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Sonochemical decolorization of wastewaters containing Rhodamine 6G using ultrasonic bath at an operating capacity of 2 L

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ABSTRACT

In the present work, the sonochemical decolorization of wastewater containing a basic dye, Rhodamine 6G (Rh 6G) has been investigated using an ultrasonic bath at an operating capacity of 2 L. Effect of initial concentration, pH, and use of different additives, such as CCl_4, H_2O_2, air, and UV light in combination with ultrasound on the extent of decolorization has been investigated. The experimental results show that an increase in dye concentration leads to a decrease in the decolorization rate, whereas basic conditions favor the decolorization of the pollutant. Among the use of different additives, maximum effect was observed for the use of hydrogen peroxide where the extent of decolorization was 77.8%. Use of air and CCl_4 as an process intensifying additive leads to a moderate increase in the extent of decolorization whereas combination of ultrasound and ultraviolet irradiations resulted in lower effectiveness as compared to the combination of ultrasound and hydrogen peroxide. Kinetic studies have also been carried out for each of the treatment approach to quantify the rate constants for the degradation. It has been demonstrated in the present work that sonochemical reactors in combination with optimized concentration of hydrogen peroxide can be effective in removing Rh 6G dye from the effluent streams.

Keywords: Rhodamine 6G; Ultrasound; Decolorization; Sonophotolysis; Additives; Process intensification

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1. Introduction

Textile industry can be classified into three categories viz., cotton, woolen, and synthetic fibers depending on the raw materials used in the processing. The cotton textile industry is one of the oldest industries in India with over 1,000 industries (or mills) mainly centered in Mumbai, Surat, Ahmedabad, Coimbatore, and Kanpur. The water consumption and wastewater generation from the textile industry depend on the processing operations employed during the conversion of raw materials to final textile fabric, and it has been reported that significantly large volume of colored effluents, which are toxic and nonbiodegradable, are produced from these textile processing industries leading to severe problems for the local water

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reservoirs [1]. The problem is applicable globally as the wastewater from a typical cotton textile industry is characterized by obnoxious color and high values of Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) [2]. Because of the high BOD and obnoxious colors, the untreated textile wastewater can cause rapid depletion of dissolved oxygen, if it is directly discharged into the surface water sources. The effluents with high levels of COD are toxic to biological life [3], thereby decreasing the effectiveness of the biological oxidation stage that can be applied by the processing industries. The high alkalinity and traces of chromium (employed in dyes) adversely affect the aquatic life and also interfere with the biological treatment process. The high color renders the water unfit for use at the downstream of the disposal point [4]. The presence of dyes can create severe environmental pollution problems by releasing toxic and potential carcinogenic substances into the aqueous phase. In view of all these adverse effects, it is very important to develop efficient treatment strategies so that the textile industry effluent is effectively treated and can be discharged according to the standards prescribed under the applicable Central Water Act (Prevention and Control of Pollution) or in general according to the pollution control norms existing worldwide. Various chemical and physical processes such as precipitation, adsorption, air stripping, flocculation, reverse osmosis, and ultrafiltration can be used for the removal of dyes from the textile effluents [5–8]. However, these techniques are nondestructive, since they only transfer the nonbiodegradable matter into sludge, giving rise to new type of pollution, which again needs further treatment [9–11]. Also the efficacy of biological oxidation for treatment of dyes is lower due to the biorefractory nature of certain dyes. Recent experimental investigations have revealed that reactive dyes can be decolorized by advanced oxidation processes [12–13] involving the generation of powerful oxidizing agent like hydroxyl radicals ($OH^{\cdot}$), which can completely destroy the pollutants in wastewater. Heterogeneous photocatalysis through illumination of UV [14] or solar light [15] on a semiconductor surface has also been reported as an attractive advanced oxidation process that can be applied for dye treatment. Cavitation generated by use of ultrasound has also been recognized as an effective approach for generating hydroxyl radicals and its subsequent use in the wastewater treatment applications [16].

Rhodamine 6G (Rh 6G) has a molecular formula, $C_{28}H_{31}N_2O_3Cl$ with appearance of dark reddish purple color and is highly toxic in nature. Rh 6G is a basic dye used to dye wool, cotton, silk, and paper where brilliant shades with fluorescence effects are required. A careful analysis of the literature indicates that there have been no studies related to use of ultrasonic irradiations for the decolorization of Rh 6G containing wastewater. Among the advanced oxidation processes, earlier reports dealing with decolorization of Rh 6G dye are based on the use of Photocatalysis [17] and heterogeneous-Fenton like degradation [18].

The objective of this work was to investigate the sonochemical decolorization of Rh 6G containing wastewaters using cavitation-based treatment strategies and also to intensify the operation by using additives that aid the radical mechanism of decolorization. The novelty of the work is established due to the fact that even though the toxicity of Rh 6G is well established, not much work has been reported related to the decolorization of Rh 6G using ultrasound. The present work mainly concentrated on maximizing the decolorization of the wastewater containing Rh 6G based on the engineering approach of using different additives as well as selecting desired operating parameters in terms of the operating pH and concentration of the dye.

2. Materials and methods

2.1. Materials

Rh 6G ((abbreviation: Rh 6G; C.I. No. 45160, dark reddish purple color, molecular formula: $C_{28}H_{30}N_2O_3$ Cl, molecular weight: 479.02 g mol^{-1}, IUPAC name [9-(2-ethoxycarbonylphenyl)-6-(ethylamino)-2, 7-dimethylxanthen-3-ylidene]-ethylazanium chloride) was obtained from Loba Chem. Pvt. Ltd., Mumbai, India. The dilute solutions of different chemicals with required concentrations were prepared using distilled water for experimental studies. Hydrogen peroxide (30%, w/v), carbon tetrachloride (CCl_4) and sodium chloride (all of AR grade) were obtained from Merck Specialties Pvt. Ltd, Mumbai, India. All the experimental runs (except for the understanding of effect of pH) were carried out at pH 12.5, and it was adjusted using 1 N KOH. For investigating the effect of pH, the solution pH was adjusted using 1 N H_2SO_4 or 1 N KOH aqueous solutions as required in the operation. All the chemicals were analytical grades (AR) and were used as received from the suppliers.

2.2. Equipment and procedure

The experimental setup based on cavitational reactor consists of an ultrasonic bath equipped with three transducers fitted at the bottom horizontally along the length of the bath. The ultrasonic bath was procured from the Medica Instrument Mfg. Co., Pune, India. The ultrasonic bath has an operating frequency of 50 kHz and rated power output of 170 W. The dimensions of ultrasonic bath are 25.5 cm length, 16 cm width, and 5 cm height. The reactor body is made up of stainless steel. Calorimetric study was carried out for the sonochemical reactors to quantify the energy efficiency of the reactor [19]. The actual power dissipated in the system as investigated by using calorimetric measurements was observed to be 31 W giving an energy efficiency of approximately 18%. The operating capacity of the reactor as used in the present work was 2000 ml which was kept constant throughout the experiment. For experiments involving the combined use of ultrasound and ultraviolet irradiations, an UV lamp was purchased from Philips India Pvt. Ltd., Mumbai (Model PL-S) with a power rating of 9 W.

The initial concentration of Rh 6G solution was 10 mg L^{-1} for all the experiments, except for those carried out to examine the effect of initial dye concentration. The effect of different additives was investigated over the concentration range of 0.2–1%. The temperature of the solution was maintained constant at the required value with circulating water. Aqueous samples were taken from the solution and the concentrations of Rh 6G were determined using a UV–vis spectrophotometer (Chemito Spectrascan UV 2,600 double beam) at wavelength, $\lambda = 523$ nm [17].

Experiments have been repeated twice to check the reproducibility of the obtained data for the extent of degradation for all the sets. It has been observed that experimental errors were within ± 2% of the average value reported in the figures and discussion.

3. Results and discussion

3.1. Effect of initial dye concentration

The effect of initial concentration has been investigated at different initial concentrations i.e. 10, 20, and 50 ppm and the obtained results have been given in Fig. 1. It has been observed that the extent of decolorization was higher at lower concentration of dye and hence lower initial concentration, specifically 10 ppm, has been selected in the further work on parameter optimization and investigating the effect of additives. The initial decolorization rate can be expected to be dependent on the concentration of $OH^{\cdot}$ radicals produced and the concentration of the dye molecules at the interface of the cavitation bubble. At the surface of the collapsed bubble, the $OH^{\cdot}$ radical concentration is remarkably high [20]. With higher concentration of the dye, the formation of hydroxyl radicals is controlling and hence lower extent of decolorization is observed at higher loadings. Similar results have been also reported by Kansas et al. [17] and Neppolian et al. [21] though for the process of dye decolorization using the photocatalytic oxidation. The kinetic analysis for the decolorization of Rh 6G at different initial concentrations of 10, 20, and 50 ppm has been shown in the Fig. 2. The kinetics of Rh 6G decolorization can be described by the first-order kinetic model, $\ln(C_0/C) = k \times t$, where C_0 is the initial concentration and C is the concentration at any time, t. The semilogarithmic plots of the concentration data gave a straight line with slope being equal to the first-order kinetic rate constant. The correlation constant for the fitted line

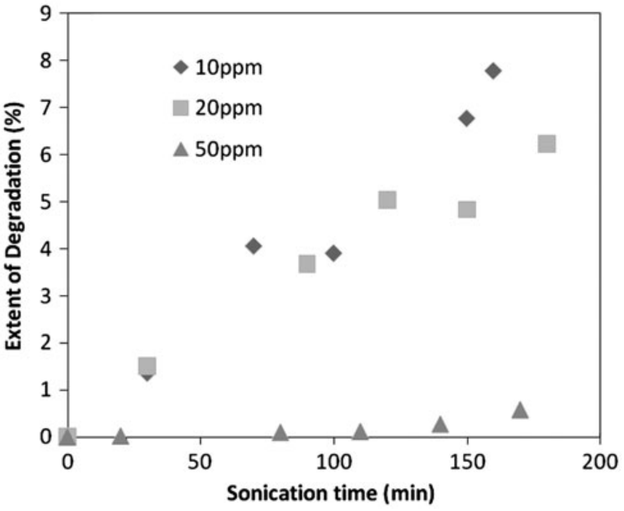

Fig. 1. Study of initial concentations (10/20/50 ppm) for sonochemical degradation of Rh 6G (sonication time = 180 min; pH 12.5).

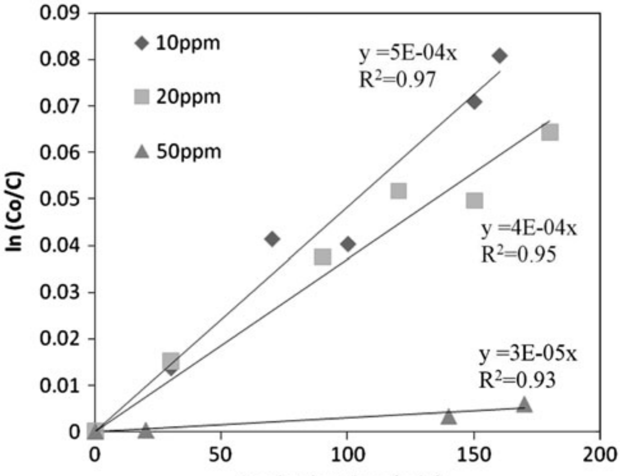

Fig. 2. Kinetic study of initial concentrations (10/20/50 ppm) of Rh 6G.

Table 1
Kinetic rate constants with regression value for different sets of degradation of Rh 6G

Sr. No.	Parameters	Kinetic rate constant, min^{-1}	Regression values i.e. R^2
1	Initial concentration (10 ppm)	5.0×10^{-4}	0.97
2	Initial concentration (20 ppm)	4.0×10^{-4}	0.95
3	Initial concentration (50 ppm)	3.0×10^{-5}	0.93
4	Hydrogen peroxide H_2O_2 (1 g/l) + US	1.25×10^{-2}	0.94
5	Hydrogen peroxide H_2O_2 (0.6 g/l)) + US	5.2×10^{-3}	0.92
6	Hydrogen peroxide H_2O_2 (0.4 g/l)) + US	4.1×10^{-3}	0.95
7	Hydrogen peroxide H_2O_2 (0.2 g/l)) + US	2.5×10^{-3}	0.97
8	Hydrogen peroxide H_2O_2 (1 g/l)) + Stirring	1.90×10^{-3}	0.98
9	CCl_4 (1 g/l) + US (12.5 pH)	1.82×10^{-3}	0.96
10	Air Sparging + US (12.5 pH)	2.30×10^{-3}	0.97
11	UV only (12.5 pH)	1.75×10^{-5}	0.94
12	CCl_4 + Sonophotolysis	2.10×10^{-3}	0.93
13	US + UV + H_2O_2 (1 g/l) (12.5 pH)	1.15×10^{-2}	0.93

was calculated to be $R^2 = 0.97$, and rate constant was calculated to be 5.0×10^{-4} min^{-1} for an initial concentration of 10 ppm of Rh 6G. The data for the kinetic rate constants for different set of experiments have been given in Table 1.

3.2. Effect of pH

The effect of pH was investigated using 10 ppm Rh 6G at different pH over the range 1.5–13.5. Fig. 3 shows the effect of pH on sonochemical decolorization of Rh 6G. The obtained results indicate that the ultrasonic decolorization rates over higher operating pH (pH 11.5–12.5) are higher than strong acidic conditions (pH 1.5–3.5). Decolorization rates decrease from pH 1.5 to 6.5 and again increase under strong alkaline conditions i.e. from pH 9.5 to 12.5 with maximum extent of decolorization being obtained at pH of 12.5. The obtained results can be attributed to the fact that Rh 6G is known to exist in two principal forms, viz. ionic (Rh $6G^+$) and non-ionic (Rh 6G) form as indicated in the Fig. 4. The generation of hydroxyl radicals under the effect of ultrasonic irradiations and its oxidation capacity generally depends on the operating pH and is favored under acidic conditions [22]. These two counteracting mechanisms decide the net extent of degradation. Under alkaline conditions, there is a possibility of lesser hydroxyl radicals generated using ultrasonic irradiations but the reactivity is higher due to the non-ionic form of the dye. While in the case of acidic conditions, the Rh 6G exists in ionic form which may lead to reduced extent of degradation, which is partially compensated by the higher reactivity of the hydroxyl radicals. In the present work, maximum extent of degradation has been obtained at pH of 12.5, which can be attributed to

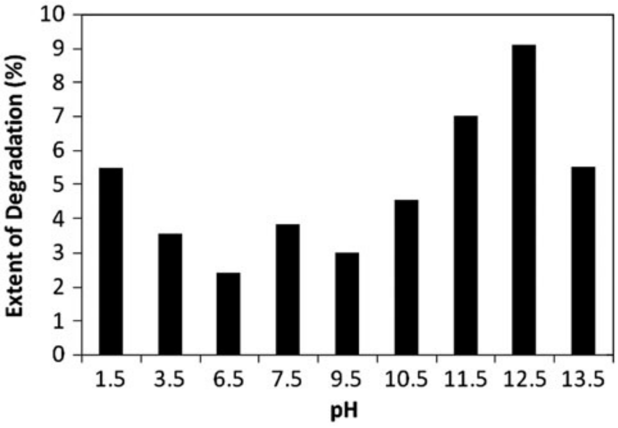

Fig. 3. Effect of pH (range pH 1.5–13.5) for sonochemical degradation of Rh 6G (sonication time = 120 min; initial concentration of Rh 6G = 10 ppm).

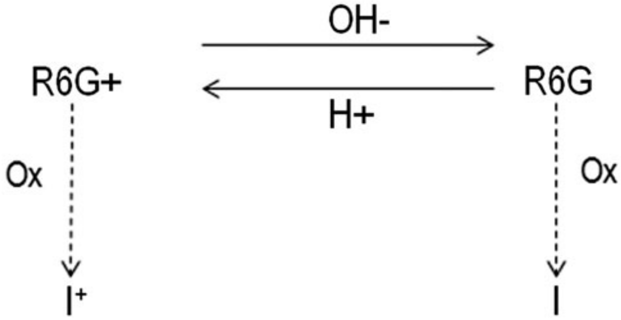

Fig. 4. Rh 6G equilibrium and intermediates of the oxidation.

dominating effect of the form of the dye under basic conditions. Due to the non-ionic form of the dye under basic conditions, higher quantum of dye is expected at the site of cavity collapse leading to higher decolorization rates. The enhancement in the decolorization rate under strong basic conditions (pH 12.5) may be also caused by the hydrophilic property of the dye as compared to it being hydrophobic under acidic condition [23]. Though not many studies related to decolorization of Rh 6G using sonochemical reactors are available, credence to the fact that basic conditions favor decolorization of Rh 6G using advanced oxidation processes in general, can be obtained from a recent work by Kansal et al. [17] who reported similar results using photocatalytic oxidation with maximum extent of degradation being obtained at pH 10. Similar behavior has also been reported for the photocatalytic decolorization of azo dyes [24].

3.3. *Effect of hydrogen peroxide addition*

In order to investigate the effect of the addition of H_2O_2, the sonochemical decolorization of Rh 6G at 10 ppm initial concentration was studied in the range of 0.2–3 g L^{-1} loading of H_2O_2 at initial pH of 12.5. Also, using the optimized loading of H_2O_2 at pH of 12.5, decolorization was investigated using mechanical stirring in the absence of ultrasonic irradiations. The obtained results for the extent of degradation are illustrated in Fig. 5 whereas Table 1 gives the obtained kinetic rate constants for different data sets involving the use of hydrogen peroxide. The rate of dye decolorization increased due to the addition of H_2O_2 in the ultrasonic reactor, which can be explained on the basis of the decomposition of hydrogen peroxide into hydroxyl radicals [25]. The extent of decolorization increased with an increase in the H_2O_2 concentration till an optimum loading of 1 g L^{-1} as also confirmed by the rate constant values given in the Table 1. The loading of 1 g L^{-1} of H_2O_2 concentration gives maximum extent of decolorization with a kinetic rate constant as 1.25×10^{-2} min^{-1}. The obtained rate constant is about 25 times more in the presence of hydrogen peroxide as compared to that obtained only using ultrasound. The extent of decolorization using optimum loading of 1 g L^{-1} H_2O_2 with stirring was only about 20% clearly indicating the formation of hydroxyl radicals in the presence of ultrasonic irradiations leading to enhanced extents of degradation. As the addition of hydrogen peroxide in the presence of ultrasound enhances the decolorization rate of Rh 6G due to additional free radical generation, it can be concluded that the controlling mechanism of Rh 6G decolorization is the free radical attack. The maximum decolorization of 77.8% was obtained for 1 g L^{-1} H_2O_2 loading. Beyond the optimum loading of hydrogen peroxide, it was observed that as the concentration of H_2O_2 increases from 1 to 3 g L^{-1}, the extent of decolorization decreases. The observed decrease in the degradation rate in the presence of high concentrations of H_2O_2 may be attributed to the increased level of hydroxyl radical scavenging by H_2O_2 itself as indicated by the following reaction:

$$H_2O_2 + {}^{\cdot}OH \rightarrow H_2O + HO_2^{\cdot} \qquad (1)$$

When H_2O_2 concentration reaches above a critical value, $^{\cdot}OH$ and $^{\cdot}H$ generated by the thermolysis of water in the solution medium preferentially reacts with H_2O_2, which acts as a $^{\cdot}OH$ scavenger. The scavenging action of hydrogen peroxide has been confirmed by Golash et al. [26] for the degradation of dichlorvos. It has been reported that the extent of degradation increased with initial addition of hydrogen peroxide and a maximum extent of degradation was observed to be 62.5% at a loading of 15 ppm, beyond which marginal decrease in the extent of degradation has been observed. Merouani et al. [27] and Teo et al. [28] have also reported that an optimum concentration of H_2O_2 exists where maximum degradation of organic pollutants is observed and excessive amounts of H_2O_2 could reduce the degradation rate.

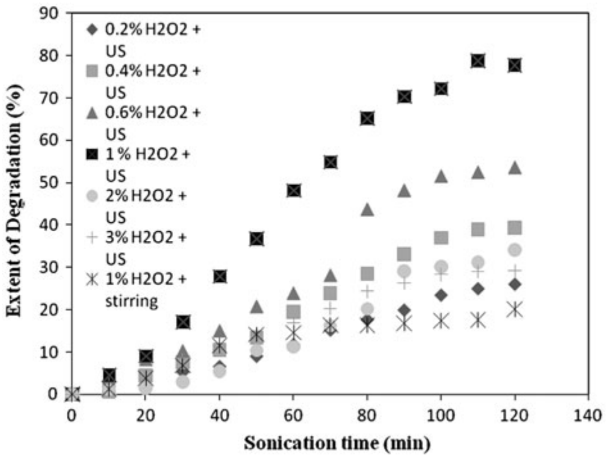

Fig. 5. Effect of H_2O_2 (0.2–1%) addition on sonochemical degradation of Rh 6G (sonication time = 120 min; initial concentration of Rh 6G = 10 ppm; pH 12.5).

3.4. *Effect of CCl_4 addition*

Carbon tetrachloride undergoes dissociation in the presence of ultrasonic irradiations and results in the generation of additional oxidizing species in the reaction system [29,30]. It is believed that CCl_4 is entrapped in the cavitating bubble and is dissociated into Cl^- and CCl_3^-. CCl_3 further dissociates into Cl and CCl_2 radicals. Cl^- and Cl^- can also combine to form stronger oxidizing agent as Cl_2. Chlorine so produced during pyrolysis can further combine with H_2O to form HOCl and HCl. It is also possible that $^-CCl_3$ combines with H^- and form $CHCl_3$. Cl_2 and HOCl are strong oxidizing agents that are independently capable of oxidizing the organic compound present in the solution.

In order to investigate the effect of the addition of CCl_4, the sonochemical decolorization of Rh 6G at 10 ppm initial concentration has been studied in the presence of 0.5 and 1 g L^{-1} CCl_4 at initial pH of 12.5. The obtained results for the variation of extent of degradation with treatment time are illustrated in Fig. 6. It is clear that the decolorization increased with an increase in the concentration of CCl_4. It was found that the extent of decolorization was 12.2% with the addition of 0.5 g L^{-1} of CCl_4 which doubled to about 22% for 1 g L^{-1} loading of CCl_4. The kinetic rate constant at 1 g L^{-1} addition was 1.82×10^{-3} min^{-1}, which is about 3.6 times more as compared to that obtained in the absence of the additive. The improvement in the decolorization of dye is due to the dissociation of CCl_4 by pyrolytic cleavage in cavitation bubbles, which results in the release of oxidizing agents that can react with dye molecules. The sonolytic degradation of CCl_4 generates $^{\cdot}Cl$ radicals that will lead to a series of reactions resulting in the formation of additional active species, such as HClO, Cl_2 and chlorine containing radicals such as $Cl^{\cdot}$, $^{\cdot}CCl_3$, having strong oxidizing property, which accelerates the decolorization of Rh 6G in aqueous solutions as discussed earlier. The overall reaction mechanism can be written as [29,30].

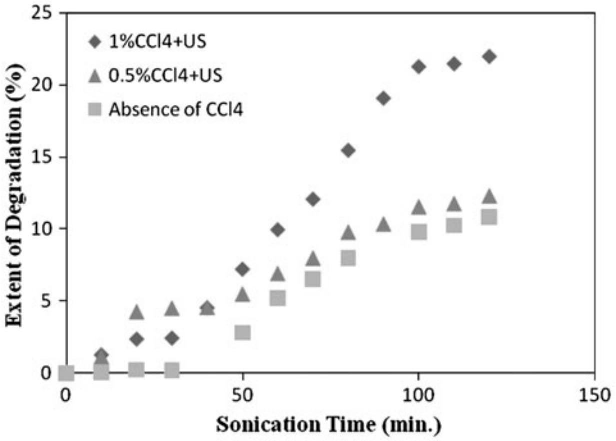

Fig. 6. Effect of CCl_4 (0.5–1%) addition on sonochemical degradation of Rh 6G (sonication time = 120 min; initial concentration of Rh 6G = 10 ppm; pH 12.5).

$$CCl_4 \rightarrow CCl_3 + Cl^{\cdot} \quad (2)$$

$$CHCl_3 \rightarrow Cl^{\cdot} + ^{\cdot}CHCl_2 \quad (3)$$

$$CH_2Cl_2 \rightarrow Cl^{\cdot} + ^{\cdot}CH_2Cl \quad (4)$$

These reactions occur in the cavitating bubble, bubble/water interface and/or bulk liquid and the $Cl^{\cdot}$ generated from decomposition of chloroalkanes, at organic/water interface, takes part in overall oxidation process. Thus, chloroalkanes can be useful additive in improving the efficacy of cavitational reactors especially when the controlling mechanism is the free radical attack. Higher extent of decolorization was achieved at concentration of 1 g L^{-1} CCl_4 which is attributed to the fact that enhanced presence of CCl_4 in the system leads to formation of higher quantum of oxidizing species. It is important to note here that the observed trend should not be generalized, and there can be an optimum concentration of CCl_4 based on the fact that presence of higher quantum of CCl_4 in the cavitating bubble leads to formation of vaporous cavities due to highly volatile nature of the additive, and this can substantially decrease the net release of energy during the cavitational collapse leading to reduced formation of oxidants [31]. Comparison of the obtained results with some of the literature illustrations also reveals interesting facts. Okitsu et al. [32] have depicted that the decomposition of methyl orange increased by 4.8 times due to the addition of 100 ppm of CCl_4 and with addition of 250 ppm, it has been observed that decolorization was increased by 14 times than calculated with addition of lower concentration. Wang et al. [33] have also reported, with investigations on methyl orange decolorization using ultrasonic horn of 20 kHz frequency, that the rate of sonochemical decomposition of methyl orange was enhanced more than 100 times by adding CCl_4 into the dye solution. Ghodbane and Hamdaoui [34] have reported that for an initial dye concentration of 50 mg/L, the use of CCl_4 significantly increased the initial rate of decolorization of anthraquinonic dye acid Blue 25. The rate of degradation was 0.1467 mg/L in the presence of only ultrasonic irradiations, whereas the addition of CCl_4 at two different loadings i.e. 399 and 798 mg/L increased the rate of degradation to 15.6 and 17.3 mg/L, respectively. It is important to note here that the use of CCl_4 as an additive depends on the pollutant under question and hence cannot be generally recommended especially considering the toxicity associated with CCl_4 itself.

3.5. Effect of introduction of air

Experiments were also performed to study the decolorization of Rh 6G in the presence of air. The air was introduced with the help of fish pond aerator with a flow rate of 31.25 cm^3/s. The obtained results for the effect of introduction of air are given in Fig. 7. It has been observed that the presence of air increases the extent of decolorization to 22.8% under similar operating conditions. The kinetic rate constant in the presence of air was 2.3×10^{-3} min^{-1}, which is about five times more as compared with that obtained in the absence of the additive. The observed results are attributed to the fact that the presence of the dissolved gases in the liquid significantly increases the cavitational effects by supplying nuclei for the process. Due to the introduced heterogeneity in the system, the generation of cavitation nuclei is favored leading to enhanced number of cavitational events, and hence, the overall cavitational intensity is increased.

3.6. Sonophotolytic decolorization

The obtained results for the degradation of Rh 6G using combination of both the modes of irradiation in the presence and absence of hydrogen peroxide is shown in Fig. 8. It has been observed from the figure that combined operation of US and UV irradiations marginally improved the extent of decolorization as compared to the use of ultrasonic irradiations alone, which can be attributed to higher quantum of free radicals being produced in the system. Also, it can be concluded from the figure that the use of combination of ultrasound and UV irradiation with the addition of H_2O_2 at optimum loadings results in significantly higher decolorization than the combination of US and UV or the individual operation of ultrasound. The decolorization of Rh 6G increased to 70.8% when the experiments were carried out in the presence of 1% H_2O_2 under combination of US and UV. The kinetic rate constant for the combination was 1.15×10^{-2} min^{-1}, which is about 23 times more as compared to that obtained using ultrasound alone. The beneficial effect of coupling photocatalysis with sonolysis as well as adding hydrogen peroxide can be attributed to the increased production of hydroxyl radicals in the reaction system through the following steps, as given in the reactions (5)–(10) [35–38]: (i) water sonolysis (reactions (5) and (6)), (ii) reaction of hydrogen peroxide with the hydrogen atoms formed from water sonolysis (reaction (7)), (iii) hydrogen peroxide photolytic dissociation (reaction (8)), (iv) reaction of hydrogen peroxide with the superoxide radical anions formed during photocatalysis (reaction (9)), (v) reaction of hydrogen peroxide with conduction band electrons (reaction (10)):

$$H_2O + \text{ultrasound} \rightarrow H^{\cdot} + HO^{\cdot} \quad (5)$$

$$H_2O + \text{ultrasound} \rightarrow 1/2H_2 + 1/2H_2O_2 \quad (6)$$

$$H_2O_2 + H^{\cdot} \rightarrow H_2O + HO^{\cdot} \quad (7)$$

$$H_2O_2 + hv \rightarrow 2HO^{\cdot} \quad (8)$$

$$H_2O_2 + O_2^{\cdot} \rightarrow HO^{\cdot} + HO^{-} + O_2 \quad (9)$$

$$H_2O_2 + e_{cb}^{-} \rightarrow HO^{\cdot} + HO^{-} \quad (10)$$

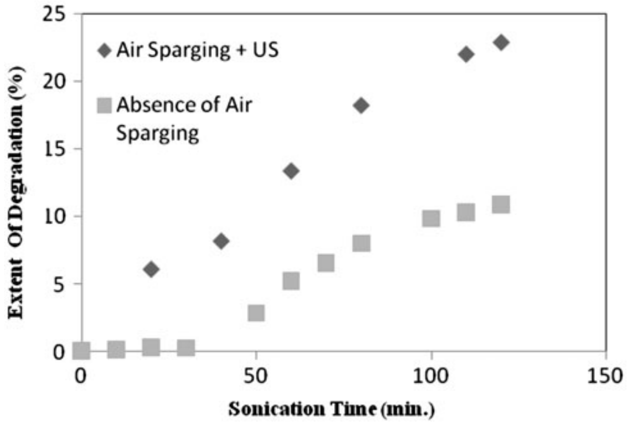

Fig. 7. Effect of air sparging on degradation of Rh 6G (sonication time = 120 min; initial concentration of Rh 6G = 10 ppm; pH 12.5).

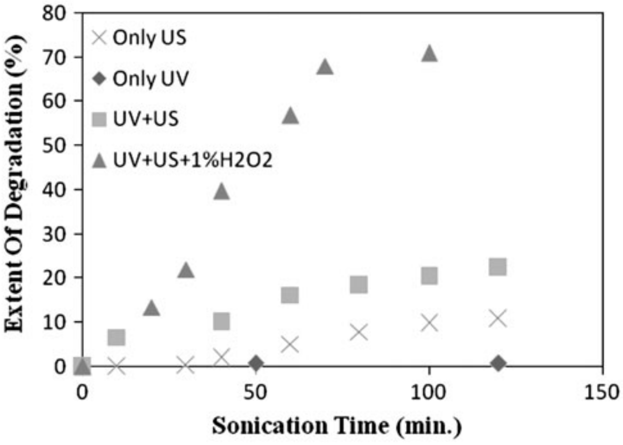

Fig. 8. Sonophotolytic degradation of Rh 6G (sonication time = 120 min; initial concentration of Rh 6G = 10 ppm; pH 12.5).

3.7. Use of CCl_4 in combination with sonophotolysis

Additional experiments were also carried out to study the decolorization of Rh 6G employing ultrasound and UV irradiations in the presence of 1% loading of CCl_4. The results have been illustrated in Fig. 9. It can be concluded that the decolorization of dye was enhanced by addition of CCl_4. It has been observed from the figure that the extent of decolorization increased to 23.5% with 1% loading of CCl_4, whereas 12% decolorization was obtained in the absence of CCl_4. The kinetic rate constant at 1% loading was 2.1×10^{-3} min^{-1}, which is about four times more as compared to that obtained using only ultrasonic irradiations. This improvement is due to the degradation of CCl_4 by pyrolytic cleavage in cavitation bubbles, which conducts to the release of oxidizing agents that can react with dye molecules as discussed in details earlier.

A comparison of the results obtained for CCl_4 as an additive for sonophotocatalytic oxidation with hydrogen peroxide as an additive clearly confirm the superiority of hydrogen peroxide indicating the free radical generation (at limiting and optimized concentration of hydrogen peroxide) and its subsequent attack on the pollutant molecules plays a key role in deciding the extent of dye decolorization. To confirm this hypothesis, additional studies were also carried out in the presence of radical scavengers.

3.8. Effect of $NaHCO_3$ addition on sonochemical decolorization of R6G

To understand the controlling mechanism for the sonochemical decolorization i.e. pyrolytic or free radical attack, additional studies have been performed considering the effect of various concentrations of sodium bicarbonate (radical scavenger) in the range from 0.05 to 2 g/L. It has been observed that as the concentration of sodium bicarbonate increases, decolorization of Rh 6G decreases significantly confirming that sodium bicarbonate behaves as a radical scavenger and the main driving force for the decolorization of Rh 6G is indeed free radical attack. At lower concentration of sodium bicarbonate i.e. 0.05 g/L the extent of decolorization of Rh 6G was 7.1%, which is marginally lower than that obtained in the absence of sodium bicarbonate. It is important to note here that at very low concentrations, sodium bicarbonate can also promote the generation of free radicals. Petrier et al. [39] have reported that the initial decolorization rate for bisphenol A increased by a factor 3.2 at low concentration of bisphenol-A ($0.022\,\mu\text{mol}\,\text{l}^{-1}$) in the presence of bicarbonate ions in water. It appears that the enhancement is not the controlling factor in the present case also indicating that mostly the reaction seems to occur around the cavitating bubble, and hence, a scavenging action of the bicarbonate ions has been observed. Further, for 0.2 g/L, the extent of decolorization was nearly half of the extent of decolorization obtained by the addition of 0.05 g/L of $NaHCO_3$. Also it has been observed that with addition of 2 g/L of $NaHCO_3$ the extent of decolorization was negligible. In the presence of $NaHCO_3$, the different reactions that can occur are given as follows:

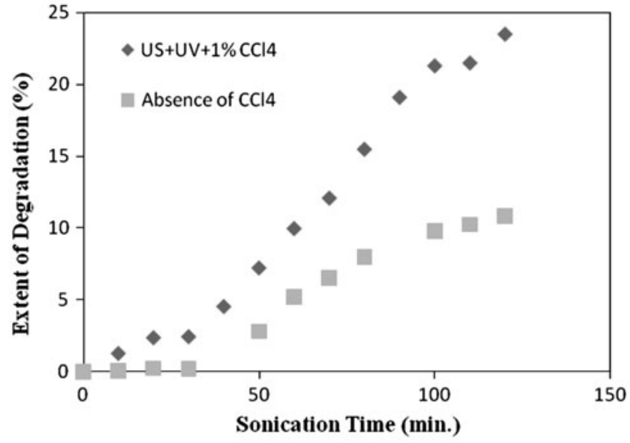

Fig. 9. Use of CCl_4 in combination with sonophotolysis (sonication time = 120 min; initial concentration of Rh 6G = 10 ppm; pH 12.5).

$$NaHCO_3 \rightarrow Na^+ + {}^-HCO_3 \qquad (11)$$

$$^-HCO_3 \rightarrow H + CO_3^{2-} \qquad (12)$$

$$^-HCO_3 + {}^*OH \rightarrow H^+ + CO_3^- \qquad (13)$$

$$CO_3^{2-} + {}^*OH \rightarrow CO_3^- + {}^-OH \qquad (14)$$

$$2CO_3^- + H_2O \rightarrow 2CO_2 + HO_2^- + OH^- \qquad (15)$$

$$OOH^- + OH \rightarrow^- OH + OOH \qquad (16)$$

The scavenging effect of sodium bicarbonate could be due to the reactions 13, 14, and 16. Also the formation of carbon dioxide in the system can deteriorate the onset of cavitational effect thus leading to an overall decrease in the extent of decolorization of Rh 6G. This study, with the presence of sodium bicarbonate has clearly established that the controlling mechanism of the sonochemical decolorization of Rh 6G is indeed, the free radical attack.

4. Conclusions

This work has shown that Rh 6G, a basic dye, can be effectively removed from water by using ultrasound based treatment strategies involving the use of additives. Initial studies related to effect of pH and initial concentration indicated that the higher concentration and basic conditions favored the extent of decolorization. Use of CCl_4 as an additive did not give satisfactory results as marginal intensification was observed as compared to other additives; also using higher concentrations of CCl_4 resulted in higher extents of decolorization but these may not be recommended considering the toxicity associated with CCl_4. The presence of air also intensified the decolorization due to the increased number of cavitational events in the reactor. Use of ultrasonic irradiation with H_2O_2 at optimum level was the most efficient approach for the oxidation of Rh 6G dye. It has been concluded from the studies related to the effect of the addition of H_2O_2 that the maximum extent of Rh 6G dye decolorization was obtained as 77.8% under optimized conditions. It has also been clearly established in this study that the ultrasound-based treatment strategies would depict much better option for degradation of Rh 6G and also provides satisfactory evidence for large capacity application of sonochemical reactors for industrial wastewater treatment.

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