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Removal of Rhodamine 6G from wastewater using solar irradiations in the presence of different additives

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ABSTRACT

The present work investigates the intensification aspects for the solar-induced photocatalytic degradation of basic dye Rhodamine 6G (Rh 6G) using different additives. The effect of basic operating parameters as pH and initial concentration has been investigated initially followed by studies related to understanding the effect of different additives and deciphering the controlling mechanism for intensification of degradation. The effect of catalysts such as TiO_2, CuO and CaO as well as process intensifying additives such as $FeSO_4$ and $CuSO_4$ over the loading range of 1.5–4.5 g/L has been investigated. Among the different additives investigated in the work, TiO_2 was observed to give maximum effectiveness for process intensification. The effect of radical scavengers such as methanol (CH_3OH), *n*-butanol (n-C_4H_9OH) and Na_2CO_3 has also been investigated to elucidate whether the free radical attack is the controlling mechanism of degradation. The extent of degradation was significantly affected at higher loadings of the radical scavengers confirming the major role of hydroxyl radicals in deciding the extent of degradation. Overall, it has been observed that maximum degradation as 96.5% was obtained under optimal conditions of pH as 12.5 and initial concentration of 10 ppm using the photocatalytic approach based on TiO_2 as the catalyst and $CuSO_4$ as additive.

Keywords: Rhodamine 6G degradation; Solar photocatalysis; Process intensification; Type of catalyst; Additives

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1. Introduction

In the beginning of the twenty-first century, there has been significant shortage of usable water resources and the problem has become severe due to the ever increasing pollution levels due to the discharges from both domestic and industrial sources. According to WHO, shortage or even lack of water supply affects more than 40% of the world population. Besides, more than 25% of the world population suffers from health and hygienic problems related to water. The extensive use of dye stuff compounds in the textile industry produces large amounts of coloured water, which has to be treated to avoid adverse environmental effects due to the toxicity of compounds and the colour that is imparted to the water bodies. It has become necessary for industries to use and develop efficient techniques to decolourize the effluents before disposal into the water bodies. Many physical and chemical methods, such as coagulation, precipitation, floatation, chemical oxidation, solvent extraction, etc., have been tried in order to remove colour from wastewater. But these conventional approaches have not been very successful since the dyes are stable to oxidizing agents, and the conventional treatment approaches involve high operational cost and treatment times, especially for the case of biological processes. Advanced oxidation processes utilize the strong oxidising species such as OH radicals produced *in situ* and can be effectively applied for the treatment also giving advantage of less residual contaminants [1].

One of the important advanced oxidation processes is photocatalysis which can be based on the use of UV irradiations or the solar light. Dyes can be degraded in the presence of photocatalyst using the UV irradiation and also the irradiation in the visible region [2]. Use of heterogeneous photocatalysts such as TiO_2, CuO, ZnO or CaO offers significant advantage in terms of ease of separation though the catalyst loading needs to be optimized as the presence of solid catalyst can result in the scattering of incident radiations [3,4]. Use of homogeneous operations such as combination of UV with hydrogen peroxide or the photo-Fenton reactions [5] avoids the problems with the light scattering but gives separation problems and also the unutilized oxidants add to the final effluent load.

The present study is aimed at developing a simple and efficient treatment scheme based on the use of solar irradiations for degrading dyes usually present in textile industry effluents, which is a very significant problem especially considering the Indian context. Also India being a tropical country, sunlight is abundantly available natural source of energy, which can be conveniently exploited for the treatment. It is expected that sunlight would give lesser efficacy as compared to the UV irradiations but the advantage in terms of lower cost and abundant availability can give significant cost benefits and hence the work was focused on investigating the intensification aspects. The work has concentrated on understanding the effect of type and the loading of the catalyst as well as use of different process intensifying additives, which has not been reported for the case of Rh 6G containing wastewaters and hence forms an important contribution. Also, mechanistic investigations were performed on the basis of use of alcohols, which to the best of our knowledge has not been investigated for the solar light-based treatment approach. The model compound considered for the study is Rhodamine 6G, which is a basic dye used to dye wool, cotton, silk and papers where brilliant shades with fluorescent effects are required. Rh 6G is highly toxic in nature and hence development of efficient treatment strategies is very important.

2. Materials and methods

2.1. Materials

Rhodamine 6G (abbreviation: Rh 6G; C.I. No. 45160; Dark reddish purple colour; molecular formula: $C_{28}H_{31}N_2O_3Cl$; molecular weight: $479.02\ \mathrm{g\ mol^{-1}}$; IUPAC name [9-(2-ethoxycarbonylphenyl)-6-(ethylamino)-2,7-dimethylxanthen-3-ylidene]-ethylazanium chloride) was obtained from Loba Chemical Pvt. Ltd, Mumbai, India. The dilute solutions of different chemicals with required concentration were prepared using demineralized water, which was prepared freshly in the laboratory. Titanium oxide (TiO_2), copper oxide (CuO), ferrous sulphate ($FeSO_4$), copper sulphate ($CuSO_4$), sodium carbonate (Na_2CO_3), calcium oxide (CaO), methanol (CH_3OH) and *n*-butanol (*n*-C_6H_5) were obtained from Merck Specialties Pvt. Ltd, Mumbai, India. All the chemicals were used as received from the supplier.

2.2. Equipment and procedure

Experiments to study the photolytic degradation of Rhodamine 6G (Rh 6G) in water were performed using a solar photoreactor with capacity of 3 L. The aqueous dye solution (volume of 2 L) was introduced into the reactor. The catalyst or additives were added as per the experimental protocol and the suspension was uniformly mixed using magnetic stirrer for about 15 min. Using the preliminary kinetic studies, it was established that 15 min was the required time to reach the equilibrium for the adsorption of the dye over the catalyst surface. For this study, initial concentration of Rhodamine 6G was selected as 10 ppm with catalyst loading of 1.5 g/L. Once the equilibrium was reached, the first sample was withdrawn for the analysis. Irradiation was then started and the suspension was exposed to the sunlight for a total treatment time of 180 min with samples being withdrawn at regular intervals for analysis. The experiments were performed in a reaction vessel at starting time of 10.30 AM so as to utilize the maximum intensity of the incident sunlight. For each of the withdrawn sample, the catalyst was separated from the dye solution using a Millipore filter paper. The filtration was performed as quickly as possible such that the contact time between filter paper and the dye solution is the minimum. The absorption spectra were recorded for the withdrawn samples and rate of degradation with respect to the change in concentration was quantified at $\lambda_{\max}$ for the Rh 6G dye. The concentration of Rh 6G was measured using a UV-spectrophotometer (Chemito Spectrascan UV 2600 double beam) at wavelength, $\lambda = 523$ nm [6].

Different catalyst concentrations over the range of 1.5–4.5 g/L have been considered in the present work for understanding the effect of catalyst loading, while the initial dye concentration was kept constant at 10 ppm for these studies. The size of TiO_2 used in the work was in the range of 1–1.5 μm and it was mainly in anatase form with tetragonal structure. The size of other catalysts used in the work was over the range of 1–3 μm [7]. Experiments for understanding the effect of dye concentration were also performed over the initial concentration range of 10–50 ppm. All the experiments were repeated at least two times to check the reproducibility and average values have been reported in the figures. The observed variation in the data was within 2% of the reported average value.

3. Results and discussion

3.1. Effect of catalyst type and loading on degradation using solar energy

The effect of catalyst type has been investigated using three different catalysts as titanium oxide (TiO_2), copper oxide (CuO) and calcium oxide (CaO) with an objective of determining the best photocatalyst among different commercially available materials being reported commonly in the literature [8–11]. Also the effect of catalyst loading was investigated over the loading range of 1.5–4.5 g/L to obtain the optimum loading for maximum effects. The initial concentration of the pollutant was kept constant as 10 ppm concentration and the operating pH as 2.5. Control experiments were also performed in the absence of any catalyst. The obtained results for the effect of type of catalyst and loading are shown in Fig. 1.

It has been observed that the extent of degradation without using any catalyst was very low at 9% and addition of catalyst increased the extent of degradation significantly. The extent of increase was found to be dependent on the type of catalyst. For the case of TiO_2, an increase in the amount of catalyst from 1.5 to 3.0 g/L increased the dye degradation sharply from 38 to 72% during the constant treatment time as 180 min. Kinetic studies revealed that first-order mechanism fits the obtained data well and it was observed that the rate constant also increased from 5.6×10^{-3} to 7.9×10^{-3} min^{-1} for a similar increase in the catalyst loading. The data for the kinetic rate constants have been given in Table 1. The observed enhancement in the removal rate could be ascribed to the increase in the amount of catalyst which increases the number of active sites available for the reaction leading to generation of higher extent of free radicals and hence the extent of degradation increases. However, with a continued increase in the loading from 3.0 to 4.5 g/L (Fig. 1), the rate of degradation of Rh 6G was found to decrease. This may be attributed to the enhanced light reflectance by the catalyst resulting in decreased light penetration. Particle–particle interaction becomes significant as the number of particles in the solution increases. This reduces the site density for surface holes and electrons and hence the quantum of free radicals generated reduces [12,13]. The rate of degradation decreases as a result of decreased surface area due to agglomeration (particle–particle interactions) at high solid loading. The results obtained in this work, are in good agreement with reported trends in the literature [14–20]. Suri et al. [16] investigated the destruction of toluene, trichloroethylene and methylethylketone using different initial pollutant concentration and TiO_2 loading. The optimum catalyst loading was found to be dependent on the initial pollutant concentration. Thus, higher amount of the catalyst may not be useful both in view of the possible aggregation as well as reduced irradiation intensity due to increased light scattering. The photocatalytic destruction of phenol also exhibited the same dependency on catalyst loading [16]. Shirgaonkar and Pandit [18] also reported that the extent of degradation of tricholrophenol was higher (16.8%) at 0.1 g/L of TiO_2 loading as compared to that obtained in the absence of catalyst (10.2%), though a further increase in the loading gave marginal effect on extent of degradation.

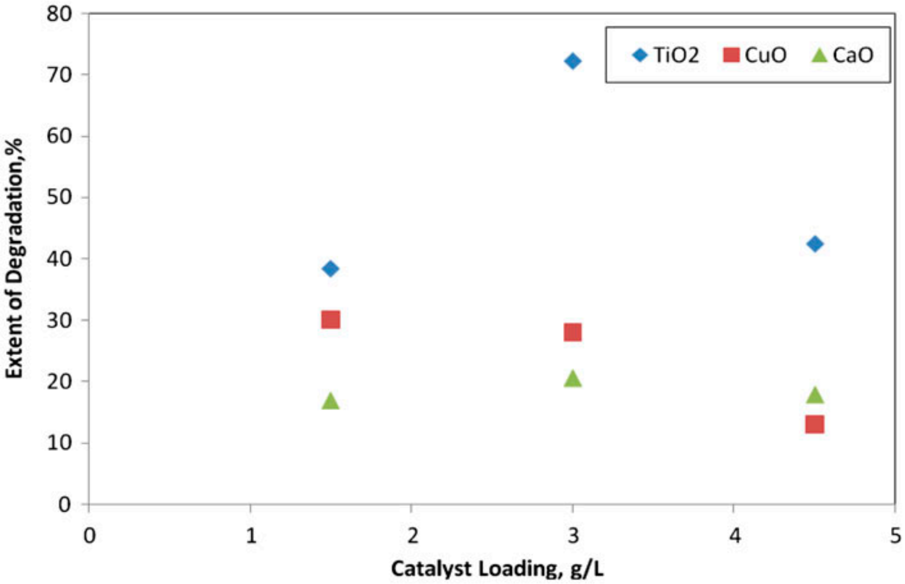

Fig. 1. Effect of catalyst type and loading on degradation of Rh 6G using solar energy. (Irradiation time 180 min; pH 12.5; 10 ppm initial concentration of dye.)

Fig. 1 also shows the obtained trends for the two other catalysts investigated in the work as CuO and CaO. For the case of CuO, it was observed that the maximum extent of degradation was 30.2% and rate constant was 4.6×10^{-3} (min^{-1}) at 1.5 g/L of catalyst loading, which were definitely higher as compared to the treatment without catalyst. It has been also observed that there was a marginal change in the extent of degradation for an increase in the loading from 1.5 to 3 g/L and beyond this, the extent of degradation decreased. Similarly, the depicted results for the case of CaO as the catalyst also confirmed that the optimum loading was 3 g/L.

Among the different catalysts, it is clearly seen that TiO_2 is the best catalyst with about three to four times higher extent of degradation at the optimum loading as compared to the other catalysts used in the work. Titanium dioxide is known to be the best semiconductor giving maximum photocatalytic activity. Also, TiO_2 is non-toxic, relatively inexpensive and stable in aqueous solution [19,20]. The better results for the photocatalyst TiO_2 can also be attributed to the higher surface area as compared to other catalysts, which is dependent on the size of the solid particles. The detailed characterization of the size of TiO_2 particles including the SEM images has been reported earlier [7] and it has been established that TiO_2 particles are extremely fine and crystalline which can possibly offer higher active surface area. TiO_2 also has a band gap of 3.2 eV corresponding to a wavelength of 385 nm. The photocatalyzed degradation of a dye in solution is driven by the photo excitation of the semiconductor, followed by the formation of electron–hole pair on the surface of catalyst [21]. The reaction mechanisms for the direct oxidation of the dye based on the use of holes can be given by the following equations:

$$(\text{Rh 6G}) + \text{hv} \rightarrow (\text{Rh 6G})\left(e_{cb}^{-} + h_{vb}^{+}\right) \tag{1}$$

$$h_{vb}^{+} + \text{dye} \rightarrow \text{dye}^{+} \rightarrow \text{oxidation of the dye} \tag{2}$$

Another mechanism which is responsible for the degradation is the formation and subsequent attack of hydroxyl radical ($OH^{\cdot}$). It is either formed by the decomposition of water (3) or by reaction of the hole with OH^{-} (4). Hydroxyl radical is an extremely strong and non selective oxidant ($E^0 = +3.06$ V) which leads to the partial or complete mineralization of several organic chemicals. The initiation reactions leading to the formation of free radicals and its attack on the parent molecules can be given as follows:

$$h_{vb}^{+} + H_2O \rightarrow H^{+} + OH^{-} \tag{3}$$

$$h_{vb}^{+} + OH^{-} \rightarrow OH^{\cdot} \tag{4}$$

Table 1
Comparative data for the percentage degradation of Rh 6G for different sets of experiments

Sr. no.	Studies	Extent of decolourization (%)
1	Solar only	9.2
2	1.5 g/L TiO_2	38.45
3	3 g/L TiO_2	72.3
4	4.5 g/L TiO_2	42.5
5	1.5 g/L CuO	30.2
6	3 g/L CuO	28.1
7	4.5 g/L CuO	13.0
8	1.5 g/L CaO	16.9
9	3 g/L CaO	20.6
10	4.5 g/L CaO	17.9
11	1.5 g/L $FeSO_4$	26.7
12	3 g/L $FeSO_4$	22.6
13	4.5 g/L $FeSO_4$	12.4
14	1.5 g/L Na_2CO_3	32.5
15	3 g/L Na_2CO_3	16.4
16	4.5 g/L Na_2CO_3	12.1
17	1.5 g/L $CuSO_4$	30.7
18	3 g/L $CuSO_4$	27
19	4.5 g/L $CuSO_4$	19.4
20	1.5 ml/L methanol	20.1
21	3 ml/L methanol	15.4
22	4.5 ml/L methanol	12.6
23	1.5 ml/L *n*-butanol	25.4
24	3 ml/L *n*-butanol	14.4
25	4.5 ml/L *n*-butanol	12.3
26	Optimal TiO_2 + optimal $FeSO_4$	94.6
27	Optimal TiO_2 + optimal $CuSO_4$	96.5
28	Optimal TiO_2 + optimal Na_2CO_3	92.8
29	Optimal CuO + optimal $FeSO_4$	84.3
30	Optimal CuO + optimal $CuSO_4$	89.4
31	Optimal CuO + optimal Na_2CO_3	79.4
32	Optimal CaO + optimal $FeSO_4$	79
33	Optimal CaO + optimal $CuSO_4$	73.6
34	Optimal CaO + optimal Na_2CO_3	71.8

$$\mathrm{OH}^{\cdot} + \mathrm{Dye} \rightarrow \text{Degradation of the dye} \qquad (5)$$

It would be also worthwhile to compare the obtained trends for the use of CuO and CaO particles. In the case of these catalysts, the extent of degradation of Rh 6G was found to depend on the particle size due to the similar catalytic activities. CuO catalyst was shown to give higher extent of degradation as compared to the CaO attributed to the lower size and hence higher surface area being available for the generation of free radicals.

Overall it can be established that presence of solid catalyst has both negative and positive impacts on the degradation. It is essential to determine the optimum amount of catalyst required in order to avoid unnecessary excess loading and also to ensure total absorption of photons for efficient degradation. In the present work, the optimal loading was observed to be 3 g/L for all the catalysts.

3.2. Effect of initial concentration of the dye

The effect of initial concentration of dye solution on the extent of degradation of Rh 6G was investigated for all the catalysts used in the work (TiO_2, CuO and CaO) by varying the initial concentration over the range of 10–50 ppm. The obtained results have been depicted in Table 2. It was found that with an increase in the initial concentration, the extent of degradation decreases for all the catalysts investigated in the work. After 180 min treatment, the extent of degradation of

Rh 6G of decreased from 87.6% at 10 ppm concentration (kinetic rate constant is 8.4×10^{-3} min^{-1}) to 61.4% at initial concentration of 50 ppm for the operation at optimal loading of catalyst TiO_2 as 3 g/L. Similar trend was observed for photocatalytic degradation in the presence of other metal oxides viz. CuO and CaO. The degradation rate constant was observed to decrease from 6.3×10^{-3} to 3.4×10^{-3} min^{-1} for CuO catalysed oxidation and from 7.4×10^{-3} to 2.5×10^{-3} min^{-1} for CaO catalysed oxidation for an increase in the concentration from 10 to 50 ppm. The obtained results can be attributed to the fact that as the initial concentration of the dye increases, the amount of light penetrating and utilized for excitation of the catalyst decreases thereby reducing the generation of free radicals. Also, the path length of photons entering the solution decreases, which thereby reduces the photon absorption by the catalyst at higher concentration giving lower extent of reduction [22]. This suggests that as the initial concentration of the dye increases, the requirement of catalyst surface needed for the effective degradation also increases. Since illumination time and amount of catalyst are constant, the OH radical (primary oxidant) formed on the surface of catalyst and being available for reaction is lower as compared to the available pollutant molecules thereby reducing the rate of degradation [23,24]. The obtained results are consistent with those reported by Matthews [20] for the photocatalytic degradation of methylene blue dye with TiO_2 catalyst. As higher extents of degradation rate constant were obtained at lower initial concentrations of the pollutant, further studies were performed at 10 ppm initial concentration of the pollutant.

3.3. Effect of pH

The solution pH is another important factor that can influence the degradation of various organic pollutants using solar/UV irradiation. Hence, the effect of pH on the degradation of dye in the presence of solar light has been investigated by performing experiments at various initial pH values over the range from 2.5 to 13.5 at constant initial dye concentration (10 ppm) and catalyst loading (3 g/L). In all the experiments, the pH values were adjusted by adding appropriate amount of 1 mol/L HCl and 1 mol/L NaOH aqueous solutions. The obtained results for the effect of pH have been given in Table 3 and it can seen from the table that the extent of degradation of Rh 6G increased from 56.5 to 91.4% (kinetic rate constant from 5.3×10^{-3} to 9.4×10^{-3} min^{-1}) with an increase in the pH from 2.5 to 12.5 and then a marginal decrease was observed at pH 13.5 for the case of catalyst as TiO_2. Similar results have also been observed for other metal oxides as CuO and CaO, where the extent of degradation increased from 43.4 to 78.7% and from 42.3 to 66.4%, respectively, for an increase in pH from 2.5 to optimum pH as 12.5.

The decreased rate of degradation of Rh 6G at higher pH (13.5) as compared to optimum is attributed to the fact that at very high pH values the hydroxyl radicals are rapidly scavenged and hence the availability for the selective oxidation of Rh 6G dye decreases [2,25]. The pH affects not only the surface properties of TiO_2, but also the formation of hydroxyl radicals. The experimental results revealed that higher degradation of the dyes occurred under basic conditions as compared to the acidic conditions. This may be attributed to the electrostatic interactions between the positive catalyst surface and dye anions leading to strong adsorption of the latter on the metal oxide. Sakthivel et al. [26] observed similar behaviour in their studies on degradation of Acid Brown 14 dye.

The interpretation of pH effect on the efficiency of the photodegradation process is a very difficult task, because three possible mechanisms can contribute to the dye degradation, namely, hydroxyl radical attack, direct oxidation by the positive hole and direct

Table 2
Effect of initial concentration on the extent of degradation of Rh 6G at optimal loading of metal oxides

		Optimal TiO_2 3 g/L		Optimal CuO 1.5 g/L		Optimal CaO 3 g/L	
Sr. no.	Concentration (ppm)	Extent of degradation (%)	Kinetic rate constant (min^{-1})	Extent of degradation (%)	Kinetic rate constant (min^{-1})	Extent of degradation (%)	Kinetic rate constant (min^{-1})
1	10	87.6	8.4×10^{-3}	65.4	6.3×10^{-3}	62.3	7.4×10^{-3}
2	20	79.5	7.8×10^{-3}	61.3	5.8×10^{-3}	53.4	5.1×10^{-3}
3	30	72.4	7.1×10^{-3}	56.3	5.3×10^{-3}	47.8	3.9×10^{-3}
4	40	66.7	6.4×10^{-3}	47.5	4.3×10^{-3}	41.6	3.4×10^{-3}
5	50	61.4	6.0×10^{-3}	41.1	3.4×10^{-3}	36.4	2.5×10^{-3}

Table 3
Effect of pH on the extent of degradation of Rh 6G at optimal loading of metal oxides

		Optimal TiO_2 3 g/L		Optimal CuO 1.5 g/L		Optimal CaO 3 g/L	
Sr. no.	pH	Extent of degradation (%)	Kinetic rate constant (min^{-1})	Extent of degradation (%)	Kinetic rate constant (min^{-1})	Extent of degradation (%)	Kinetic rate constant (min^{-1})
1	2.5	56.4	5.3×10^{-3}	43.4	4.3×10^{-3}	42.3	4.4×10^{-3}
2	6.5	64.9	6.8×10^{-3}	48.3	4.8×10^{-3}	53.4	5.1×10^{-3}
3	8.5	73.4	7.6×10^{-3}	56.3	5.3×10^{-3}	57.8	5.9×10^{-3}
4	10.5	85.7	8.3×10^{-3}	67.5	6.3×10^{-3}	61.2	6.4×10^{-3}
5	12.5	91.4	9.4×10^{-3}	78.7	7.4×10^{-3}	66.4	6.5×10^{-3}
6	13.5	87.3	8.6×10^{-3}	74.4	7.5×10^{-3}	63.7	6.3×10^{-3}

reduction by the electron in the conducting band. The importance of each one depends on the substrate nature and pH [27]. In the present case, it can be presumed that the main reaction is controlled by the hydroxyl radical attack, which can be favoured in general at higher operating pH. It is important to note that due to the counteracting mechanisms controlling the effect of pH, optimum is likely to exist (as also demonstrated in the present work) and the value is likely to depend on the pollutant under question. The approach presented in the work would be very useful for establishing the optimum pH for maximum degradation.

3.4. Effect of inorganic ions

The presence of inorganic ions in the industrial wastewater is relatively common and hence it is important to establish the effect of these inorganic ions on the photocatalytic degradation of dye. Experiments were performed to understand the effect of sulphate ions (using $FeSO_4$ and $CuSO_4$) and carbonate ions (using Na_2CO_3) at a loading of 1.5–4.5 g/L. The obtained results for the variation in the extent of degradation of Rh 6G in the presence of different salts have been depicted in Fig. 2. It can be seen from the figure that the obtained extent of degradation is higher at 1.5 g/L loading as compared to other additive concentrations and also as compared to the basic extent of degradation obtained using the solar photolysis only. As the loading of additives increased beyond 1.5 g/L, the degradation rate of Rh 6G was found to decrease.

In the case of addition of $FeSO_4$, the maximum extent of degradation as 26.7% (rate constant 9.0×10^{-4} min^{-1}) was observed at 1.5 g/L loading of $FeSO_4$. The extent of degradation obtained for 3 g/l and 4.5 g/l loading of $FeSO_4$ was 22.6% (rate constant 8.0×10^{-4} min^{-1}) and 12.4% (rate constant 7.0×10^{-4} min^{-1}), respectively. The initial increase in the extent of degradation due to the use of $FeSO_4$ can be attributed to splitting of the added salt into ferrous ion (Fe^{2+}) and sulphate ion (SO_4^{2-}) in the presence of solar irradiations, which give additional oxidation mechanisms. Sulphate ions being very strong oxidant produce hydroxyl radicals ($OH^{\cdot}$) under solar irradiation which result in enhanced degradation of Rh 6G [28,29]. At higher loadings, too much salt content can create a salting out effect thereby reducing the interactions of the pollutant with generated free radicals and the extent of degradation reduces.

Similar results have also been observed when additional experiments were carried out using $CuSO_4$ at various concentrations. It was observed that in the case of $CuSO_4$ also, the maximum extent of degradation of Rh 6G (30.7%) is obtained at lower loading i.e. 1.5 g/L which is slightly higher than $FeSO_4$. Copper sulphate can also undergo dissociation in the presence of solar irradiations as follows [30,31] generating additional oxidants which enhance the overall degradation.

$$CuSO_4 \rightarrow Cu^{2+} + SO_4^{2-} \tag{6}$$

$$SO_4^{2-} + OH^{0-} \rightarrow SO_4^{0-} + OH^- \tag{7}$$

$$2SO_4^{0-} \rightarrow S_2O_8^{2-} + 2e^- \tag{8}$$

$$SO_4^{0-} + \text{Dye} \rightarrow SO_4^{2-} + \text{dye}^{0+} \text{ (intermediate)} \tag{9}$$

$$\begin{aligned} &SO_4^{0-} + \text{dye}^{0+} \text{ (intermediate)} \\ &\quad \rightarrow SO_4^{2-} + CO_2 + \text{other inorganics} \end{aligned} \tag{10}$$

The effect of addition of Na_2CO_3 on the degradation of Rh 6G was also investigated and it can be discerned from Fig. 2 that after the initial increase (as compared to the case of absence of Na_2CO_3), the extent of

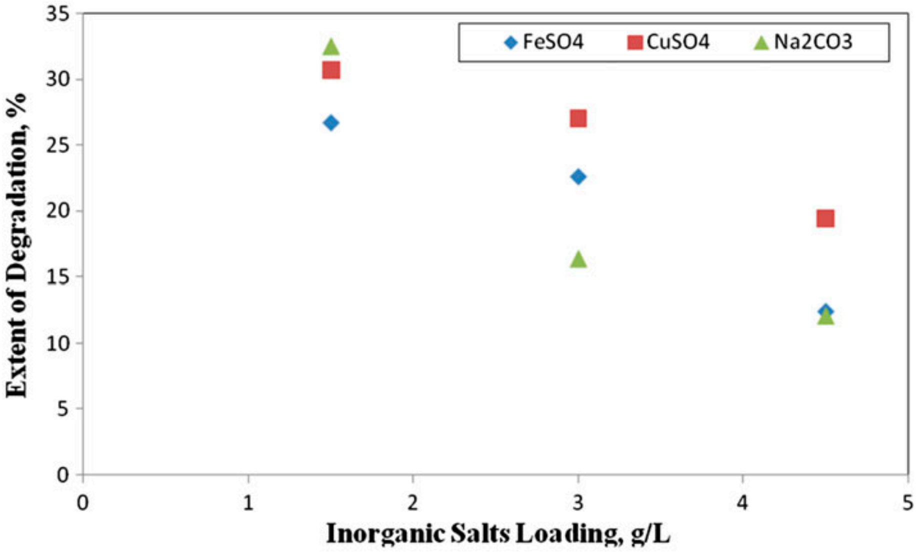

Fig. 2. Effect of inorganic salts on degradation of Rh 6G using solar energy. (Irradiation time 180 min; pH 12.5; 10 ppm initial concentration of dye.)

degradation decreases rapidly. Beyond the optimum loading of Na_2CO_3 as 1.5 g/L, the extent of degradation decreased significantly which can be attributed to the rapid scavenging action of Na_2CO_3 [32]. The obtained results clearly confirm that the main driving force for the decolourization of Rh 6G is indeed free radical attack.

3.5. Combined effect of metal oxides and inorganic salts

The possibility of combining the metal oxides as catalysts and additives at optimum loading with various combinations of metal oxide catalyst as TiO_2, CuO and CaO and the inorganic salts viz. $FeSO_4$, $CuSO_4$ and Na_2CO_3 at optimal conditions for obtaining maximum process intensification was also investigated. The obtained results for the various combinations have been given in Table 1. It is observed that the efficacy of the photocatalytic process using solar irradiation for degradation of Rh 6G dye is enhanced due to the use of additives. Maximum degradation of 96.5% was obtained at optimal conditions of TiO_2 and $CuSO_4$. The kinetic rate constant of 4.6×10^{-3} was obtained for this optimum combination of $TiO_2 + CuSO_4$ which was higher as compared to the combination of TiO_2 and Na_2CO_3 as well as combination of $TiO_2 + FeSO_4$. As mentioned earlier, TiO_2 helps in enhancing the production of free radicals, which is augmented by the use of $CuSO_4$ through the generation of the sulphate ions under the solar irradiation. The enhanced production of hydroxyl radicals increases the rate of degradation of the organic compound as compared to the individual operations.

3.6. Effect of radical scavengers

In order to determine the effect of strong radical scavengers such as methanol and butanol, experiments were performed by varying the concentration from 0.15 to 0.45% (by volume). The degradation efficacy for Rh 6G at various concentrations of methanol and butanol has been depicted in Fig. 3. It can be clearly seen that the extent of degradation decreases with an increase in the concentration of methanol as well as butanol. The extent of degradation obtained at 0.15% concentration of *n*-butanol was only 25.4% (rate constant 7.3×10^{-4} (min^{-1}) which further decreases when the loading was increased to 0.45% concentration of *n*-butanol. Similarly trends have also been observed for the case of methanol.

4. Mineralization studies of dyes

Chemical oxygen demand (COD) is used as a measure of the oxygen equivalent of the organic content in a sample that is susceptible to oxidation by a strong oxidant. The dichromate reflux method was used to estimate COD [33]. As the reduction of COD reflects the extent of mineralization of an organic species, the percentage removal in COD was studied for dye Rh 6G samples (concentration 10 ppm) under optimized conditions (optimum loading of TiO_2,

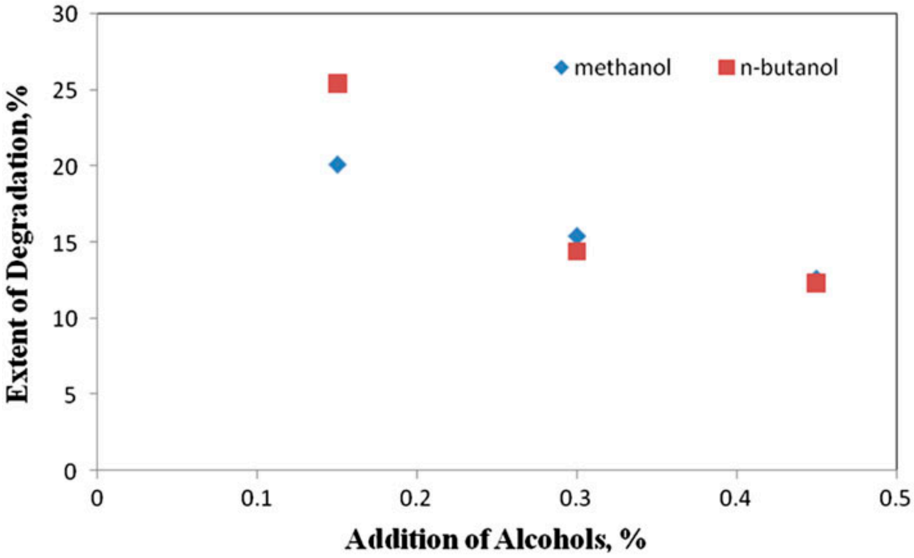

Fig. 3. Effect of alcohols on degradation of Rh 6G using solar energy. (Irradiation time 180 min; pH 12.5; 10 ppm initial concentration of dye.)

Table 4
Percentage of COD removal of Rh 6G under optimum conditions

Sr. no.	Studies	% Removal of COD
1	3 g/L TiO_2	74
2	1.5 g/L CuO	45
3	3 g/L CaO	34
4	1.5 g/L $FeSO_4$	42
5	1.5 g/L Na_2CO_3	45
6	1.5 g/L $CuSO_4$	45
7	4.5 ml/L methanol	34
8	4.5 ml/L *n*-butanol	42
9	10 ppm + 3 g/L TiO_2	84
10	12.5 pH + 3 g/L TiO_2	90
11	Optimal TiO_2 + optimal $CuSO_4$	92

CaO, CuO, Na_2CO_3, $FeSO_4$, $CuSO_4$, methanol and *n*-butanol, pH 12.5, reaction time 180 min). The maximum COD removal of 92% was obtained for the combination of $TiO_2 + CuSO_4$ at optimum conditions of pH as 12.5, TiO_2 loading as 3 g/L and initial concentration of pollutant as 10 ppm. The obtained results for the other sets of experiments are depicted in Table 4. It can be seen that under solar irradiation, the percentage reduction of COD was maximum at optimal TiO_2 loading as compared to other catalysts similar to trends observed for the pollutant concentration.

5. Conclusions

It has been established that the photodegradation of Rh 6G in an aqueous solution or in general, the textile industry wastewater using the solar light is feasible with near complete removal of the colour along with the mineralization under optimum conditions. The solar energy-based treatment may emerge as an alternative cost-effective approach because of the abundance of the light energy and non-hazardous nature. The use of various catalysts and additives for enhancing the extent of degradation is possible but establishing optimum concentration is an important requirement for effective operation. Additives such as methanol and *n*-butanol as well as salts at higher loadings act as a radical scavenger and hence the treatment approach should be designed properly to overcome the effects. The maximum COD removal was observed for the approach of photocatalytic oxidation with TiO_2 in combination with $CuSO_4$. Overall the work has clearly demonstrated that the combined treatment schemes based on solar photocatalysis can be effective in decolourization of dye containing wastewaters.

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