red B		Reactive Red 2		Direct Blue 6	
experiments	C_R (ppm)	β %	C_R (ppm)	β %	C_R (ppm)	β %
100 mL solution (10 ppm) + 25 mg TiO_2	8.18	18.20	8.73	12.70	8.07	19.30
100 mL solution (10 ppm) + 25 mg TiO_2 + 1 mM SDS	9.81	1.90	9.93	0.70	9.15	8.50

[a] η = percentage of the initial dye degraded in 90 min of sonication (calculated as $(C_o - C_R) \times 100/C_o$), where C_o is the initial dye concentration and C_R is residual dye concentration.

1. Compared to degradation with sonication alone (category 1), addition of TiO_2 to the medium increases the degradation. However, the extent of increase in degradation is different for the three dyes. With addition of 25 mg TiO_2, % degradation of Acid Red B and Direct Blue 6 show about ~30−35% increase in degradation, while degradation of Reactive Red 2 shows only with marginal rise ~10% rise. Smaller rise in degradation of Reactive Red 2 could be attributed to its lesser adsorption on TiO_2, as evident from results given in Table 2(B).

2. With doubling of the quantity of TiO_2, the extent degradation does not show a proportionate, or even close to proportionate, rise. For Acid Red B, a significant rise of ~50% in degradation is seen; however, for Reactive Red 2 and Direct Blue 6, the degradation stays practically unchanged (with a trivial rise of ~10%).

3. Addition of the surfactant SDS (1 mM) drastically reduces the extent of degradation of all 3 dyes. The highest reduction is seen for Reactive Red 2, where practically zero degradation is seen with SDS, while for Acid Red B and Direct Blue 6, a marginal degradation is seen in presence of SDS.

4. In Category 4, experiments (25 mg TiO_2 with varying concentrations of SDS), an interesting trend is seen. For 0.5 mM SDS, the extent of degradation rises with TiO_2 addition for all three dyes (as compared to category 3 in which 1 mM SDS is added to dye solution prior to sonication). However, increase in SDS concentration to 1 mM, with TiO_2 quantity fixed, reduces the degradation for Acid Red B and Reactive Red 2. Nonetheless, the degradation of Direct Blue 6 stays unchanged. With SDS concentration further rising to 2 mM, degradation of Acid Red B and Reactive Red 2 shows some rise; however, degradation of Direct Blue 6 stays practically unchanged, as compared to degradation with 0.5 mM SDS added solutions.

5. Essentially same trends as in Category 4 are seen in Category 5, where quantity of TiO_2 is doubled for same concentrations (0.5, 1, and 2 mM) of SDS. Quite interestingly, the extent of degradation for the three dyes is more or less same in presence of double quantity of TiO_2.

6. About 3−6-fold reduction in extent of degradation is also seen with addition of alcohols. All three dyes show greater degradation in presence of 1-butanol than 2-propanol. However, marked difference is seen in the extent of degradation seen for the three dyes. For Acid Red B, almost 3-fold difference is seen in degradation in presence of two alcohols, while for Direct Blue 6, the difference is only 10%. Comparing among the dyes, we find degradation is the order of Direct Blue 6 > Reactive Red 2 > Acid Red B.

4.3. Analysis. The result of the experiments presented in previous section gives us strong hints about the relative contributions of sonolysis and photocatalysis in the overall degradation of dyes.

1. Marginal rise in the degradation with addition of TiO_2, as compared to sonolysis alone give an indication that the contributions of photocatalyst to degradation could be low. Small change in extent of degradation of three dyes with doubling the quantity TiO_2 further strengths this indication.

2. Minimum degradation shown by all three dyes with increasing concentrations of SDS is basically a consequence of 3 independent phenomena associated with SDS. As noted earlier, SDS being a surface active solute, adsorbs on bubble interface causing declustering of bubbles, which increases the active bubble population in the medium. These "active" bubbles increase both sonoluminescence intensity as well as radical production. However, SDS itself is a good scavenger of radicals. Therefore, it consumes the radicals generated from cavitation bubbles, before they can attack the dye molecules. Second, SDS molecules reduce the adsorption of dye on TiO_2, because of which the concentration of dye in bulk solution (with very dilute concentration of dye 10 ppm) increases. This is likely to reduce the probability of dye—radical interaction leading to reduction in degradation. However, addition of surfactant reduces the surface tension of the solution, because of which cavitation threshold (the minimum acoustic pressure amplitude needed to generate cavitation) decreases;[39] or in other words, the energy needed to initiate cavitation decreases. Consequently, for the same ultrasound intensity (or same energy input), the number of active bubbles generated in the medium increases with increase in surfactant concentration. Thus, the minima in extent of degradation with increasing concentration of SDS would be explained in terms of (1) rise in number of active bubbles at 0.5 mM concentration because of declustering of bubble clouds (along with reduction in adsorption rise of dye on TiO_2), (2) extensive scavenging of radicals by SDS at 1 mM concentration, (3) rise in "active bubbles" at 2 mM because of lowering of surface tension with consequent decrease of transient cavitation threshold. As all of the three phenomena are independent of TiO_2 concentration in the bulk medium, it is rather obvious that trends observed in results of Category 4 and 5 are essentially the same, with minor quantitative differences.

3. Reduction in degradation with addition of alcohol is strong indicating that the degradation of dye is essentially because of the radicals generated from cavitation bubbles only. Like SDS, alcohol molecules also adsorb on bubble interface and reduce sonoluminescence. However, proven by Tronson et al.,[30] this phenomenon is not seen at low frequencies of 20 kHz, similar to that used in this study. Therefore, the sonoluminescence intensity in the medium is not changed. This would also mean that production of $^\bullet$OH radicals due to activation of photocatalyst by sonoluminescence radiation would also stay unchanged. Nonetheless, alcohols are powerful scavengers of $H^\bullet$ and $^\bullet$OH radials. Therefore, the radicals released by cavitation bubbles in the bulk medium are consumed (at a much higher rate than SDS) by alcohol molecules, the consequence of which is seen in drastic reduction of degradation. Like SDS, alcohols also adsorb on TiO_2, resulting in desorption of dye. This factor may also contribute to reduction in degradation. Higher degradation seen for 1-butanol than 2-propanol indicates that the scavenging of radicals by longer chain alcohol, due to which larger number of $OH^\bullet$ radicals are available for degradation of dye. 1-Butanol, being larger molecule than 2-Propanol, would have higher tendency to adsorb on support such as TiO_2. If TiO_2 would have been generating $OH^\bullet$ radicals, the adsorbed butanol would consume them, before they would attack the adsorbed dye molecules. This would mean that the extent of degradation, if caused by the radicals generated from photocatalyst (under sonoluminescence light emission), would be lower for 1-butanol than 2-propanol. However, a reverse trend is seen, which indicates that the TiO_2 does not contribute to the generation of radicals through photocatalysis, and that the degradation of dye almost entirely is due to the radicals from cavitation bubbles.

5. OVERVIEW

The analysis of experimental results vis-à-vis effect of surface active solutes indicates that the expected synergy between sonolysis and photocatalysis is not obtained in sonophotocatalysis reaction system. The sonoluminescence light emission is not able to activate TiO_2 to generate additional radicals. This would also mean that an external source of UV radicals is essential in such systems to activate the photocatalyst. In absence of such a source, the role of TiO_2 is mere physical in that it acts as an adsorbent for the dye molecules or as investigated by previous authors,[37] TiO_2 may provide site for cavitation (that would generate more "active" bubbles) in the system, because of the gas pockets trapped in the crevices of the particles.

It remains to be discussed, as what is the possible mechanism underlying enhancement of degradation when sonolysis and photocatalysis (with an external source of UV irradiation) are applied together. It appears from the results of present study that the enhancement is merely due to the additive effects of degradation caused by two techniques, acting more—or—less independently. An alternative answer to this question could also be in terms of the physical effect of ultrasound and cavitation, that is, generation of intense microconvection in the system that facilitates the transport processes (essentially rendering equilibration of adsorption/desorption faster) in the system. The microconvection due to ultrasound and cavitation would facilitate the transport of pollutant molecules to the surface of the photocatalyst, where it can adsorb, and react with the $^\bullet$OH radicals generated by reaction of holes with adsorbed H_2O molecules. The microconvection may also assist desorption of the product from photocatalyst surface, making it accessible to the next molecules. Another possible contribution of ultrasound and cavitation could be in terms of deagglomeration of the TiO_2 particles. This would increase the effective surface area of these particles, with consequent increase in extent of adsorption of dye molecules.

The results of this study have, thus, provided strong hints that the role of TiO_2 in sonophotocatalytic reactions (without external UV) is merely physical. The synergy between the two mechanisms is also of physical nature.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: vmoholkar@iitg.ernet.in. Fax: +91 361 258 2291.

■ REFERENCES

(1) Robinson, T.; McMullan, G.; Marchant, R.; Nigam, P. Remediation of Dyes in Textile Effluent: A Critical Review on Current Treatment Technologies with a Proposed Alternative. *Bioresour. Technol.* **2001**, *77*, 247.

(2) Andreozzi, R.; Caprio, V.; Insola, A.; Marotta, R. Advanced Oxidation Processes (AOP) for Water Purification and Recovery. *Catal. Today* **1999**, *53*, 51.

(3) Suslick, K. S. Sonochemistry. *Science* **1990**, *247*, 1439.

(4) Kamath, V.; Prosperetti, A.; Egolfopoulos, F. N. A Theoretical Study of Sonoluminescence. *J. Acoust. Soc. Am.* **1993**, *94*, 248.

(5) Prasad Naidu, D. V.; Rajan, R.; Kumar, R.; Gandhi, K. S.; Arakeri, V. H.; Chandrasekaran, S. Modeling of a Batch Sonochemical Reactor. *Chem. Eng. Sci.* **1994**, *49*, 877.

(6) Hart, E. J.; Henglein, A. Sonochemistry of Aqueous Solutions: Hydrogen−Oxygen Combustion in Cavitation Bubbles. *J. Phys. Chem.* **1987**, *91*, 3654.

(7) Colussi, A. J.; Weavers, L. K.; Hoffmann, M. R. Chemical Bubble Dynamics and Quantitative Sonochemistry. *J. Phys. Chem. A* **1998**, *102*, 6927.

(8) Yasui, K. Alternative Model for Single−Bubble Sonoluminescence. *Phys. Rev. E* **1997**, *56*, 6750.

(9) Storey, B. D.; Szeri, A. J. Water Vapor, Sonoluminescence and Sonochemistry. *Proc. R. Soc. Lond. Ser. A* **2000**, *456*, 1685.

(10) Wang, S.; Gong, Q.; Liang, J. Sonophotocatalytic Degradation of Methyl Orange by Carbon Nanotube/TiO$_2$ in Aqueous Solutions. *Ultrason. Sonochem.* **2009**, *16*, 205.

(11) Abbasi, M.; Asl, N. R. Sonochemical Degradation of Basic Blue 41 Dye Assisted by NanoTiO$_2$ and H$_2$O$_2$. *J. Hazard. Mater.* **2008**, *153*, 942.

(12) Kubo, M.; Matsuoka, K.; Takahashi, A.; Kitakawa, N. S.; Yonemoto, T. Kinetics of Ultrasonic Degradation of Phenol in the Presence of TiO$_2$ Particles. *Ultrason. Sonochem.* **2005**, *12*, 263.

(13) Shimizu, N.; Ogino, C.; Dadjour, M. F.; Murata, V. Sonocatalytic Degradation of Methylene Blue with TiO$_2$ Pellets in Water. *Ultrason. Sonochem.* **2007**, *14*, 184.

(14) Chen, Y. C.; Smirniotis, P. Enhancement of Photocatalytic Degradation of Phenol and Chlorophenols by Ultrasound. *Ind. Eng. Chem. Res.* **2002**, *41*, 5958.

(15) Ge, M.; Guo, C.; Zhu, X.; Ma, L.; Han, Z.; Hu, W.; Wang, Y. Photocatalytic Degradation of Methyl Orange Using ZnO/TiO$_2$ Composites. *Frontiers Environ. Sci. Eng. China* **2009**, *3*, 271.

(16) Kaur, S.; Singh, V. Visible Light Induced Sonophotocatalytic Degradation of Reactive Red Dye 198 Using Dye Sensitized TiO$_2$. *Ultrason. Sonochem.* **2007**, *14*, 531.

(17) Pradhan, A. A.; Gogate, P. R. Degradation of *p*-Nitrophenol Using Acoustic Cavitation and Fenton Chemistry. *J. Hazard. Mater.* **2010**, *173*, 517.

(18) Zhang, Z.; Yuan, Y.; Liang, L.; Fang, Y.; Cheng, Y.; Ding, H.; Shi, G.; Jin, L. Sonophotoelectro Catalytic Degradation of Azo Dye on TiO$_2$ Nanotube Electrode. *Ultrason. Sonochem.* **2008**, *15*, 370.

(19) Wang, J.; Jiang, Z.; Zhang, Z.; Xie, Y.; Wang, X.; Xing, Z.; Xu, R.; Zhang, X. Sonocatalytic Degradation of Acid Red B and Rhodamine B Catalyzed by Nanosized ZnO Powder Under Ultrasonic Irradiation. *Ultrason. Sonochem.* **2008**, *15*, 768.

(20) Kritikos, D. E.; Xekoukoulotakis, N. P.; Psillakis, V.; Mantzavinos, D. Photocatalytic Degradation of Reactive Black 5 in Aqueous Solutions: Effect of Operating Conditions and Coupling with Ultrasound Irradiation. *Water Res.* **2007**, *41*, 2236.

(21) Pandit, A. B.; Gogate, P. R.; Mujumdar, S. Ultrasonic Degradation of 2,4,6 Trichlorophenol in the Presence of TiO$_2$ Catalyst. *Ultrason. Sonochem.* **2001**, *8*, 227.

(22) Davydov, L.; Reddy, E. P.; France, V.; Smirniotis, P. G. Sonophotocatalytic Destruction of Organic Contaminants in Aqueous Systems on TiO$_2$ Powders. *Appl. Catal. B: Environ.* **2001**, *32*, 95.

(23) Iida, Y.; Kozuka, T.; Tuziuti, T.; Yasui, K. Sonochemically Enhanced Adsorption and Degradation of Methyl Orange with Activated Aluminas. *Ultrasonics* **2004**, *42*, 635.

(24) Wang, J.; Guo, B.; Zhang, X.; Zhang, Z.; Han, J.; Wu, J. Sonocatalytic Degradation of Methyl Orange in the Presence of TiO$_2$ Catalysts and Catalytic Activity Comparison of Rutile and Anatase. *Ultrason. Sonochem.* **2005**, *12*, 331.

(25) Li, F.; Lu, X.; Mei, P. Sono-photocatalytic Degradation of Azo Dye Reactive Brilliant Red X-3B. *Environ. Sci. Technol.* **2009**, *2* (Pt. B), 1285.

(26) Dai, Z.; Chen, A.; Kisch, H. Efficient Sonochemical Degradation of 4-Chlorophenol Catalyzed by Titanium Dioxide Hydrate. *Chem. Lett.* **2005**, *34*, 1706.

(27) Vinu, R.; Giridhar, M. Kinetics of Sonophotocatalytic Degradation of Anionic Dyes with Nano TiO$_2$. *Environ. Sci. Technol.* **2009**, *43*, 473.

(28) Ashokkumar, M.; Grieser, F. The Effect of Surface Active Solutes on Bubbles in an Acoustic Field. *Phys. Chem. Chem. Phys.* **2007**, *9*, 5631.

(29) Ashokkumar, M.; Hall, R.; Mulvaney, P.; Grieser, F. Sonoluminescence from Aqueous Alcohol and Surfactant Solutions. *J. Phys. Chem. B* **1997**, *101*, 10845.

(30) Tronson, R.; Ashokkumar, M.; Grieser, F. Comparison of the Effects of Water−Soluble Solutes on Multibubble Sonoluminescence Generated in Aqueous Solutions by 20- and 515-kHz Ultrasound. *J. Phys. Chem. B* **2002**, *106*, 11064.

(31) Segebarth, N.; Eulaerts, O.; Reisse, J.; Crum, L. A.; Matula, T. J. Correlation Between Acoustic Cavitation Noise, Bubble Population and Sonochemistry. *J. Phys. Chem. B* **2002**, *106*, 9181.

(32) Sunartio, D.; Ashokkumar, M.; Grieser, F. The Influence of Acoustic Power on Multibubble Sonoluminescence in Aqueous Solution Containing Organic Solutes. *J. Phys. Chem. B* **2005**, *109*, 20044.

(33) Sunartio, D.; Ashokkumar, M.; Grieser, F. Study of the Coalescence of Acoustic Bubbles as a Function of Frequency, Power, and Water-Soluble Additives. *J. Am. Chem. Soc.* **2007**, *129*, 6031.

(34) Rahal, R.; Pigot, T.; Foix, D.; Lacombe, S. Photocatalytic Efficiency and Self-Cleaning Properties Under Visible Light of Cotton Fabrics Coated with Sensitized TiO$_2$. *Appl. Catal. B:Environ.* **2011**, *104*, 361.

(35) Sivasankar, T.; Paunikar, A. W.; Moholkar, V. S. Mechanistic Approach to Enhancement of the Yield of a Sonochemical Reaction. *AIChE J.* **2007**, *53*, 1132.

(36) Sivasankar, T.; Moholkar, V. S. Mechanistic Approach to Intensification of Sonochemical Degradation of Phenol. *Chem. Eng. J.* **2009**, *149*, 57.

(37) Tuziuti, T.; Yasui, K.; Iida, Y.; Taoda, H.; Koda, S. Effect of Particle Addition on Sonochemical Reaction. *Ultrasonics* **2004**, *42*, 597.

(38) Rico, V.; Lopez, C.; Borras, A.; Espinos, J. P.; Gonzales-Elipe, A. R. Effect of Visible Light on the Water Contact Angles on Illuminated Oxide Semiconductors Other Than TiO$_2$. *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 2944.

(39) Mason, T. J.; Lorimer, J. P. *Applied Sonochemistry: The Uses of Power Ultrasound in Chemistry and Processing*; Wiley: Coventry, U.K., 2002.

11494

dx.doi.org/10.1021/ie201127v |*Ind. Eng. Chem. Res.* 2011, 50, 11485–11494