

ZnO Mediated Degradation of Reactive Brilliant Orange 3R by Visible Light

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Abstract

Visible light induced degradation of Reactive Brilliant Orange 3R, RBO, has been done in presence of 0.5 g to 1.7 g ZnO in 45 mL aqueous suspensions containing 3×10^{-5} M to 6.5×10^{-5} M dye at fixed pH (5.59). The process of its removal was monitored by recording the change of absorbance at $\lambda_{max} = 493$ nm with time. Molar absorptivity (ϵ) was found to be 1.91×10^4 L/mol cm at 30 °C. The photo degradation has been suggested to be initiated by electronic injection from the photo activated absorbed dye to ZnO followed by creation of different radicals. These radicals are responsible for ultimate mineralization of the dye. The initial rate of ZnO mediated photo degradation of RBO is affected by its initial concentration and the amount of ZnO. The photo degradation kinetics follows model indicating that degradation occurs at the surface of the ZnO particles. More than 51% color of 3×10^{-5} M in 45 mL suspension containing 1.50 g ZnO vanished within an hour of illumination. The products of mineralization of RBO by visible light in presence of ZnO are suggested to be CO₂, H₂O, SO₄²⁻, NO₃⁻, Cl⁻ and N₂. This suggests that the present technique can be optimized for industrial application to photo-mineralize dyes from the dyeing-house effluents.

Keywords: Visible light, photo degradation, Reactive Brilliant Orange 3R, surface catalyst.

Introduction

Dye, at present, is an inseparable component of our daily life. The application of dyes is widespread. Dyes are used in textile industries, coloring foods, candles, confectioneries, drugs, cosmetics, and pulp and paper industries. Furthermore, coloration of leather and rubber goods; printing inks, oils; waxes, varnishes and lipsticks require dye. The dye producing and dye using/consuming industries are discharging huge effluent which contains raw materials, unused dyes, and dye intermediates without pre-treatment. These are carried into the big rivers through canals, drains, etc. As dyes are non biodegradable, they are contaminating the

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surface water and consequently polluting the aquatic system. Therefore dye is a major pollutant of water. It is high time that we protected our aquatic system from the pollution caused by dye. Aqueous toxic waste is a global problem that needs to be given careful attention. Processes need to be developed for the detoxification of various classes of chemical wastes. The photo assisted detoxification processes can be developed that are industrially and economically feasible. During the last two decades, extensive research programs have been persuaded in the area of heterogeneous photo catalysis with semiconducting particulate systems for the photodecomposition of liquid waste and polluted water. Most of the works found in the literatures regarding heterogeneous photo catalytic processes deals with aqueous suspensions. Semiconductors used as photo-catalysts include TiO_2 [1-6], ZnO [7], CdS [8-9] and Fe_2O_3 [10-11]. The visible light excites the dyes [12] in the bulk solution and also the dyes adsorbed on catalyst particles [13]. On the other hand UV light of appropriate wavelength initiates other processes by generating electrons and holes [14-15] in the photo catalyst particles in the aqueous suspensions. Various physical, chemical and biological treatment techniques can be employed to remove color from dye containing wastewaters. In general, each technique has advantages and limitations. Dye removal strategies consist therefore mostly of a combination of different techniques which are delineated in (Fig.1).

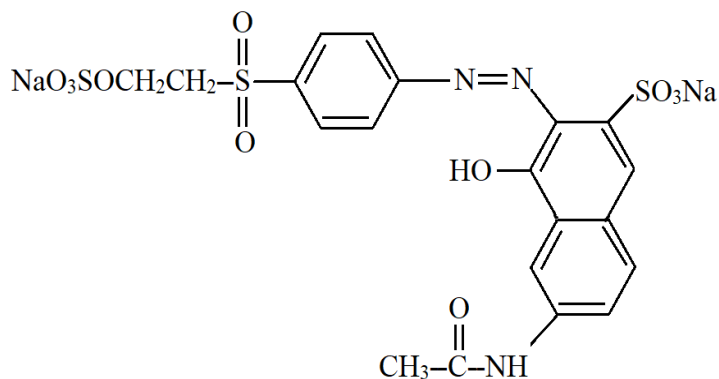


Figure 1. Reactive Brilliant Orange 3R

Experimental

Materials and methods

RBO was used as received without further purification; chemical used in this study were of analytical grade.

Analysis of RBO

Double-beam UV-visible spectrophotometer (UV-1601PC, Shimadzu, Japan), Electronic balance (SHIMADZU, AUY 220), pH meter (OAKTON, Singapore), Laboratory centrifuge machine (Labofuge, 200, Germany), Visible light source (11W Fluorescent lamp), Magnetic stirrer. Muffle furnace (ISUZU Seisakusho) were used for the analysis of RBO solution using $\lambda_{max} = 493$ nm with $\epsilon = 1.92 \times 10^4$ L/mol cm at 25°C. Initial rate, R_i , was determined from the following equation (Eq. 1):

$$R_i = -\frac{d}{dt} [RBO] = k' [RBO]_0 \quad (1)$$

The initial rate of degradation was determined from the slope of the tangent drawn at the initial absorbance (of RBO) versus time profile. It is assumed that all light is completely absorbed by the system. Percent decolorization of RBO was calculated by the following equation (Eq. 2), where A_o is initial absorbance at $[RBO]_o$, the concentration of RBO at time $t = 0$ and A_t = absorbance of RBO at time 't' during the experiment.

$$\% \text{ of RBO degradation} = \frac{A_o - A_t}{A_o} \times 100 \quad (2)$$

Photochemical reactor and light source

The reactor consisted of an open beaker made of pyrex glass. An energy saving bulb (11 W) was focused on the reactor surface horizontally which was arranged in a wooden box with Al-foil inside lining. The lamp was switched on before the experiment started and the temperature inside the box rose to 30 °C. The temperature remained 30 °C during the experiment. The volume of suspension in the reactor was kept constant and the reactor was maintained at fixed position so that the intensity of the incident light remains the same for all the experiments. No significant weight loss of the contents was recorded up to one hour of photolysis.

Photo degradation

1.5 g ZnO powder was taken in a beaker. 45 mL RBO of definite concentration was added to it. Then the beaker was placed into the box for photolysis. During photolysis the contents of the reactor were also stirred magnetically so that the suspension does not change its state. 5.0 mL solution was withdrawn from the beaker into the centrifuge tube at every five minutes and centrifuged. The clear solutions from the centrifuge tube were taken to measure the concentration spectrophotometrically. Photo degradation of dyes was studied with different initial concentration of RBO, with different amount of ZnO at the usual initial pH (5.59) of the solution and different initial pH of the medium. Fig. 2 and Fig. 3 show the pattern of the change of absorbance with time. The change in absorbance represents decolorization of the dye.

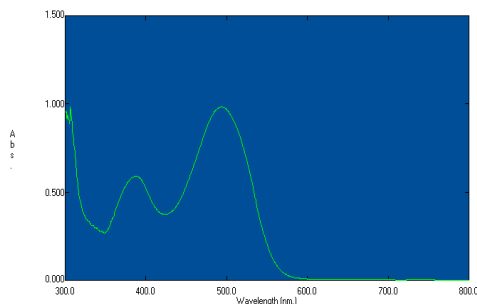


Figure 2. UV-Visible absorption spectrum of RBO in aqueous solution (Reference water)

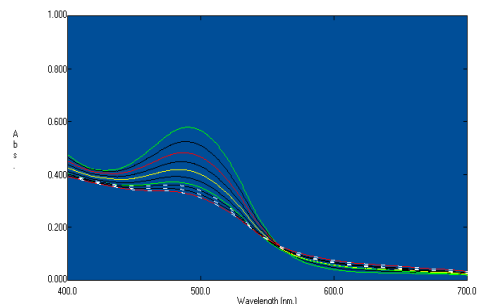


Figure 3. The pattern of degradation of RBO over the course of 60 min (Reference water)

[RBO] was measured at different times and the pseudo first order rate constant (k' , min^{-1}) was obtained from the slope of $\ln A$ versus time plot according to following equation (Eq. 3). Therefore, the initial rate of degradation, R_i is $R_i = -\frac{d[RBO]}{dt} = k' [RBO]_0$ (3)

Result and discussion

The photo degradation of RBO by visible light is quite insignificant (Fig .4) in absence of ZnO. This is why the RBO molecule was degraded by visible light in presence of ZnO. The absorbance of RBO solution changes with time of photolysis and solution is decolorized if it is illuminated for

sufficiently long time in the presence of ZnO [16]. For example, more than 51% color of 5.50×10^{-5} M RBO in 45 mL suspension containing 1.5g ZnO disappears within 60 minutes of illumination. The decrease in disappearance indicates fragmentation of the dye molecules. Disappearance of RBO suggests that the mineralization occurs slowly. Fragmentation of dye in absence of ZnO (Fig .4) and in presence of ZnO is shown below:

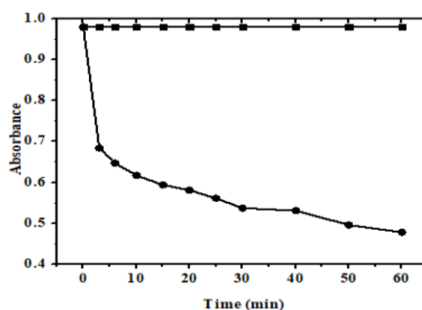


Figure 4. Effect of light on RBO solution in absence (upper plot) and in presence of ZnO (lower plot); RBO = 5.50×10^{-5} M, ZnO = 1.5 g

The effect of mediator concentration

It is important from both the mechanistic and application point of view to investigate the dependence of photo catalytic reaction rate on the concentration of ZnO suspension. The effect of ZnO concentration in the range of 0.5 to 1.5 g on the photodegradation of 45 mL of 5.50×10^{-5} M RBO solution (pH 5.59) was investigated. Fig. 5 shows the variation of absorbance of photo degraded solution with irradiation time. Under this condition the initial rate of degradation of RBO solution increases with the increase in concentration of ZnO suspension (Fig. 5).

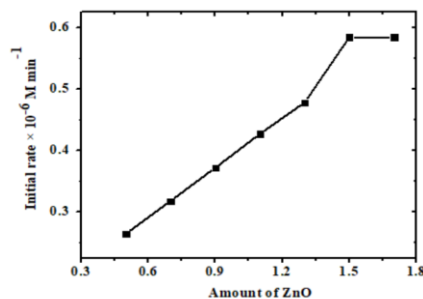


Figure 5. Initial rate of RBO photodegradation vs amount of ZnO used.

Fig. 5 shows increase of the percentage of degradation with the increase of irradiation time for different concentration of ZnO suspension. The highest degradation of RBO solution is observed at 1.50 g/45 mL concentration of suspension. The initial increase of degradation may be due to the increase of total active surface area as the catalysts dosage increases. It facilitates the active sites on catalyst's surface.

The effect of initial pH of the medium

Solution pH is an important parameter in the evaluation of aqueous-phase mediated photo catalytic reaction [17]. Experiments were carried out at various pH values, ranging from 3.50-6.21 using the 5.50×10^{-5} M concentration of RBO in 1.50 g/45 mL concentration of ZnO suspension. The results shown in the Fig. 6 and Fig. 7 indicates that the pH of the medium have no significant influence on the absorbance and photo degradation of RBO, respectively.

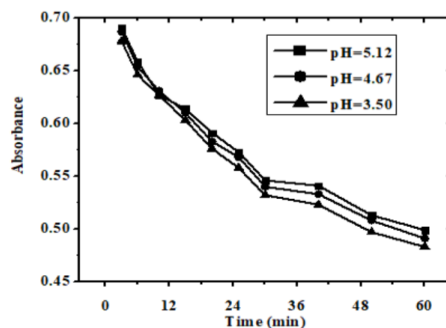


Figure 6. Variation of absorbance of RBO with time for different pH of the solution

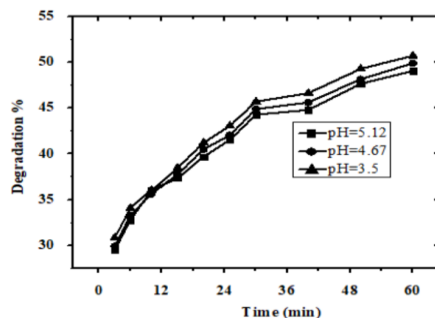


Figure 7. Percentage of degradation of RBO with time for different pH of the solution

The effect of concentration of the dye on its photo degradation

The photo catalytic degradation of RBO was investigated by varying the initial concentration of RBO over the range of 3.00×10^{-5} M to 6.50×10^{-5} M. The percentage of degradation of RBO solution is decreased with increase of RBO concentration. Table 1 shows that in case of 3.00×10^{-5} M of RBO solution 59% and for 6.50×10^{-5} M RBO solutions about 49% degradation is found after 60 minutes. However, as the concentration of RBO is increased, the initial rate of photo degradation increases, as shown in Fig. 8. The reason for increase in initial rate of degradation with concentration might be due to the increased initial adsorption of RBO molecules on catalyst surface. The overall percentage of degradation decreases with increase of initial concentration of RBO (Table 1).

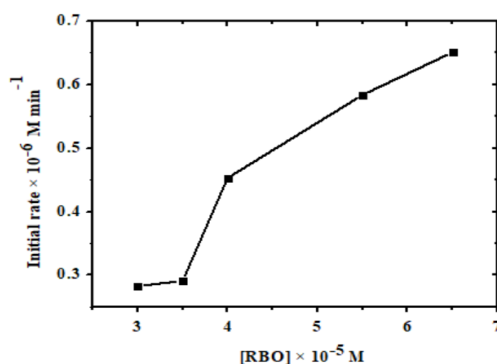


Figure 8. Initial rate of RBO degradation vs RBO concentration

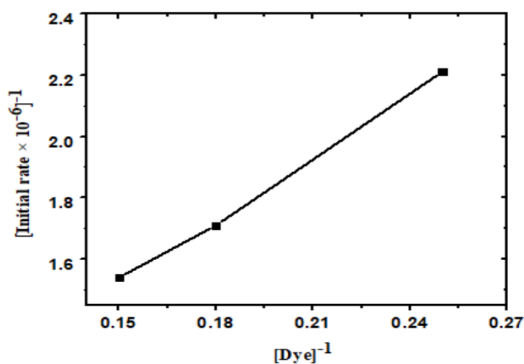


Figure 9. $[\text{Initial rate}]^{-1}$ vs $[\text{DYE}]^{-1}$ plot for photo degradation of RBO in presence of ZnO

This result indicates that degradation efficiency is inversely affected by the RBO concentration. As the RBO concentration increases, the equilibrium adsorption of RBO on the catalyst surface sites increases hence competitive adsorption of $\bullet\text{OH}$ in same sites decreases, meaning a lower rate of formation of $\bullet\text{OH}$ radical which is the principle oxidant necessary for high degradation efficiency. On the other hand, considering the Beer-Lambert law, as the initial RBO concentration increases, the path length of photon entering the solution decreased, resulting in lower photon adsorption on catalyst particles and, consequently, a lower photo degradation rate.

Table 1. Effect of various parameters on degradation of RBO

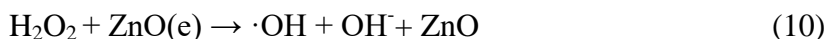
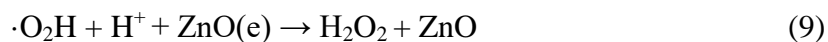
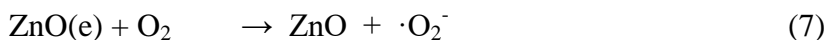
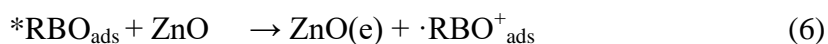
RBO $\times 10^{-5}$ M	Catalyst (g/45 mL)	pH	% Degradation after 60 min
3	1.5	5.59	66.09
3.5			59.46
4			54.27
5.5			51.22
6.5			48.96
5.5	1.5	3.5	49.08
		4.01	49.39
		4.67	49.90
		5.12	50.71
		5.59	51.22
		6.21	44.39

The initial rate (R_i) of mediated photo degradation of the dye or any other organic substrate in aqueous solution matches Langmuir-Hinshelwood kinetic model [18]. This model was applied to photo degradation of RBO as illustrated in Eq. 4, Where R_i is the initial disappearance rate of color of RBO. $[\text{RBO}]_0$ is the initial concentration of RBO. K is the apparent Langmuir adsorption constant or Langmuir-Hinshelwood coefficient of the dye on the oxide mediator. k is the proportionality constant suggesting a measure of the intrinsic reactivity of the photo activated surface with the dye. k is the proportional to the intensity of the light. k is also proportional to the fraction of O_2 absorbed on the surface. Adsorption coefficient for O_2 is noncompetitive as it remains exclusively adsorbed at the preferred sites on the oxide surface.

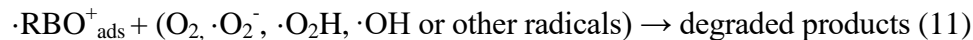
$$\frac{1}{R_i} = \frac{1}{k} + \frac{1}{kK[\text{RBO}]_0} \quad (4)$$

Mechanisms of mediated photo degradation

The visible light cannot excite ZnO (band gap energy 3.2 eV), but it can excite RBO (*RBO) adsorbed on ZnO surface. *RBO can subsequently inject an electron to the conduction band of ZnO. This also happens in the case of TiO₂ when it is used as photo catalyst. Considering the comparable band gap energy, ZnO is likely to behave as TiO₂ and the steps involved in the photo degradation of dyes may be similar. Assuming this, we propose the following steps (Eq. 5 – Eq. 11) that may be involved in the photo degradation of RBO on ZnO [19-21].



Finally,



RBO_{ads} is the dye adsorbed on the surface of ZnO and ZnO indicates an electron trapped in the ZnO matrix. Since photolysis was carried out in an open reactor there was generous involvement of aerial oxygen in the process. The final step (Eq. 11) is the significant step that degrades RBO adsorbed on the surface of the mediator. However, there could be reactions in the bulk producing RBO⁺, which can participate in the reactions with radicals, oxygen, etc.

Conclusion

We have studied ZnO-mediated photodegradation of an industrially important dye, RBO, in presence of visible light. Our thorough investigation has shown that the presence of ZnO in the degradation medium has a tremendous impact on the degradation of RBO, with the percentage of degradation increasing with an increasing amount of ZnO. However, the pH of the medium was found to play no role in changing the

percentage of degradation. Furthermore, the percentage of dye degradation was found to be inversely proportional to the increasing concentration of dye. A detailed mechanism behind the degradation of RBO in presence of ZnO was laid out. Since the dyes, specially, RBO, have many uses in our daily life and they have also been causing serious environmental problems, the implementation of our study can lessen the impact of RBO and other industrially relevant dyes on our environment and water.

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