



PHOTOCATALYTIC DEGRADATION OF REMAZOL BRILLIANT BLUE DYE BY ZnO/UV PROCESS

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ABSTRACT

The photocatalytic degradation of Remazol Brilliant Blue dye (RBB) has been investigated under UV irradiation in aqueous suspension of zinc dioxide under a variety of conditions. The degradation was studied by monitoring the change in dye concentration using UV spectroscopic technique. The effects of key operation parameters such as initial dye concentration, catalyst loading, as well as light intensity on the decolorization extents were studied. The decolorization of the organic molecule followed a pseudo-first-order kinetics.

Key words: Zinc dioxide, Textile dye, Remazol brilliant blue.

INTRODUCTION

Organic dyes are one of the largest groups of pollutants in wastewaters and most of them are produced from the textile industry, which use them in conjunction with a wide range of auxiliary chemicals for various dyeing and finishing process. It is estimated that approximately 12% of dyes are lost annually during manufacturing and the processing operations. The discharge of these colored wastewaters in the ecosystem without treatment can cause serious problems due to the toxicity of some dyes to the aquatic life and damaging to the aesthetic nature of the environment¹.

Several techniques such as activated carbon and other adsorbents²⁻⁶ have been used to solve the problems caused by the toxic substance contained in these colored wastewaters. However, all of these treatments mentioned above have a major disadvantage of simple transferring the pollutants from one phase to another phase rather than destroying them, which consequently leads to secondary pollution. Semiconductor photocatalytic oxidation is

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a famous modern water treatment technology. It has many advantages such as high efficiency, low energy-consumption, moderate condition, extensive applicability and decrease in secondary pollution. It can be used as catalyst and photocatalyst under the ultraviolet radiation ($\lambda \leq 368$ nm) to resist bacteria, eliminate odor, disinfect, refine and protect the environment. Therefore, ZnO will play an important role in the treatment of contamination⁷.

Therefore, many research groups have paid attention to the degradation of these colored wastewaters in recent years⁸⁻¹¹. The photocatalytic mechanism of AOPs employing ZnO was investigated in details elsewhere. Briefly, when aqueous ZnO suspension is irradiated in light energy greater than the band gap energy of the semiconductor ($E_g > 3.2$ eV), conduction band electrons (e^-) and valance band holes (h^+) are generated. If charge separation is maintained, the electrons and holes may migrate to the catalyst surface where they participate in redox reaction with the adsorbed species. The photogenerated electrons react with the adsorbed molecule O_2 on the Zn(II)-site and reduce it to superoxide radical anion ($O_2^{\cdot-}$), while the photogenerated holes can oxidize the H_2O or OH^- ions adsorbed at the ZnO surface to OH^{\cdot} radicals. These radicals together with other highly oxidant species (e.g. peroxide radicals) will act as strong oxidizing agents that can easily attack the adsorbed organic molecules or these located close to the surface of the catalyst, thus resulting in their complete degradation into small inorganic species. The dye derivative Remazol Brilliant Blue has been widely used in textile industry and its structure is presented in Fig. 1. To the best of our knowledge few efforts have been made to investigate the photocatalytic degradation of this dye. Therefore, a detailed investigation on the photodegradation of Remazol Brilliant Blue (RBB) was carried out in the present study.

In the present work, we report the photocatalytic degradation of RBB dye with ZnO and the effect of operational parameters such as catalyst loading, the initial dye concentration, and light intensity on the decolorization were studied to optimize the process for maximum degradation.

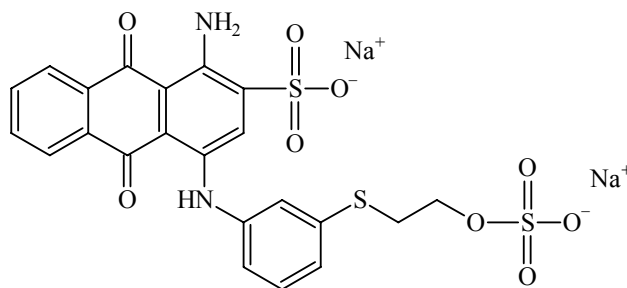


Fig. 1: Chemical structure of remazol brilliant blue dye

EXPERIMENTAL

Materials

Commercial ZnO powder were purchased from (Sigma-Aldrich, Germany). Remazol Brilliant Blue dye (RBB) was supported by Hilla Company of textile dyes, Iraq. All chemicals used in this study were analytical grade and used directly without further purification.

Photocatalytic experiments

The photocatalytic activity of the ZnO photocatalyst was evaluated by the degradation of RBB dye wastewater.

All experiments were carried out in a photo-reaction vessel, with 250 mL of total capacity. A 125 W high-pressure mercury lamp with the strongest emission at 365 nm was used as light source. The beakers were put under the ultraviolet light maintaining the distance between the light source and the surface of the solution controlled by using UVA-meter (Dr. Honle, Germany). Prior to each test, the lamp was turned on and warm up for about 10 min in order to get a constant output. Batch tests were performed as the following procedure, 0.3 g ZnO photocatalyst was added into 200 mL dyes solutions, the mixture was stirred in dark for 30 min to allow the physical adsorption of dyes molecules on catalyst particles reaching the equilibrium.

Subsequently, the mixture was poured into the photoreactor and began the photocatalytic degradation tests. The reaction solution was mixed by an air diffuser, which was placed at the bottom of the reactor to uniformly disperse air into the solution with a flow rate of 0.1 mL/min.

Samples were collected at regular intervals and were immediately centrifuged to remove particles for analysis. The concentration of RBB was determined by measuring the absorption intensity at its maximum absorbance wavelength of $\lambda = 620$ nm, by using a UV-Vis spectrophotometer (1650 Shimadzu, Japan) with a 1 cm path length spectrometric quartz cell, and then calculated from calibration curve.

Effect of various operational parameters such as amount of catalyst ($0.5\text{--}2.5\text{ g L}^{-1}$), light intensity ($1.92\text{--}6.64\text{ mW cm}^{-2}$), and concentration of dye ($100\text{--}400\text{ mg L}^{-1}$) on the photodegradation efficiency was studied. The percentage removal of photocatalytic

degradation of RBB dye and apparent first order rate constant were calculated using the following relationships.

$$\text{PDE (\%)} = 100 \times (C_0 - C_t)/C_0 \quad \dots(1)$$

$$\left(\frac{C_t}{C_0} \right) = e^{-kt} \quad \dots(2)$$

Where, C_0 and C_t are the initial and photolyzed concentration (mg/L), respectively, PDE (photocatalytic degradation efficiency), t is time of irradiation (min.) and k is the apparent first order rate constant (min^{-1}).

RESULTS AND DISCUSSION

Effect of mass dosage

To investigate the effect of catalyst loading on the final decolorization efficiency, a series of experiments were carried out by varying the catalyst from 0.5 to 2.5 g/L in the solution with 20 mg/L dye concentration, reaction temperature = 30°C, time = 1 hr. The profile behaviour of photocatalytic degradation is illustrated in Fig. 2.

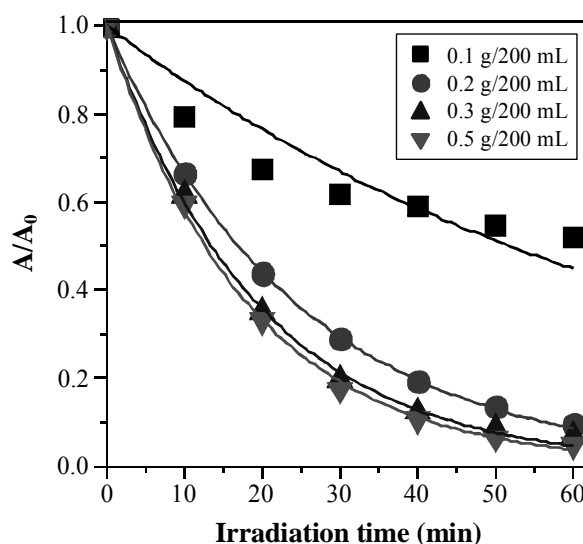


Fig. 2: Photocatalytic degradation of RBB dye at different mass dosage. Experimental Conditions: Initial conc. 400 mg.L⁻¹, Temp. 30°C, and L.I. 2.42 mW.cm⁻²

Fig. 3 shows the relationship between the catalyst loading and the degradation rate, and the photocatalytic degradation efficiency of the dye, respectively. From Fig. 3, it is clear that when the amount of the catalyst increases, the degradation rate goes up first and then keeps unchangeable in certain scale, but when the amount exceeds 1.5 g/L, the degradation rate not change. It is probably due to the aggregation of the free catalyst particles and the “screening” effect¹².

The result is consistent with many other researches that there are an optimal amount of catalyst loading¹³. When the concentration of the catalyst is below the optimal value, the effective surface of the catalyst and the absorption of the light are the main factors, which determine the photocatalytic degradation rate^{13,14}.

The initial increase in rate of dye degradation with increase in amount of catalyst is due to increase in number of active sites on the surface of photocatalyst. Due to this, there is an increase in number of photogenerated electron-hole pair, which results in an increase in number of hydroxyl radicals responsible for dye degradation¹⁴⁻¹⁶.

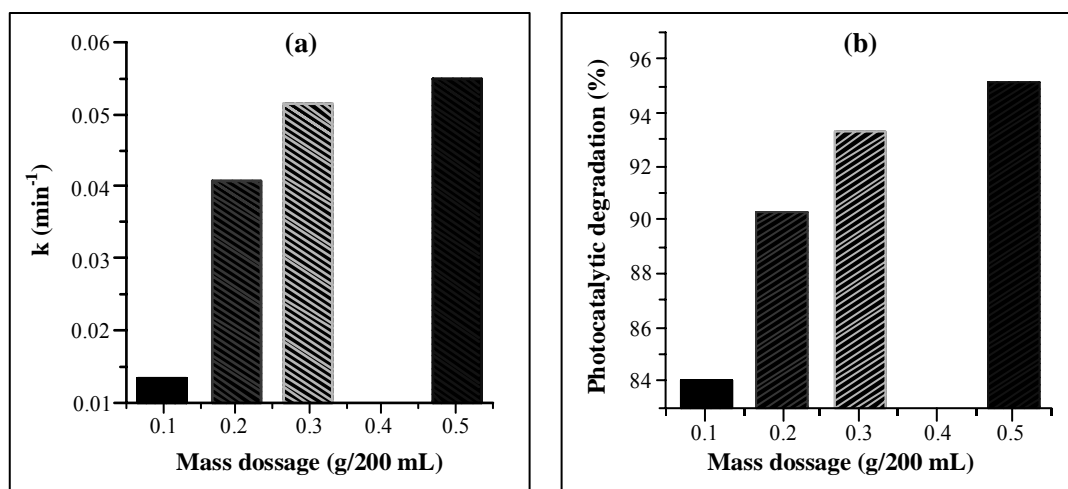


Fig. 3: Remazol brilliant blue RBB: (a) degradation rate constant (b) photocatalytic degradation efficiency under different catalyst loading. Experimental conditions: Initial conc. 400 mg.L⁻¹, Temp. 30°C, and L. I. 2.42 mW.cm⁻²

Effect of concentration of dye

The initial concentration of dye solution plays a pivotal role in deciding the rate of dye degradation^{15,17-19}. In present studies, the initial concentration of dye was varied

100 mg.L⁻¹ to 400 mg.L⁻¹ in the steps of 50 at a constant catalyst loading of 1.5 g/L. Fig. 4 shows the time dependence of photocatalytic degradation of RBB dye under different concentrations.

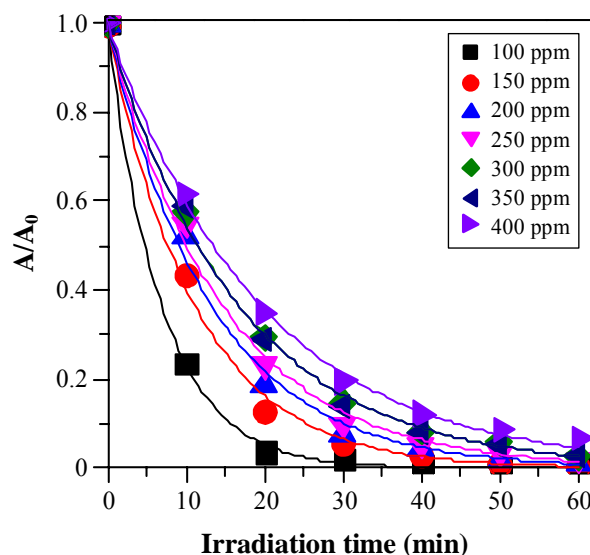


Fig. 4: Photocatalytic degradation of RBB dye at different initial concentration.
Experimental conditions: mass amount 1.5 g.L⁻¹, Temp. 30°C,
and L.I. 2.42 mW.cm⁻²

Fig. 5 shows the rate of photocatalytic degradation of RBB dye, it is clear from Fig. 5a that when the initial concentration of RBB dye increased the rate of photocatalytic degradation decreased, in vise versa of Fig. 5b that shows demonstrates the effect of initial dye concentration on the photocatalytic degradation efficiency by varying the initial concentration from 100 to 400 mg/L with the constant ZnO catalyst loading (1.5 g.L⁻¹) and pH values. The results reveal that the initial dye concentration influences the degradation efficiency severely. With the increase of initial dye concentration, the degradation efficiency decreases remarkably, especially when the initial dye concentration varies from 300 to 400 mg/L. The negative effects of the initial dye concentration are ascribed to the competence between dye and OH⁻ ion adsorption on the surface of catalyst. The adsorption of dye depresses the OH⁻ ion adsorption, which results in the reduction on the formation of hydroxyl radicals. At the same time, as the initial dye concentration increases, the path length of photons entering the solution decreases. Hence, in the solution with constant catalyst concentration, the formation of hydroxyl radicals that can attack the pollutants decreases, thus leading to the lower decolorization efficiency^{20,21}.

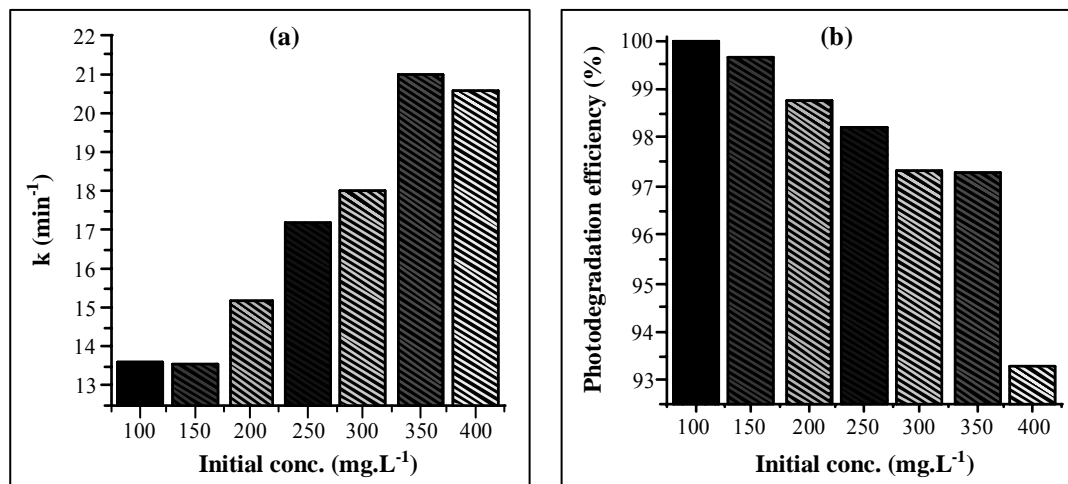


Fig. 5: Effect of initial dye concentration (a) rate constant, (b) photocatalytic degradation efficiency on the photocatalytic degradation of RBB dye. Experimental conditions: mass amount 1.5 g.L⁻¹, Temp. 30°C, and L.I. 2.42 mW.cm⁻²

Light intensity and wavelength

Light intensity determines the extent of light absorption by the semiconductor catalyst at a given wavelength. The rate of initiation of photocatalysis, electron-hole formation in the photochemical reaction is strongly dependent on the light intensity²².

Light intensity distribution within the reactor invariably determines the overall pollutant conversion and degradation efficiency²³. Consequently, the dependency of pollutant degradation rate on the light intensity has been studied in numerous investigations of various organic pollutants. While in some cases the reaction rate exhibited a square root dependency on the light intensity, others observed a linear relationship between the two variables²⁴.

Experiments were conducted by varying I from 1.92 to 6.64 mW cm⁻². The time dependence of the photocatalytic degradation on light intensity was shown in Fig. 6. The rate of photocatalytic degradation and the photocatalytic degradation efficiency were illustrated in Fig. 7. It is clear from results in Fig. 7 that the rate of photocatalytic degradation and photodegradation efficiency increased with increasing is increasing with increasing UV light intensity as more radiation is available to excite the catalyst and hence more charge carriers are generated resulting in a higher rate of photocatalytic removal.

However, the relation between the light intensity and the photocatalytic removal was

found to be nonlinear due to the fact that at high photon flux the recombination rate of the charge carriers also increases as compared with a lower photon flux²⁵.

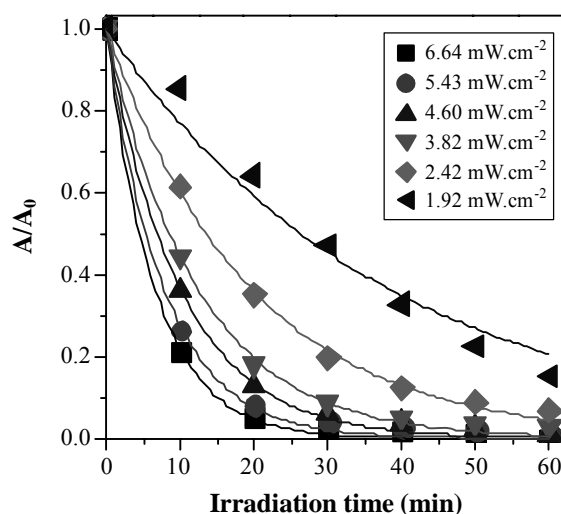


Fig. 6: Photocatalytic degradation of RBB dye at different light intensities.
Experimental conditions: Initial conc. 400 mg.L⁻¹, Temp. 30°C,
and mass amount 1.5 g.L⁻¹

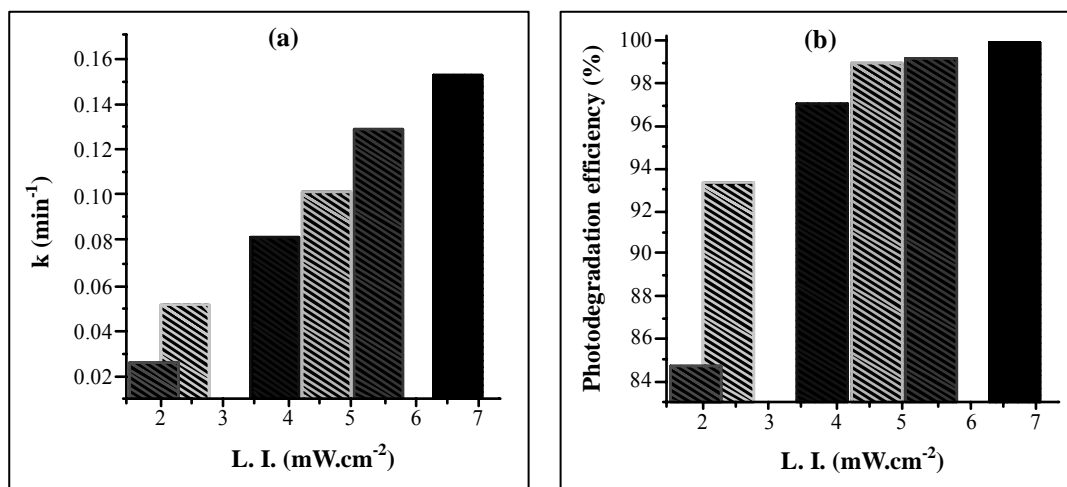
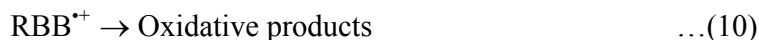
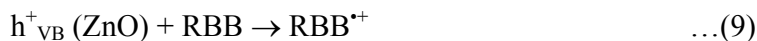
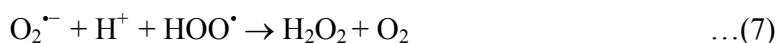
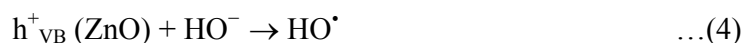
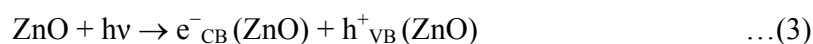


Fig. 7: Effect of light intensity (a) rate constant, (b) photocatalytic degradation efficiency on the photocatalytic degradation of RBB dye.

Experimental conditions: mass amount 1.5 g.L⁻¹, Temp. 30°C,
and initial concentration 400 mg.L⁻¹

Mechanism of dye degradation

In a photodegradation process, when ZnO is irradiated by light with energy greater than or equal to its band gap, an electron in the valence band can be excited to the conduction band, with the simultaneous generation of hole in the valence band (Eq. 3). These photogenerated electron-hole pair can interact separately with other molecules. The holes in the valence band can react with water on the surface of ZnO to form highly reactive hydroxyl radicals, while electrons are accepted by adsorbed oxygen to form superoxide radical anion. This radical anion further forms hydroxyl radicals which is a powerful oxidizing agent and attacks the dye molecule to give the oxidized product. The reactions are summarized in Eqs. (3-10)^{15,16}.



CONCLUSION

The obtained results show that Remazol Brilliant Blue can be easily degraded by a ZnO assisted process in aqueous dispersions under UV irradiation. The photodegradation of the dye follows first order kinetics and parameters like the ZnO concentration, light intensity and initial dye concentration affect the photodegradation effect. The results indicated that the catalyst loading, light intensity and the initial dye concentration affected the degradation efficiency of ZnO powders obviously. We learned that the photodegradation efficiency is enhanced with the increase of catalyst loading and the reverse effect is obtained with the increase of initial dye concentration in our experiments. The photocatalytic decomposition of remazol brilliant blue dye was most efficient in the solution at lower initial concentration, and higher light intensity.

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