Improved Photocatalytic Activity of TiO_2 Coupling Ultrasound for Reactive Blue 19 Degradation

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Summary: The degradation of Reactive Blue 19 (RB 19) using photolysis, photocatalysis and sonophotocatalysis in aqueous solutions was investigated. Emphasis was given on the effects of different operating conditions viz. catalyst concentration, pH, initial dye concentration, ultrasonic power and reaction time) on RB 19 degradation. The extent of photocatalytic and sonophotocatalytic degradation was increased by decreasing pH, initial dye concentration and increasing catalysts loading and ultrasonic power. Ultrasound combined with photocatalysis was found efficient than the respective individual processes due to the enhanced formation of reactive hydroxyl radicals as well as the possible ultrasound-induced increase of the active surface area of the catalyst. The sonophotocatalytic efficiency was increased in acidic conditions as compare to individual processes at same experimental conditions (100 mg L^{-1} of dye concentration, 300 mg L^{-1} of TiO_2 concentration, 240 W ultrasonic power and at pH 4). The kinetic study of RB 19 degradation under different experimental conditions apparently followed first order reaction. The intermediates and end products formed during the degradation were identified using gas chromatography/mass spectrometry (GC/MS) and a possible degradation pathway of RB 19 was proposed.

Keywords: Photocatalytic degradation, Sonophotocatalytic degradation, RB 19 dye, ultrasonic cavitation, GC/MS intermediates and products, wastewater treatment

Introduction

Water is one of the fundamental requirements of life and addition of any foreign material from different sources like agricultural runoff, industrial effluents and chemical spills leads to its contaminations [1]. These effluents contained many toxic and non-biodegradable organic substances like, pesticides, herbicides and dyes, which are highly stable to natural decomposition and persistent to environment [2]. Of all these compounds, dyes having their carcinogenic nature constitute a major threat to the environment [3]. Earlier studies have shown that during dyeing and washing processes of textile goods, a significant amount of dyestuff i.e. 15% exhausted in the effluents [4]. The release of wastewater containing the dye poses a dramatic source of water pollution, eutrophication and perturbation of aquatic life [5]. Therefore, the removal of such pollutants from the effluents is important for sustainability of environment [6].

Several methods have been investigated like biological and chemical oxidation [7], adsorption, photolysis, electrochemical and sonolysis [8, 9] for the treatment of dyes wastewater. An advanced oxidation process (AOP) involving the generation of powerful oxidizing agent like hydroxyl radical has gained much attention for treatment of contaminated industrial, ground and surface water in the recent years [10, 11]. Some recent trends revealed the superiority of using combined or sequential methods over single technique for the treatment of dye wastewater. The concept of compatible combined techniques has proven to be more successful keeping in view the complex nature of real industrial effluents. Heterogeneous photocatalysis and sonochemical are two such techniques having potential to degrade dye molecules using $\cdot OH$ radicals [12, 13]. Photocatalysis process utilizes the UV radiation to photo-excite a semiconductor catalyst for the generation of $\cdot OH$ radicals while sonochemical effect is based upon the nucleation, growth and collision of micro bubbles in the liquid. These bubbles collisions bring about localized supercritical conditions of high pressure and temperature that further resulted in the cleavage of water molecules to produce H and OH radicals as a consequence [14]. The oxidation potential of $\cdot OH$ (2.8 V) is considerably higher than other oxidizing species such as O_3 (2.07 V) and H_2O_2 (1.77 V). The

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rule of thumb is the higher the oxidation potential, the greater the decomposing capability of the material. Photocatalysis and sonolysis, the two process under investigation contribute towards the production of ·OH as a dominant free radical which is mainly responsible for increasing the rates of reaction. Thus, the expected synergism between these two modes of irradiation can possibly attributed to:

1. Cavitational effects leading to increase in the temperatures and pressure at the localized micro void cavity implosion sites.
2. Cleaning and sweeping of the TiO_2 surface due to acoustic micro streaming allows more active catalyst sites at any given time.
3. Mass transport of the reactants and products is increased at the catalyst surface and in the solution, due to the facilitated transport by shockwave propagation.
4. Surface area is increased by fragmentation or pitting of the catalyst.
5. Cavitation induced radical intermediates participate in the destruction of organic compounds.
6. The organic substrate reacts directly with the photo generated surface holes and electrons under cavitating conditions [15].

Despite having comparable mode of action the combined effect of the two advanced oxidation techniques are rarely studied for Reactive Blue 19 dye and yet need to be exploited. In the present study, an attempt has made to examine the degradation through photocatalysis and the combined effect of photocatalysis and sonolysis as an efficient tool. For practical applications effect of different parameters such as pH, catalyst loading, dye concentration and ultrasonic power was also studied.

Results and Discussions

Photocatalytic Degradation

A number of controlled experiments were conducted on RB 19 dye (100 mg L^{-1}) under Ultraviolet (UV) irradiations, Titanium dioxide (TiO_2) and TiO_2/UV irradiation over a reaction time of 120 min. No significant change in concentration of the dye was observed by UV light or TiO_2 alone. In the presence of TiO_2 along with UV light 35 % of the dye decolorization was observed within 120 min of irradiation as shown in Fig. 1.

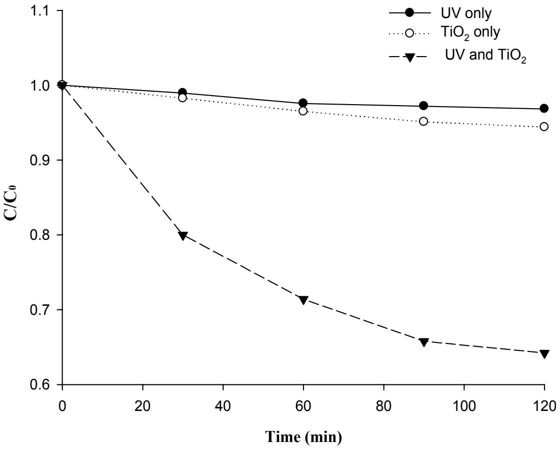

Fig. 1: Degradation of RB 19 dye in the presence of different experimental conditions.

Effect of Catalysts

In order to avoid the excessive use of catalyst, the optimum dose was determined using concentrations (20, 50, 100, 200, 300, 400 and 500 mg L^{-1}) of TiO_2 under UV light. It was found that rate of degradation initially increases with the increase in catalyst concentration, but beyond a certain level it remained almost constant. In present case 300 mg L^{-1} was found to be the optimum catalyst concentration [4]. The increase in catalysts concentration has a positive influence on the number of photons absorbed and number of dye molecules adsorbed. This in turns enhances the rate of dye degradation. Above a certain catalysts concentration the numbers of substrate molecules are not sufficient to fill the surface active sites of TiO_2. Hence, further addition of catalyst does not lead to the enhancement of degradation rate. This is may be due to the reduction in the penetration of light with surplus amount of TiO_2. The surplus addition of the catalyst makes the solution more turbid and light penetration is hindered from the sample [16, 17].

Effect of Initial pH

The solution pH is an important parameter and the effect of different pH conditions (3 to 10) on the degradation of RB 19 dye was investigated (Fig. 2). The degradation of dye was increased in acidic conditions and decreased with the increased in pH of the solution. Therefore the photodegradation experiments were conducted in the acidic pH conditions.

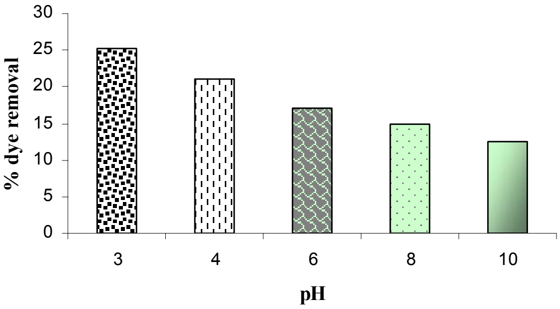

Fig. 2: Effect of pH on photodegradation of dye

The RB 19 dye used in this study have negatively charged sulfonic group in the structure, thus at acidic solution interaction between catalyst surface and dye favors the adsorption. On the other hand, at high pH values, titanium dioxide surface is negatively charged and adsorption of the dyes does not occur [18]. In the acidic pH, the surface of TiO_2 acquire a positive charge thereby attracting the RB 19 dye, leading to the greater adsorption and increasing the degradation rate in acidic media. The reverse effect was observed in the basic medium where the TiO_2 surface is negatively charged which repels the dye and decreased the degradation rate as shown in Eq. (1, 2).

$$TiOH + H^+ \rightarrow TiOH_2^+ \quad (1)$$

$$TiOH + {}^-OH \rightarrow TiO^- + H_2O \quad (2)$$

Effect of Initial Concentration

The effect of dye concentration on the decolorization rate of RB 19 dye was also investigated by changing the initial dye concentration (50 to 250 mg L^{-1}) in the presence of optimum quantity of TiO_2 catalyst and pH. The results showed that the degradation rate decreased with the increase in initial dye concentrations (Fig. 3). The optimum concentration of dye was found 100 mg L^{-1}. This was due to the reason as the initial concentration of the dye increased the concentration of unabsorbed dye in the solution increased, which lead to less penetration of light through the solution on to the surface of TiO_2, thereby decreased the concentration of ·OH radicals on the surface and hence decreased the degradation rate. However, there is a reverse effect at lower dye concentration, where the light intensity and time irradiation is same but the interception of photons to the catalyst surface is increased leading to the formation of more ·OH radicals, hence increase rate of degradation [17].

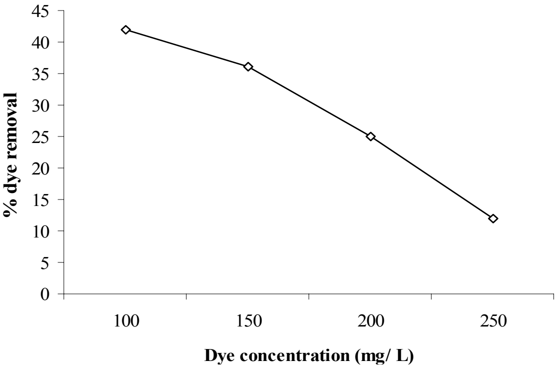

Fig. 3: Effect of dye initial concentration on percentage degradation of RB 19 by photocatalysis process, Reaction conditions: initial pH = 4, TiO_2 conc. = 300 mg L^{-1}

Sonophotocatalytic Degradation

Under optimized conditions of dye concentration (100 mg L^{-1}), catalysts concentrations (300 mg L^{-1}) and pH 4, further experiments were conducted under sonolysis (US), photocatalysis ($UV+TiO_2$) and sonophotocatalysis ($US+UV+TiO_2$) processes to study their effect on degradation rates. It is found from the results (Fig. 4) that after 120 min, 73%, 35% and 12% dye degradation takes place under sonophotocatalysis, photocatalysis and sonolysis processes respectively.

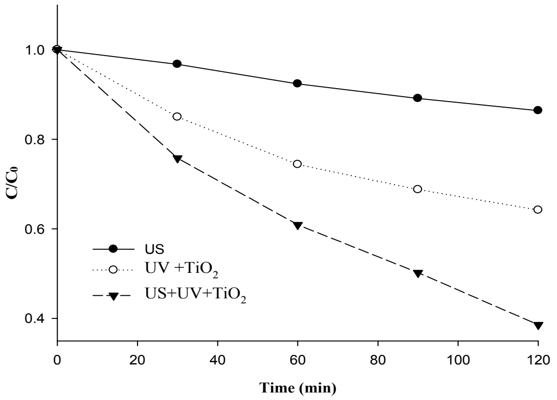

Fig. 4: Comparison of sonolysis, photocatalysis and sonophotocatalysis processes for degradation of RB 19, Reaction conditions: initial pH = 4, dye conc. = 100 mg L^{-1}, TiO_2 conc. = 300 mg L^{-1}, US power = 240 W

The dye degradation under photocatalysis is enhanced by ultrasound. Both in photocatalysis and sonophotocatalysis the dye is decomposed mainly through the generation of ·OH radicals. In sonophotocatalysis process, ·OH radicals are generated from splitting of water molecules under extreme conditions created by collision of cavitational bubbles. In photocatalysis process the ·OH radicals are generated by UV radiation to photo-excite a semiconductor catalyst. The combine effect thus increases the amount of reactive radical species inducing oxidation of dye molecules [4].

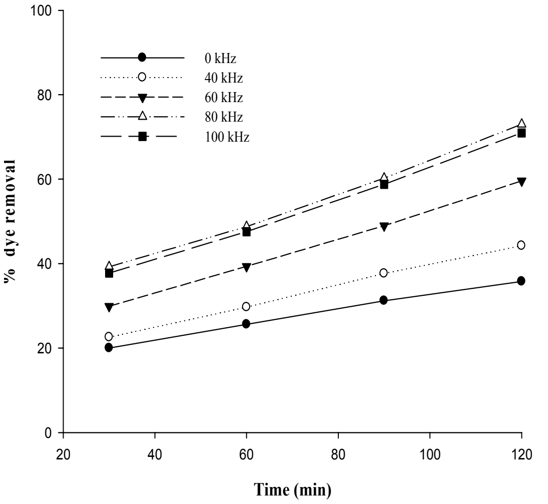

Fig. 5: Effect of ultrasonic power settings on percentage degradation of RB 19 by sonophotocatalysis process, Reaction conditions: initial pH = 4, dye conc. = 100 mg L^{-1}, TiO_2 conc. = 300 mg $L^{-1.}$

Effect of Ultrasonic Power

To investigate the effect of ultrasonic power sonophotocatalytic experiments are conducted with optimized conditions of dye and TiO_2 concentrations at pH 4 with different ultrasonic power settings ranged from 120-300 W (Fig. 5). The results show that the increase in ultrasonic power causes a decrease in the residual dye concentration. The maximum 73% dye degradation is observed at 240 W after 120 min. Ultrasound produces its sonochemical effects through the formation of cavitation bubbles. The increase in ultrasonic power has a significant effect on the collapse of cavitation bubbles. At higher power, the life time of bubbles is shorter and collapse occurs very quickly with the production of ·H and ·OH radicals, thus enhancing the possibility of radical's attack on dye molecule. In general, an increase in ultrasonic power results in an increase in the rate of reaction [19]. However, by increasing ultrasonic power from 240 to 300 W, no significant increase in dye degradation is observed. This was due to the reasons that a maximum rate of reaction can be obtained in any chemical reaction when an optimum acoustic power exists therefore a great number of cavitational bubbles are generated at higher ultrasonic power [19].

Kinetics Studies

Under different experimental conditions of sonolysis (US), photocatalysis (UV+TiO_2) and sonophotocatalysis (US+UV+TiO_2) order of reaction is determined. A graph of ln (C_t/C_0) vs. time is plotted. The dye degradation apparently follows 1st order of kinetics [20] (Fig. 5). The correlation between ln (C_t/C_0) and treatment time is linear (straight line). This is a typical first order reaction plot (Fig. 6). The slopes of the lines show the rate constant (k) of the reaction. The regression coefficient R^2 obtains for first order reaction at different experimental conditions which ranges from 0.97 to 0.99, confirming that degradation of RB 19 under different experimental conditions i.e. sonolysis (US), photocatalysis (UV+TiO_2) and sonophotocatalysis (US+UV+ TiO_2), follows the first order reaction.

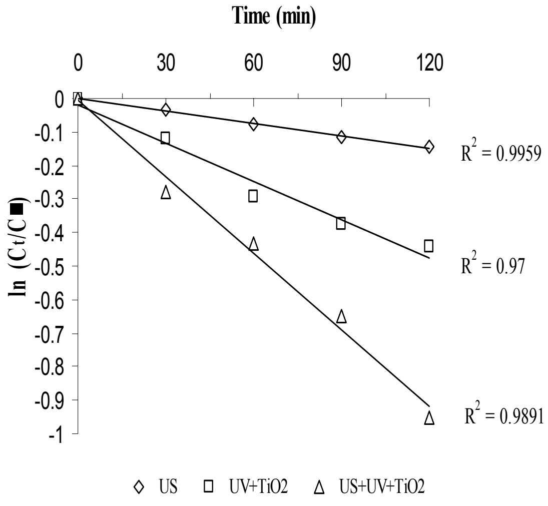

Fig. 6: First order kinetics plot of RB 19 degradation under sonolysis (US), photocatalysis (UV+TiO_2) and sono-photocatalysis (US+UV+ TiO_2), Reaction conditions: initial pH = 4, dye conc. = 100 mg L^{-1}, TiO_2 conc. = 300 mg L^{-1}, US power = 240 W

TOC Analysis

Reduction in TOC contents reflects the mineralization of organic compound. The reduction in total organic carbon is studied for sonolysis, photocatalysis and sonophotocatalysis process under optimum conditions; initial concentration of 100 mg L^{-1}, pH 4, catalysts loading of 300 mg L^{-1} and ultrasonic power 240 W under ultraviolet light. It was observed (Table 1) that the heterogeneous nature of treatment (sonophotocatalysis) permitted an overall TOC reduction of about 55% in 120 min. While individually sonolysis and photocatalysis techniques caused 7.2% and 10.18% respective reduction of TOC after 120 min.

Table-1: Reduction of the total organic carbon content.

Process	TOC reduction (%)
Sonolysis	**7.2 %**
Photocatalysis	**10.18 %**
Sonophotocatalysis	**55 %**

Reaction conditions: initial pH = 4, dye conc. = 100 mg L^{-1}, TiO_2 conc. = 300 mg L^{-1}, US power = 240 W

Degradation Pathway of the RB 19 identified by GC/MS

The products which were formed after the treatment of RB 19 were identified using GC/MS. The degradation pathway is illustrated in Fig. 7. The bonds which are most fragile in oxidation conditions as provided in this study are between C(5)–C(6), C(13)–C(14), C(6)–C(7), C(12)–C(13), C(8)–N, C(9)–S, C(11)–N, C(17)–S, C(15)–N. It is proposed that in first stage, C(11)-N is broken to give anthraquinone derivative **(1)** and product **(2)**, which further decomposes to anthraquinone **(3)**, after the cleavage of C(8)–N, C(9)–S, C(11)–N during treatment of 30 min. Further treatment time of 60 min resulted in the cleavage of C(6)–C(7), C(12)–C(13) bonds forming isobenzofuran- 1,3-dione **(4)** and 2,3-dihydronaphthalene-1,4-dione **(5)**. These compounds further degraded to smaller aromatic oxidized products like benzoic acid **(6)**, benzaldehyde **(7)**. Last products of decomposition are supposed to be small aliphatic acids e.g. acetic acid which is evident from nearly colorless solution after dye treatment.

Experimental

Materials

Reactive Blue 19 dye was a commercialized product obtained from Arzoo Textile Mill, Faisalabad and was used as received with out further purification [19]. The photocatalyst used in all experiments was titanium dioxide powder from Acros Organics, Scientific Fisher Company, Belgium.

Procedure

A sonophoto reactor was constructed as shown in Fig. 8. Degradation experiments were carried out in the reactor at room temperature. The immersion well type photo reactor was provided with water circulating jacket for maintaining reaction temperature. Irradiation was provided by 9-Watt UV-A source (Philips) lamp with wavelength of 365 nm placed vertically in the middle of the reactor. To study the effect of ultrasound, the photo reactor was immersed in a Digital Ultrasonic Bath (300W, 35 kHz- Cleaner Model Utech Products, Inc.). The acoustic power dissipated by ultrasonic bath into the solution in the reactor was measured using calorimetric method [21].

Stock solution of the dye (1000 mg L^{-1}) was prepared in distilled water. The desired concentration (100 mg L^{-1}) was obtained by dilutions using distilled water. The initial pH of the samples was maintained by using dilute HCl (1M) and NaOH (1M) solutions and was measured by pH meter (HANNA of model HI 99003). The color and concentration of dye in model solutions were determined by using UV-Visible Spectrophotometer (IRMECO of Model U2020) at scanning spectrum of 200-800 nm. TOC analyzer (Shimadzu, model TOC-V CSH) was used for determining total organic carbon (TOC) of the samples. The instrument was operated at 680 ºC furnace temperature and 20 ml sample injection. Samples after treatment were filtered by Milli pore filter (0.45 μm) [19].

The degradation products were identified using gas chromatography/mass spectrometry (GC/MS) (PerkinElmer Clarus 600). The samples were collected and were extracted according to the procedure reported in the literature [19]. The GC was equipped with an Elite-xlb column (30 m × 0.25 mm) and 0.25 μm film thickness and connected directly to MS. The GC column was operated at 40 ºC for 1.50 min which was than increased to 300 ºC at the rate of 20 ºC/min. The other experimental conditions were: helium as a carrier gas with the flow rate of 1mL, sample volume 1L, injection temperature 200 ºC, injection mode split, and split ratio is 50.

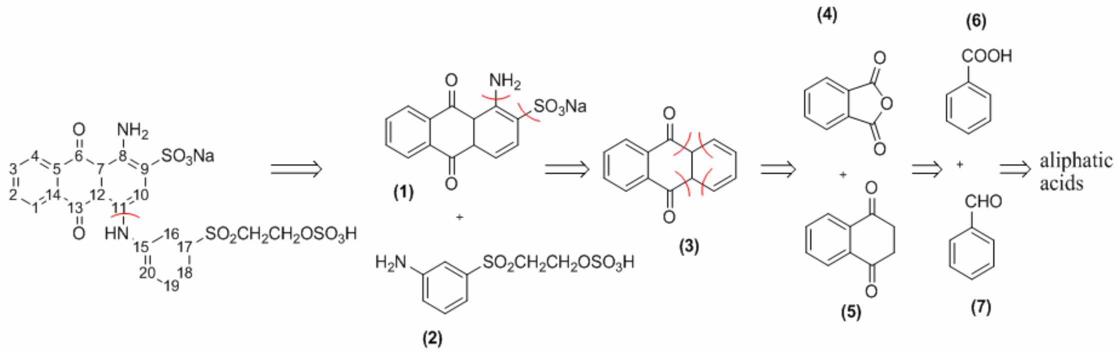

Fig. 7: Proposed pathways of sonophotocatalytic degradation of RB 19 dye identified by GC/MS. Reaction conditions: initial pH= 4, dye conc.= 100 mg L^{-1}, TiO_2 conc. = 300 mg L^{-1}, US power = 240 W

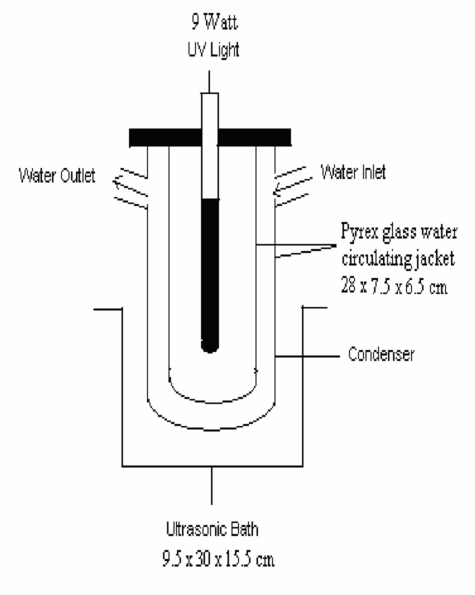

Fig. 8: The experimental set up for sonophoto reactor.

Irradiation Experiments

Dye solution 500 mL having concentration of 100 mg L^{-1} with different concentrations of TiO_2 (20, 50, 100, 200, 300, 400 and 500 mg L^{-1}) was used. The solution containing dye and TiO_2 in the reactor with the continuous exposure to UV and ultrasonic irradiation was investigated. The dye samples were taken over regular intervals of time i.e., after 30, 60, 90 and 120 min of irradiation, filtered and analyzed for the determination degradation of dye at maximum λ_{max} = 256 nm and 594 nm using UV-Visible spectrophotometer. Experiments were performed in duplication. The percentage dye decolorization and degradation were determined using the formulae reported elsewhere [19]. Reduction in percentage total organic carbon content was measured using Eq. (3) [19].

$$TOC (\%) = (TOC_{initial} - TOC_{final} / TOC_{initial}) \times 100 \qquad (3)$$

Conclusions

The degradation of Reactive Blue 19 (RB 19) using photolysis, photocatalysis and sonophotocatalysis in aqueous solutions was investigated. The extent of photocatalytic and sonophotocatalytic degradation was increased by decreasing pH, initial dye concentration and increasing catalysts loading and ultrasonic power respectively. The combined technique was found efficient than the respective individual processes due to the enhanced formation of reactive radicals as well as the possible ultrasound-induced increase of the active surface area of the catalyst. The efficiency of sonophotocatalysis was increased to about two folds in acidic conditions as compare to individual processes at same experimental conditions (100 mg L^{-1} of dye concentration, 300 mg L^{-1} of TiO_2 concentration, 240 W ultrasonic power). Further the chemical kinetics and order of reaction was investigated that showed the dye degradation followed 1st order of reaction. The intermediate and end products formed during sonophotocatalytic treatment of RB 19 were identified by GC/MS as isobenzofuran- 1,3-dione, 2,3-dihydronaphthalene-1,4-dione, benzoic acid, benzaldehyde and acetic acid.

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Conflict of Interests

The authors declare that they have no competing interests.

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