Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2016.1143404

57 (2016) 23927–23939
October

Taylor & Francis
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Combined removal of Rhodamine B and Rhodamine 6G from wastewater using novel treatment approaches based on ultrasonic and ultraviolet irradiations

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Received 28 September 2015; Accepted 22 December 2015

ABSTRACT

The present work deals with treatment of wastewater containing a mixture of basic dyes from Rhodamine family, i.e. Rhodamine B and Rhodamine 6G using different treatment approaches based on the use of ultrasonic (US) and ultraviolet (UV) irradiations. Initially, the effect of operating parameters such as pH and initial concentration of dyes on the extent of degradation of Rh-B and Rh-6G has been investigated to establish the optimum parameters for the combined treatment schemes. Sonocatalytic (US/TiO_2), photocatalytic (UV/TiO_2), and sonophotocatalytic (US/UV/TiO_2) degradation have been investigated subsequently at various loading of TiO_2 (0.1–0.4 g/L). It has been observed that the extent of degradation increases till an optimum loading of TiO_2 as 0.3 g/L for all the three approaches. Among the processes based on US UV, the maximum extent of degradation as 91% for Rh-B and 76% for Rh-6G was obtained using sonophotocatalytic (US/UV/TiO_2) treatment approach. The extent of degradation of dye also increased in the presence of additives such as hydrogen peroxide, $FeSO_4$, $CuSO_4$, and NaCl. For all the additives, optimum loading for maximum degradation has been established also confirming that the extent of intensification depends on the type of additive and the loading. The approach involving combination of advanced oxidation processes, i.e. US/UV/Fenton resulted in enhanced extent of degradation (Rh-B as 89% and Rh-6G as 84%) as compared to the individual operations (ultrasonic irradiations alone giving degradation of 32 and 52% for Rh-B and Rh-6G,

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respectively, whereas for UV irradiations alone degradation were 25 and 40% in same order). The maximum COD removal for the mixture of dye solution obtained using combined treatment strategy as US/UV/optimal TiO_2 /NaCl and US/UV/optimal TiO_2/Ferrous salt were 96 and 97%, respectively. Overall, combined treatment processes in the presence of additives has been established to be effective as compared to the individual oxidation approaches based on the use of irradiations.

Keywords: Mixture of dyes; Rhodamine B; Rhodamine 6G; Ultrasonic irradiation; Ultraviolet irradiations; Combined US/UV process

1. Introduction

Significant usage of dyes in textile, rubber, paper, plastic, leather, cosmetic, and mineral processing industries have also led to water pollution issues due to the possible discharge of dyestuff effluents leading to the presence of toxic and non-biodegradable compounds in the wastewater. Pollution due to the dyestuff compounds and other commercial colorants have created significant environmental issues and hence there has been a tremendous need for the efforts for developing effective remediation strategies [1–3]. Among the different categories of dyestuff compounds, Rhodamine B (Rh-B) and Rhodamine 6G (Rh-6G), are the most commonly used xanthene dyes, which are also known for excellent stability. Conventional methods of pollutant removal such as flocculation, physical adsorption, and biodegradation are not suitable as they are non-destructive, require significant treatment times, and can produce secondary waste by transfer of pollutants from wastewater to another form such as solids [4].

Advanced oxidation processes offer a promising alternative to the non-destructive conventional methods owing to their potential to generate hydroxyl radicals in solution [5–9], which are strong oxidizing agents. The hydroxyl radicals are short-lived and highly reactive chemical species that react non-selectively with organic matter present in the wastewater. Among different advanced oxidation processes, photocatalytic oxidation and Fenton chemistry have shown considerable promise for wastewater treatment applications and may be operated individually or in combination with other oxidation processes [10]. Cavitation generated by the use of ultrasound has also been recognized as an effective approach for generating hydroxyl radicals and showed promise for wastewater treatment [11]. The phenomena of cavitation, i.e. generation, growth, and collapse of cavities occur in extremely small interval of time, releasing large magnitudes of energy locally also generating hot spots and free radicals. Ultrasound-induced cavitation has been used for oxidative destruction of various organic compounds [12–15]. Photocatalytic oxidation based on the use of UV irradiations has also been effectively used for the degradation of dyes in wastewater [16–20]. Among the various semiconductors employed, TiO_2 and ZnO have shown better efficacy for the degradation of contaminants due to their high photosensitivity, stability, and large band gap. The present work deals with application of different treatment schemes based on the use of ultrasound and ultraviolet irradiations for the treatment of wastewaters containing mixture of two dyes as Rhodamine 6G and Rhodamine B.

Rhodamine 6G (Rh-6G) is a basic dye used to dye wool, cotton, silk, and papers where brilliant shades with fluorescent effects are required. Rhodamine B (Rh-B) is also a basic dye and it is widely used in textile, leather, jute, and food industries and is also a well-known tracer due to the fluorescence effects. Similar to Rhodamine 6G, Rhodamine B is also used to dye wool, cotton, silk, papers, etc. Thus, there is a possibility of both dyes being found in the same effluent giving higher degree of environmental problems.

In our earlier work [21–24], it has been demonstrated that Rh-B and Rh-6G (considered as individual-simulated solutions) can be degraded with varying treatment efficiency using sonolysis, photolysis, sonophotolysis, sonophotocatalysis, and hydrodynamic cavitation with intensification studies based on the use of various catalysts as well as additives. The present work deals with treatment of wastewater containing mixture of these dyes which has not been investigated at all to the best of our knowledge. An attempt has been made to effectively treat the wastewater containing mixture of Rhodamine B and Rhodamine 6G using ultrasound (US), ultraviolet (UV), and combined (US/UV) irradiations. The effect of addition of process intensifying additives such as H_2O_2 and salts such as NaCl, $FeSO_4$, and $CuSO_4$ on the extent of degradation has also been investigated. Degradation of mixture of dyes has also been investigated using the combined approach of US/Fenton, UV/Fenton, and US/UV/Fenton.

2. Material and methods

2.1. Materials

Rhodamine 6G (abbreviation: Rh 6G; C.I. No. 45,160, dark reddish purple color, molecular formula: $C_{28}H_{30}N_2O_3HCl$, molecular weight: 479.02 g/mol, IUPAC name [9-(2-ethoxycarbonylphenyl)-6-(ethylamino)-2,7-dim-ethylxanthen-3-ylidene]-ethylazanium chloride) was obtained from Loba Chem. Pvt. Ltd, Mumbai, India. Rhodamine B (abbreviation: Rh B; C.I. No. 45170; molecular formula: $C_{28}H_{31}$ N_2O_3Cl; IU PAC name ([9-(2-carboxyphenyl)-6-diethylamino-3-xanthanylidene]-diethylammonium chloride) was obtained from Kankoo Research and Fine Chemicals (India), Mumbai. The molecular structure of Rhodamine B and Rhodamine 6G have been given in Fig. 1. Titanium dioxide (TiO_2), sodium chloride (NaCl), copper sulfate ($CuSO_4$), and ferrous sulfate ($FeSO_4$) were obtained from Merck Specialties Pvt. Ltd, Mumbai, India. For investigating the effect of pH, the solution pH was adjusted using 1 N H_2SO_4 or 1N NaOH aqueous solutions as per the requirement. All the chemicals were of analytical grade (AR) and used as received from the suppliers.

2.2. Equipment and procedure

For the present experimental studies, an ultrasonic bath procured from Medica Instrument Mfg. Co. Pune, India having dimensions of 25.5 cm length, 16 cm width, and 5 cm height was used. The ultrasonic bath has an operating frequency of 50 kHz and rated power output of 170 W. The operating capacity of the reactor used in the present work was 2,000 ml which was kept constant throughout the experiment. Sonochemical reactor was filled with 2 L of aqueous solution of mixture of Rh-6G dye and Rh-B dye with desired concentrations.

For ultraviolet irradiations, a photolytic reactor was fabricated in-house with dimensions of 30 cm length, 30 cm width, and 12 cm height. The quantum of solution used in the present work was 2 L also kept constant throughout the experiments. The dye solution with photocatalyst was stirred throughout the experiment for obtaining uniform suspension of catalyst in the solution. All the experiments were performed for a constant time of 180 min. For analysis, samples were withdrawn from the solution at regular intervals of 10 min. The residual concentration of Rh-6G dye and Rh-B dye were determined using a UV–vis spectrophotometer (ChemitoSpectrascan UV 2600 double beam) at wavelength of 523 and 499 nm, respectively. Experiments have been repeated twice to check the reproducibility of the obtained data for the extent of degradation. It has been observed that experimental errors were within ±2% of the average value reported in the figures (variation indicated in the form of error bars).

3. Results and discussions

3.1. Effect of initial dye concentration

In order to study the effect of initial dye concentration on the extent of degradation of dye, experiments were performed at different initial concentrations of dye over the range of 5–50 ppm using ultrasonic (US), ultraviolet (UV), and combined ultrasonic–ultraviolet irradiations (US/UV). The variation in the extent of degradation with concentration has been depicted in Fig. 2. It has been observed that initially with an increase in the concentration of dye mixture, the extent of degradation increases till an optimum of 10 ppm, and then decreases with a further increase in the concentration for all the three approaches (US, UV, and combined US/UV). It has also been observed that higher extent of degradation for both the dyes (32% for Rh-B and 35% for Rh-6G) is achieved using combined US/UV approach as compared to individual process of US or UV irradiation. The observed trends for the extent of degradation with an increase in the initial concentration can be explained on the basis of the governing mechanisms of degradation.

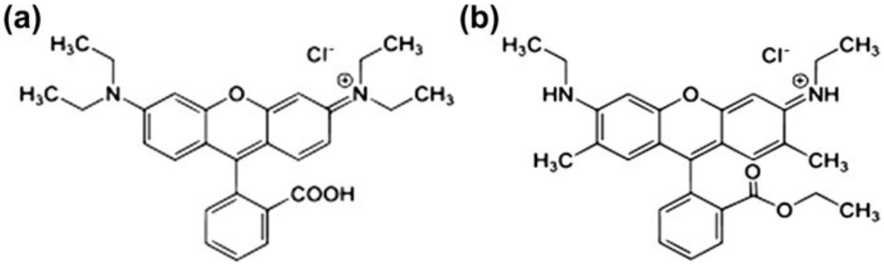

Fig. 1. Molecular structures of Rh-B and Rh-6G. (a) Structure of Rh B and (b) Structure of Rh 6G.

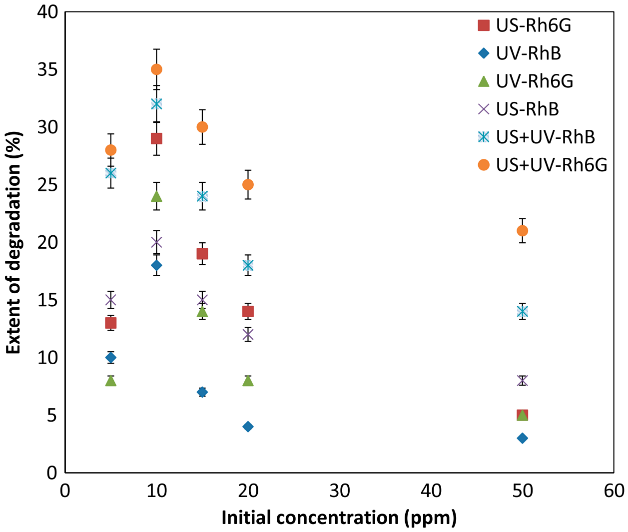

Fig. 2. Effect of initial concentration on extent of removal of Rh-B and Rh-6 using ultrasonic (US), ultraviolet (UV), and combined US/UV irradiations (irradiation time: 180 min; pH 2.5).

For the ultrasound induced degradation, generally two mechanisms, viz. pyrolytic degradation within the cavitation bubble and the attack of the OH radicals at the bubble–water interface as well as in the liquid bulk have been reported [25,26]. The initial increase in the concentration from 5 to 10 ppm leads to an enhanced presence of dye in the collapsing bubble giving enhanced rates of degradation. For a further increase in the concentration, the amount of dye in the bubble remains constant and the degradation is controlled by the rate of generation of hydroxyl radicals. When the cavitational intensity is constant, the number of cavitational events, and the cavitational intensity would be constant, but the ease of free radical generation and the oxidation capacity reduces at significantly higher concentrations of the pollutants giving reduced extents of degradation with an increase in the initial concentration beyond the optimum level. Similar results have been reported for the case of ultrasound induced degradation by Mishra et al. [22] for the degradation of Rh-B and by Banerjee et al. [21] for the case of simulated solution of Rh-6G. It is expected that similar controlling mechanisms in terms of generation of the hydroxyl radicals hold good for the UV induced degradation as well as for the combined operation giving an optimum initial concentration for maximum benefits for degradation. Similar results have also been reported by Kansal et al. [27] and Neppolian et al. [28] for the degradation of dyes using UV irradiations . Based on the obtained results in the present work, an optimum concentration of 10 ppm has been selected for further studies related to the effect of operating parameters and for the combined processes.

3.2. Effect of pH

In actual industrial operations, effluent containing dyes is generated at different pH depending on the processing conditions and hence it is important to understand the effect of pH on the degradation efficiency. Experiments were performed at various pH values over the range of 2.5–10.5 at constant optimum concentration (10 mg/L) of each dye. The obtained results for the variation in the extent of degradation have been shown in the Fig. 3 and it can be seen that the percentage removal of Rh-B and Rh-6G from the mixture is higher under acidic conditions for all the three treatment approaches (US, UV, and combined US/UV). The extent of degradation was also higher (52% for Rh-B and 61% for Rh-6G) using combined treatment approach (US/UV) as compared to US alone and UV alone at optimized value of pH as 2.5. The observed results can be attributed to the fact that under acidic conditions, generation of hydroxyl radicals from the decomposition of hydrogen peroxide formed *in situ* is favored thereby increasing the availability of the free radicals for the desired reaction of oxidation of the pollutant. Also, the oxidation capacity of hydroxyl radicals is higher under acidic conditions

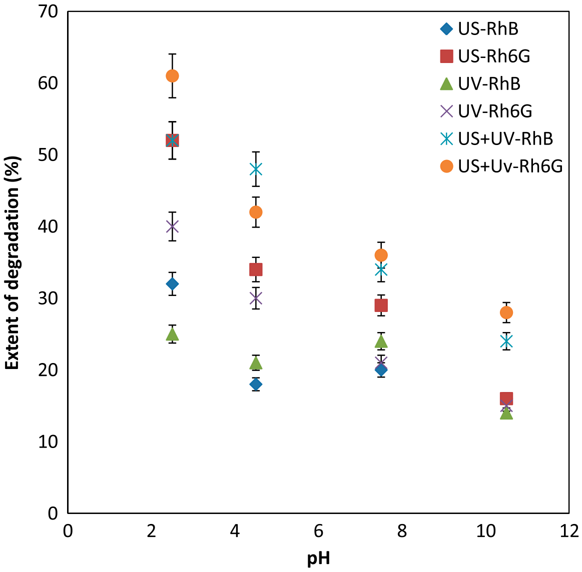

Fig. 3. Effect of pH on extent of removal of Rh-B and Rh-6 using ultrasonic (US), ultraviolet (UV), and combined US/UV irradiations (irradiation time: 180 min; initial concentration: 10 ppm).

as compared to that observed under alkaline conditions [29]. The form of the pollutant, which depends on the pK_a value for the compound, also plays a major role in deciding the extent of degradation. The dissociation constant (pK_a) for Rh-B is 3.2, whereas for the Rh-6G, it is over the range of 4.87–6.13. Under the strongly acidic conditions, Rh-B exhibits strong hydrophobic nature and hence leads to significantly higher concentrations at the interface of the collapsing bubble and hence is subjected to the pyrolytic cleavage as well as OH radical attack at maximum concentrations [30,31] giving higher rates of degradation under strongly acidic conditions.

It is important to compare the trends observed for the variation in the extent of degradation with pH for the mixture of Rh-B and Rh-6G with the trends reported in the literature for individual dyes. For the case of Rh-6G, the decolorization rate was reported to be higher under basic conditions as compared to the acidic conditions and the obtained extent of degradation under strong acidic conditions (pH of about 1.5–3.5) was about half of the degradation obtained under strongly basic conditions (pH of about 10.5–12.5) under otherwise similar conditions [21]. Kansal et al. [27] also reported that the degradation of Rh-6G increased with an increase in pH exhibiting maximum rate at pH of 10. In the case of Rh-B, most of the studies revealed that maximum degradation is achieved under acidic conditions as compared to the strongly basic conditions. In the present work where mixture of dyes was used, it is expected that Rh-B plays a dominating role in deciding the initiation reactions in terms of the radical formations. Due to the formation of radicals initiated by Rh-B dissociation, the degradation of Rh-6G also occurs at a faster rate in the mixture under acidic conditions. Due to the better results obtained under acidic conditions, operating pH of 2.5 was selected as the optimum operating pH for further studies.

3.3. Effect of addition of H_2O_2

Hydrogen peroxide can be used as an intensifying agent to enhance the extent of degradation of pollutants as it is known to dissociate into hydroxyl radicals in the presence of irradiations [32]. The effect of H_2O_2 loading on the extent of degradation of Rh-B and Rh-6G present in the mixture has been studied at optimized pH of 2.5 and initial dye concentration of 10 ppm. The hydrogen peroxide loading has been varied over the range of 0.1–0.4 g/L and the obtained results are given in the Fig. 4. It has been observed that the extent of degradation increases with an increase in the H_2O_2 loading up to an optimum of 0.2 g/L and decreases with a subsequent increase in H_2O_2 loading for both US and UV processes. The observed increase in the rate of dye decolorization due to the addition of H_2O_2 till the optimum can be explained on the basis of enhanced formation of hydroxyl radicals [33], which can be readily utilized by the dye molecules. The decrease in the extent of degradation beyond the optimum loading of 0.2 g/L can be attributed to the scavenging of hydroxyl radicals by the excess hydrogen peroxide. The reaction of hydroxyl radicals with excess H_2O_2 forms super peroxy radicals (·OOH), which are much less reactive and weaker oxidants as compared to the ·OH radicals, giving lower extents of degradation. In order to establish the efficiency of the combined US/UV process for dye degradation, experiments were carried out at optimized loading of H_2O_2 and it has been observed that the extent of degradation (72% for Rh-B and 75% for Rh-6G) obtained using combined treatment approach (US/UV) was higher as compared to US alone and UV alone process at optimized loading of hydrogen peroxide (0.2 g/L).

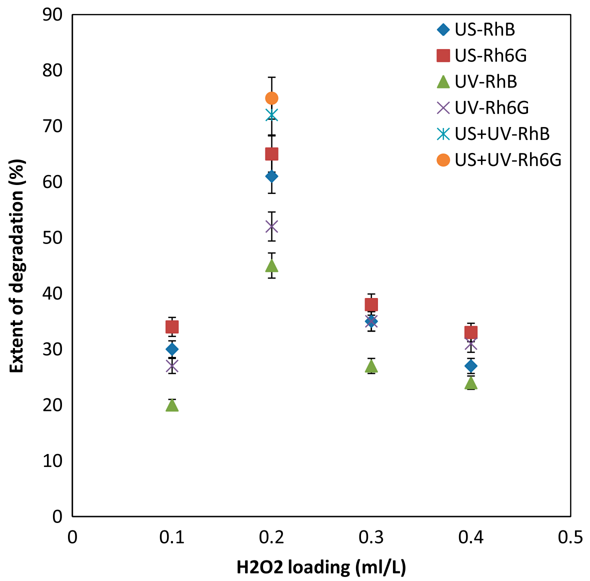

Fig. 4. Effect of H_2O_2 loading on extent of removal of Rh-B and Rh-6G using ultrasonic (US) and ultraviolet (UV) irradiations (initial concentration 10 ppm; pH 2.5; irradiation time: 180 min; for combined US/UV only optimum H_2O_2 loading was used).

3.4. Effect of US/Fenton, UV/Fenton, and US/UV/Fenton

In order to quantify the extent of degradation of mixture of dyes containing Rh-B and Rh-6G using combined process of US/Fenton and UV/Fenton, experiments were carried out at different loadings of ferrous sulfate at already optimized loading of 0.2 g/L of hydrogen peroxide. $FeSO_4$ loading was varied over the range of 0.1–0.4 g/L and the obtained results have been depicted in Fig. 5. It can be seen from the figure that the extent of degradation of Rh-B and Rh-6G increased with an increase in the $FeSO_4$ loading till 0.3 g/L, which may be attributed to the generation of enhanced quantum of hydroxyl radicals. The decrease in the extent of degradation with a further increase in the $FeSO_4$ loading (beyond the optimum) may be due to insufficient hydrogen peroxide loading for the added $FeSO_4$ loading so as to generate enhanced quantum of hydroxyl radicals. Experiment was also performed for the combined US/UV/Fenton process at the optimized loading of $FeSO_4{\cdot}7H_2O$ (0.3 g/L) at fixed loading of 0.2 g/L of hydrogen peroxide. The extent of degradation obtained using the combined process of US/UV/Fenton (Rh-B and Rh-6G as 89 and 84%, respectively) was marginally higher as compared to US/Fenton (Rh-B and Rh-6G as 83 and 82%, respectively) and significantly higher as compared to the UV/Fenton process (Rh-B and Rh-6G as 67 and 62%, respectively). It is important to note that the combination of US/UV/Fenton is not giving significantly better results in terms of extent of degradation as compared to the US/Fenton confirming that it might not be a good idea to keep on combining oxidation processes with an objective of increasing the quantum of the hydroxyl radicals if these are not being utilized by the pollutants.

3.5. Effect of addition of TiO_2

It is widely recognized that sonolysis and photolysis reactions in the presence of TiO_2 particles would be intensified giving higher extent of degradation of any pollutant, though the extent of increase and the possibility of existence of optimum concentration does depend on the specific target compound thus directing the requirement of detailed investigations. TiO_2 has the ability to enhance the production of free radicals thereby increasing the rate of degradation of the organic compound. The obtained results for varying concentration of TiO_2 over a range of 0.1–0.4 g/L for fixed initial concentration of dyes as 10 ppm and pH of 2.5 have been shown in Fig. 6 for the operation involving ultrasonic (US) and ultraviolet (UV) irradiations. It can be seen from the figure that with an increase in the TiO_2 loading, the extent of degradation increases till an optimum loading of TiO_2 (0.3 g/L) and further decreases for both the approaches (US and UV).

It can be seen from the Table 1 that the extent of degradation of Rh-B and Rh-6G were 85 and 81%, respectively, using ultrasonic irradiation in the presence TiO_2 at optimum loading of 0.3 g/L. In the case of ultrasound-induced degradation of mixture of dyes, TiO_2 provides additional nuclei for cavitation leading to enhanced degradation up to optimum loading of TiO_2 and further increase in loading lowers the extent

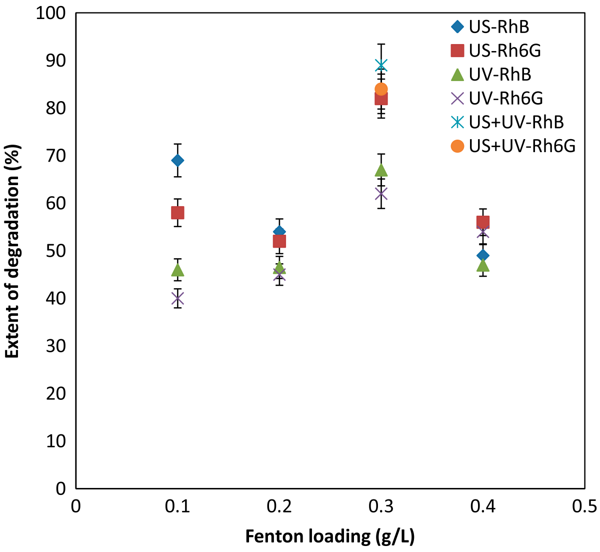

Fig. 5. Removal of Rh-B and Rh-6 using US/Fenton, UV/Fenton, and US/UV/Fenton process at fixed loading of H_2O_2 (0.2 g/L). (initial concentration 10 ppm; pH 2.5; $FeSO_4{\cdot}7H_2O$ = 0.1–0.4 g/L; irradiation time 180 min; for combined US/UV/Fenton process only optimum $FeSO_4{\cdot}7H_2O$ loading was used).

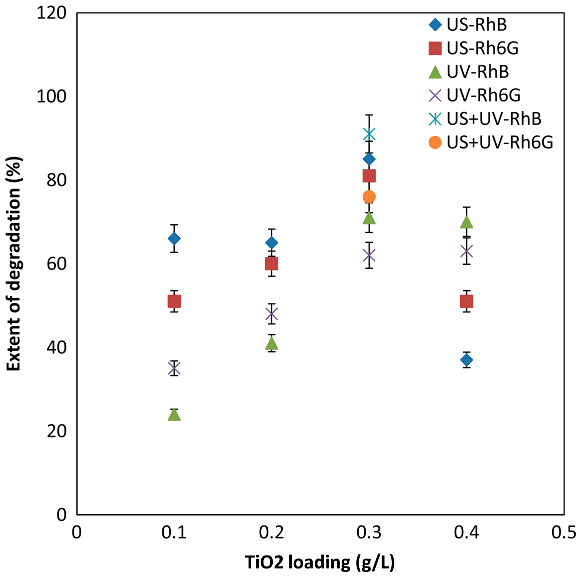

Fig. 6. Effect of TiO_2 loading on extent of removal of Rh-B and Rh-6G using ultrasonic (US), ultraviolet (UV) irradiations (initial concentration 10 ppm; pH 2.5; irradiation time 180 min; TiO_2 loading 0.1–0.4 g/L; for combined US/UV only optimum TiO_4 loading was used).

Table 1
Summary of results for Rh-B and Rh-6G degradation using US, UV, and combined US/UV process

			Extent of degradation (%)					
			US		UV		US/UV	
Sr. no	Parameters		Rh B	Rh 6G	Rh B	Rh 6G	Rh B	Rh 6G
1	Concentation (ppm)	5	15	13	10	8	26	28
		10	20	29	18	24	32	35
		15	15	19	7	14	24	30
		20	12	14	4	8	18	25
		50	8	5	3	5	14	21
2	pH	2.5	32	52	25	40	52	61
		4.5	18	34	21	30	48	42
		7.5	20	29	24	21	34	36
		10.5	16	16	14	15	24	28
3	H_2O_2 loading (g/L)	0.1	30	34	20	27		
		0.2	61	65	45	52	72	75
		0.3	35	38	27	35		
		0.4	27	33	24	31		
4	$FeSO_4{\cdot}7H_2O$ loading (g/L) at fixed H_2O_2 loading (0.2 g/L)	0.1	69	58	46	40		
		0.2	54	52	46.5	45		
		0.3	83	82	67	62	89	84
		0.4	49	56	47	54		
5	TiO_2 (g/L)	0.1	66	51	24	35		
		0.2	65	60	41	48		
		0.3	85	81	71	62	91	76
		0.4	37	51	70	63		
6	$FeSO_4{\cdot}7H_2O$ loading (g/L)	0.1	38	46	35	40		
		0.2	45	21	41	45		
		0.3	61	59	47	54	73	78
		0.4	34	41	38	43		
7	NaCl loading (g/L)	0.1	48	51	43	47		
		0.2	53	57	49	53		
		0.3	64	69	56	60	69	71
		0.4	50	53	46	51		
8	$CuSO_4$ loading (g/L)	0.1	35	38	31	34		
		0.2	39	41	35	38		
		0.3	42	48	39	43	64	67
		0.4	31	35	26	39		
9	NaCl loading (g/L) at fixed optimum 0.3 g/L of TiO_2 loading	0.1	42	51				
		0.2	84	83				
		0.3	91	91	56	64	93	95
		0.4	63	73				
10	$FeSO_4{\cdot}7H_2O$ loading (g/L) at optimum TiO_2 loading (0.3 g/L)	0.1	89	85				
		0.2	93	89	78	81	95	98
		0.3	34	56				
		0.4	32	53				

of degradation due to scattering effects on the incident sound waves leading to lower amount of energy dissipation. Similar results have also been reported for the degradation of aqueous solution of Rh-B as well as Rh-6G [22,24]. In the case of ultraviolet irradiations (UV), it has been observed that the extent of degradation of Rh-B and Rh-6G were 71 and 62%, respectively, at an optimum loading of 0.3 g/L. The observed decrease beyond the optimum can be again attributed to possibility of scattering effects and also to possible agglomeration of catalyst particles which leads to the less availability of catalyst surface for photon absorption [34]. The presence of only stirring is not able to avoid the possible agglomeration leading to uneven light transmission and reducing the quantum of free radicals generated [35].

In order to establish the efficiency of the combined US/UV/TiO_2 process for dye degradation, experiments were carried out at optimized loading of TiO_2 and it has been observed that the extent of degradation of Rh-B was 91%, whereas for the case of Rh-6G, extent of degradation was 76%. The extent of degradation is higher in the combined operation as compared to the individual operation (US/TiO_2) or (UV/TiO_2), which can be attributed to the formation of more free radicals as compared to the individual process. Also, the turbulence generated by the ultrasound-induced cavitation during the treatment increases the mass transfer of chemical species between the solution phase and the catalyst surface [36], leading to enhanced degradation.

3.6. Effect of addition of salts

Presence of salts play a major role in enhancing the efficacy of the treatment of wastewater due to multiple effects such as changing the physicochemical properties, viz. vapor pressure and surface tension, enhancing the radical formation, changing the distribution of aqueous and organic phases as well as affecting the intensity of cavitational collapse. Experiments have been performed to investigate the effect of salts such as $FeSO_4$, $CuSO_4$, and NaCl (over the loading of 0.1–0.4 g/L) on the extent of degradation of mixture containing Rh-B and Rh-6G using both ultrasonic (US) and ultraviolet (UV) irradiations. The obtained results have been depicted in the Figs. 7–9 and it has been generally observed that the removal of both Rh-B and Rh-6G increases with an increase in loading of salts up to an optimum loading of 0.3 g/L. The extent of degradation has been observed to be marginally reduced at higher loading of 0.4 g/L. In order to establish the efficiency of the combined US/UV process for dye degradation, experiments were also performed at optimized loading of salts and it has been observed that the extent of degradation of both the dyes in the presence of salts is the maximum for the combined approach of US/UV as compared to US and UV alone. At optimized loading of NaCl, $FeSO_4$, and $CuSO_4$ the maximum extent of degradation of Rh-B using the combined operation of US/UV was 69, 73, and 64%, respectively, whereas the extent of degradation for Rh-6G was 71, 78, and 67%, respectively. The obtained results can be explained on the basis of mechanisms of intensification due to the presence of salts. NaCl mainly results in preferential accumulation of the reactants at the reactive sites thereby resulting in higher extents of degradation [37]. Both $FeSO_4$ and $CuSO_4$ split into Fe^{2+}, Cu^{2+}, and sulfate ion (SO_4^{2-}). Sulfate ions being strong oxidants produce hydroxyl radicals (OH^-) under solar irradiation or ultrasound giving enhanced degradation of Rh-6G

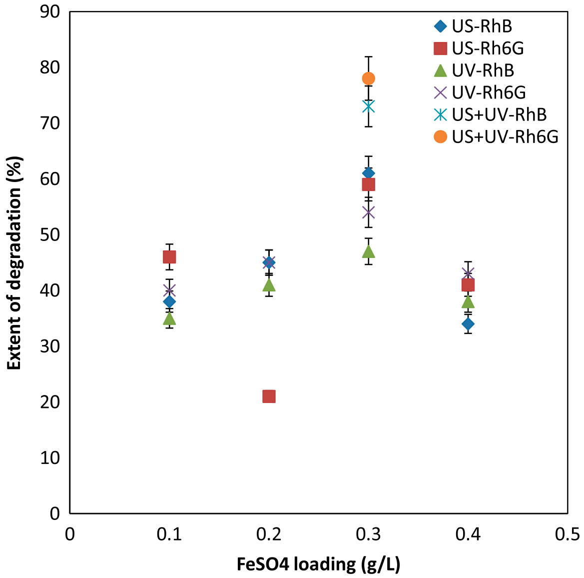

Fig. 7. Effect of $FeSO_4·7H_2O$ loading on extent of removal of Rh-B and Rh-6G using ultrasonic (US), ultraviolet (UV) irradiations (initial concentration 10 ppm; pH 2.5; irradiation time 180 min; $FeSO_4·7H_2O$ loading 0.1–0.4 g/L; for combined US/UV only optimum $FeSO_4·7H_2O$ loading was used).

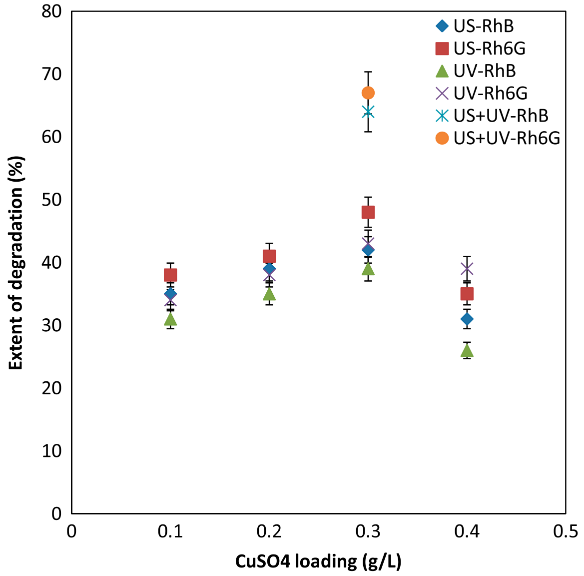

Fig. 8. Effect of $CuSO_4$ loading on extent of removal of Rh-B and Rh-6G using ultrasonic (US), ultraviolet (UV) irradiations (initial concentration 10 ppm; pH 2.5; irradiation time 180 min; $CuSO_4$ loading 0.1–0.4 g/L; for combined US/UV only optimum $CuSO_4$ loading was used).

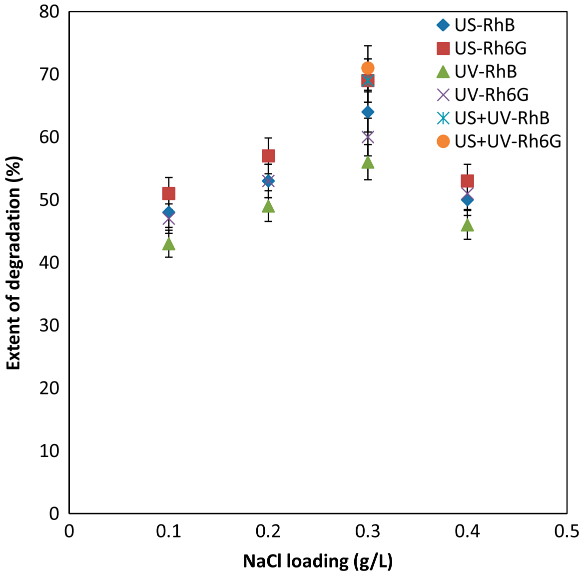

Fig. 9. Effect of NaCl loading on extent of removal of Rh-B and Rh-6G using ultrasonic (US), ultraviolet (UV), and combined US/UV irradiations (initial concentration 10 ppm; pH 2.5; irradiation time 180 min; NaCl loading 0.1–0.4 g/L; for combined US/UV only optimum NaCl loading was used).

[38]. Hydrogen peroxide formed during the process reacts with ferrous ions to accelerate the degradation of dye via the usual Fenton chemistry [39] and hence intensification effect is also observed for $FeSO_4$. The different free radical reactions occurring in the process can be given as follows:

$$FeSO_4 \rightarrow Fe^{2+} + SO_4^{-\cdot} \quad (1)$$

$$CuSO_4 \rightarrow Cu^{2+} + SO_4^{2-} \quad (2)$$

$$SO_4^{-\cdot} + H_2O \rightarrow HSO_4^{-} + OH^{\cdot} \quad (3)$$

$$HSO_4^{-} + OH \rightarrow H_2O_2 + SO_3^{-\cdot} \quad (4)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + HO^{\cdot} \quad (5)$$

$$Cu^{2+} + H_2O_2 \rightarrow Cu^{3+} + OH^{-} + HO^{\cdot} \quad (6)$$

3.7. Combined studies using US/UV/Optimal TiO_2/Salts

To obtain higher efficacy in terms of removal of Rh-B and Rh-6G from the mixture, combined treatment schemes involving catalyst as TiO_2 (at optimum loading) and NaCl/$FeSO_4 \cdot 7H_2O$ have been investigated at various loadings of the additive. The obtained results for the addition of NaCl over the range of 0.1–0.4 g/L along with optimized quantum of TiO_2 (0.3 g/L) in the case of ultrasound-assisted operation has been depicted in Fig. 10 and Table 1. Experiments using UV and combined US/UV irradiations were carried out only with optimum quantum of TiO_2 and optimized NaCl loading and results have been tabulated in Table 1. It has been observed that marginally higher degradation (93% of Rh-B and 95% of Rh-6G) is obtained using combined US/UV process at optimized loading of NaCl (0.3 g/L) as compared to individual process involving the use of US alone (91% of Rh-B and 91% of Rh-6G), whereas for the process involving UV alone, significantly lower extents of degradation were observed (56% degradation of Rh-B and 64% degradation of Rh-6G). The presence of NaCl creates a salting out effect leading to the preferential accumulation of the pollutant at the bubble–water interface where the radical concentration is significantly higher as compared to the liquid bulk [40]. Since the effect is more dominating in the case of ultrasound-induced degradation, higher degree of intensification is obtained due to the addition of NaCl in the case of US-assisted degradation in individual approach as well as combined approach of US/UV. Since UV-induced degradation is not affected significantly with addition of NaCl, the obtained degree of intensification is similar for the US and combination of US and UV irradiations. Mahamuni and Pandit

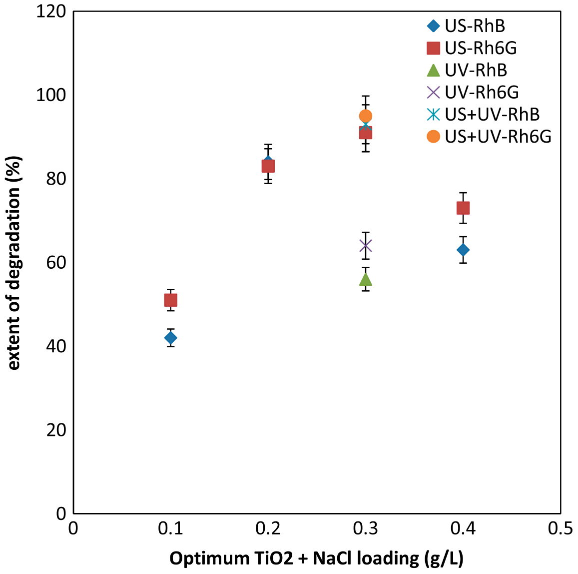

Fig. 10. Effect of various loadings of NaCl at optimal TiO_2 (0.3 g/L) on extent of removal of Rh-B and Rh-6G using ultrasonic (US) irradiations (initial concentration 10 ppm; pH 2.5; irradiation time 180 min; NaCl loading 0.1–0.4 g/L; for ultraviolet (UV) irradiations and combined US/UV only optimum NaCl and TiO_2 loading was used).

[41] studied the effect of NaCl addition on the degradation of phenol and reported that compared to the experimental runs without NaCl, the addition of NaCl at 2 and 8% increased the reaction rate by 1.1 and 1.5 times, respectively. Ghodbane and Hamdaoui [42] also reported that addition of salts such as NaCl, $CaCl_2$, $NaHCO_3$, and KI increased the degradation rate of organic pollutants.

Similarly the operation involving the combination of $FeSO_4{\cdot}7H_2O$ at different loadings over the range of 0.1–0.4 g/L along with optimized loading of TiO_2 (0.3 g/L) has also been investigated for the ultrasound-based treatment. The obtained results have been depicted in Fig. 11. Experiments were also performed for the operation of UV and US/UV only at optimized loading of $FeSO_4$, $7H_2O$ and results tabulated in Table 1 reveals that the maximum removal of 95% for Rh-B and 98% for Rh 6G is obtained at $FeSO_4$ loading of 0.2 g/L. This can be attributed to the fact that the presence of $FeSO_4$ in lower loadings results in dissociation of hydrogen peroxide formed from the recombination of hydroxyl radicals giving a Fenton-like mechanism. Due to the lower concentrations of the generated hydrogen peroxide, increasing loading of $FeSO_4$ does not give any significant effect and an optimum loading as 0.2 g/L can be established.

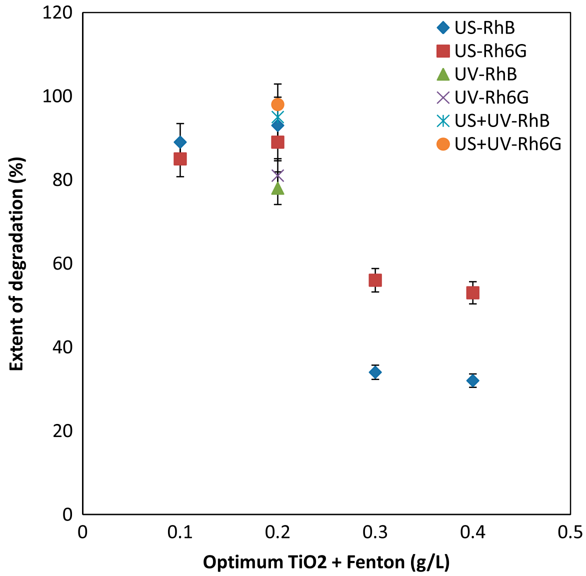

Fig. 11. Effect of $FeSO_4{\cdot}7H_2O$ loading at optimal loading of TiO_2 (0.3 g/L) on extent of removal of Rh-B and Rh-6G using ultrasonic (US) irradiation (initial concentration 10 ppm; pH 2.5; irradiation time 180 min; $FeSO_4{\cdot}7H_2O$ = 0.1–0.4 g/L; for ultraviolet (UV) irradiations and combined US/UV only optimum $FeSO_4{\cdot}7H_2O$ and optimum TiO_2 loading was used).

Overall, it has been observed that combined use of optimal loading of TiO_2 and salts gives about 95–98% extent of degradation of Rh-B and Rh-6G. Mineralization studies have also been carried for the experimental approaches where maximum extent of degradation was achieved. It has been observed that using the combination of US/UV/TiO_2/Ferrous salt, maximum COD removal of 97% was obtained at optimal loading of 0.3 g/L TiO_2 and 0.3 g/L of ferrous sulfate. With optimal loading of 0.3 g/L TiO_2 and 0.3 g/L of sodium chloride, marginally lower COD removal of 96% was obtained in US/UV/TiO_2/NaCl process.

3.8. Kinetic studies

Kinetic analysis has also been performed to establish the rate constant and order of reaction for the different approaches used in the work. Based on integral method of analysis for the calculation of order of reaction, it has been observed that the degradation of Rh-B and Rh-6G followed pseudo-first-order kinetics. The rate equation for such kinetic mechanism can be expressed as follows:

$$\frac{-\mathrm{d}[c]}{\mathrm{d}t} = k'c \tag{7}$$

where k' is the pseudo first order rate constant and c is the concentration of dye in the solution.

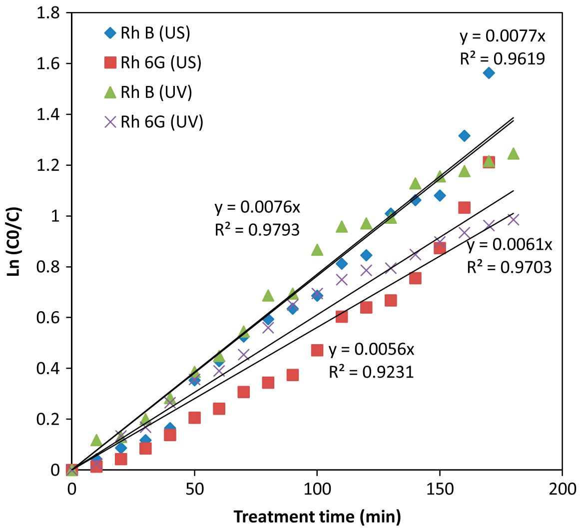

Fig. 12. Kinetic study for degradation of Rh-B and Rh-6G at optimal TiO_2 loading for ultrasound (US) and ultraviolet (UV) irradiations (initial concentration 10 ppm; pH 2.5; Irradiation time 180 min; TiO_2 = 0.3 g/L).

Table 2
Rate constant data for degradation of Rh-B and Rh-6G using US, UV, and combined US/UV process at optimal conditions, viz. concentration, pH, and additive loading

			Rate constant, $k' \times 10^3$ (min^{-1})					
			US		US + UV		UV	
S. no.	Parameter		Rh B	Rh 6G	Rh B	Rh 6G	Rh B	Rh 6G
1	H_2O_2 (ml/L)	0.2	6.0	6.5	7.1	7.8	4.2	5.1
2	$FeSO_4·7H_2O$ (g/L)	0.3	5.7	5.4	6.4	6.8	3.4	4.8
3	TiO_2 (g/L)	0.3	7.7	5.6	8.6	8.1	6.5	5.5
4	$CuSO_4·5H_2O$ (g/L)	0.3	3.5	3.8	6.5	6.8	2.3	3.4
5	NaCl (g/L)	0.3	4.6	4.9	5.6	6.0	5.3	4.9
6	Combined study 1 (TiO_2 + NaCl) (g/L)	0.3 + 0.3	8.3	7.6	9.3	9.2	1.3	1.6
7	Combined study 2 ($TiO_2 + FeSO_4·7H_2O$) (g/L)	0.3 + 0.3	9.2	9.1	9.8	9.5	6.4	6.3

Integrating Eq. (7) within limits of $c = c_0$ at $t = 0$ and $c = c$ at time $t = t$, we obtain Eq. (8):

$$\ln\frac{c_0}{c} = k't \tag{8}$$

where c is the residual concentration of dye at any time t and c_0 is the initial concentration of dye obtained under equilibrium conditions. Fig. 12 depicts the obtained results for the kinetic analysis for Rh-B and Rh-6G degradation for the specific case of optimal TiO_2 (3 g/L) loading using US and UV irradiations. The rate constants for degradation using different approaches as US/TiO_2 for the degradation of Rh-B, US/TiO_2 for the degradation of Rh-6G, UV/TiO_2 for the degradation of Rh-B, and UV/TiO_2 for the degradation of Rh-6G were established to be 7.7, 5.6, 7.6, and 6.1×10^{-3} min^{-1}, respectively. Similarly, the rate constants obtained for other sets of experiments have been given in Table 2. The values for the rate constants presented in the table match the trends in terms of the extent of degradation as explained in the earlier discussions.

4. Conclusions

The studies related to the degradation of Rh-B and Rh-6G present as mixture in the aqueous solution using US/UV-based processes have established for the first time that higher extents of removal are obtained in the combined processes and use of different additives at optimized loadings can help in achieving near complete removal of dyes along with mineralization. Following important design-related information has been established from the present study:

(1) The extent of degradation of mixture of dyes decreases with an increase in pH confirming that the production of hydroxyl radicals and oxidation capacity is more dominating as compared to the nature of the pollutant
(2) The extent of degradation of Rh-B and Rh-6G increases with an increase in initial dye concentration till an optimum value of 10 ppm and decreases at higher concentrations of dyes for all the three approaches (US, UV, and combined US/UV).
(3) The extent of degradation of Rh-B and Rh-6G increases with the addition of hydrogen peroxide till optimum loading (0.2 g/L) due to generation of enhanced quantum of free radicals in the presence of ultrasonic (US) and ultraviolet (UV) irradiations.
(4) Fenton process in combination with US and UV also results in higher removal efficiency (Rh-B, 89% and Rh-6G, 84%) as compared to individual process (US/Fenton and UV/Fenton).
(5) Optimum loading of catalyst as TiO_2 gives enhanced extent of degradation of dye using US/TiO_2, UV/TiO_2, and US/UV/TiO_2 approaches as the excess loading hinders the process of transfer of incident irradiations.
(6) Enhanced removal of Rh-B and Rh-6G from the mixtures is possible using salts such as NaCl, $CuSO_4$, and $FeSO_4$ due to multiple simultaneously acting effects. Further increase in extent of degradation is observed when combined US/UV/TiO_2/NaCl (Rh-B, 93% removal and Rh-6G, 95% removal) and US/UV/TiO_2/$FeSO_4$ (Rh-B, 95% removal and Rh-6G, 98% removal) processes are applied for treatment.

(7) The combined US/UV/TiO_2/$FeSO_4$ has been established as the best treatment approach among all the combined approaches studied in the present work. It is also important to optimize the combination of oxidation processes and additives based on the utilization of hydroxyl radicals by the pollutants present in the wastewater stream.

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