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RESEARCH ARTICLE

Photocatalytic Degradation of Textile Dye Cristal Violet Wastewater using Zinc Oxide as a Model of Pharmaceutical Threat Reductions

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Abstract

The photo catalytic degradation of Cristal Violet dye (CV) 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 decolonization extents were studied. And found 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 photo catalyst the rate of photo catalytic degradation and photo degradation efficiency increased with increasing is increasing with increasing UV light intensity.

Keywords: *Photcatalytic; Cristal Violet dye, zinc oxide*

Introduction

The photo catalytic reactions are carried out in the presence of light and semiconductor. These reactions have been classified into two categories depending upon the nature of reactants and semiconductors, homogeneous and heterogeneous. Homogeneous photo catalysis and the generation of active species in situ by light is potentially interesting [1].The attention has been mainly devoted to the chemistry originated when light observed by a photo redox process has grown enormously in recent years [2] and several physical methods are being adopted for the characterization of the catalyst films, particles and for the study of their reactions [3].

Heterogeneous photo catalysis by semiconductor through particulate systems has become an exciting and rapidly growing area of research in the last few years[4] In the last decade various oxide semiconductors [5] have been used as catalyst, phosphor, gas sensor, photo catalyst, UV-photo protector, visitor or in dye-sensitized solar cells [6]The field of applications is determined by the electrical, optical and structural properties of the semiconductors.

Among them, ZnO offers some unique optoelectronic properties due to its wide band gap of 3.3 eV and large excitonic binding energy of 60 meV. Due to the special optical properties, high transparencies in the visible domain coupled with high absorbance of the UV radiation, ZnO has been toughly investigated as a coating material, from paints to sunscreens and fabric coating [7] Zinc oxide semiconductor as a catalyst has the ability to remove from the wastewater a number of pollutants such as pesticides[8].

If the semiconductor zinc oxide irradiated by UV lamp, the electrons will promote from valance band to conduction band, producing electrons in conduction band undergo photo reduction will leave a positive hole in valance band inter photo oxidation processes

Materials and Methods

Materials

Commercial ZnO powders were purchased from (sigma-aldrich, Germany).

Remazol crystal violet dye (CV) was supported by Hilla Company of textile dyes/ Iraq.

All chemicals used in this study were analytical grade and used directly without further purification.

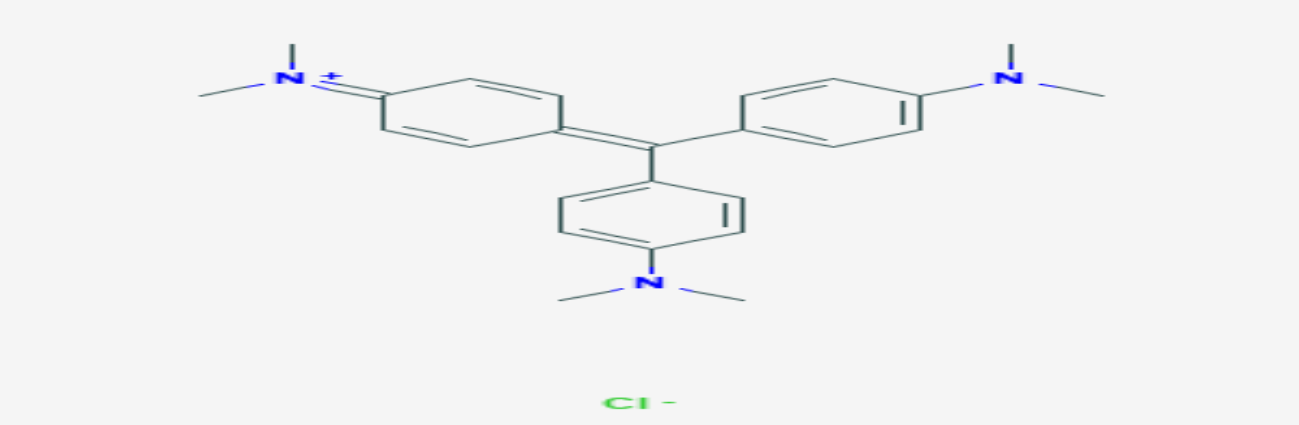

Fig. 1: Chemical structure of Cristal Violet (CV)

Photcatalytic Experiments

The photo catalytic activity of the ZnO photo catalyst was evaluated by the degradation of CV dye wastewater. All experiments were carried out in a photo-reaction vessel, with 200 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 photo catalyst 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 photo reactor and began the photo catalytic 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 CV was determined by measuring the absorption intensity at its maximum absorbance wavelength of λ CV = 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 (0.5–5.0 g L^{-1}), light intensity (2.05 – 7.90 mw cm^{-2}), and concentration of dye (10–100 mgL^{-1}) on the photo degradation efficiency was studied. The percentage removal of photo catalytic degradation of CV dye and apparent first order rate constant were calculated using the following relationships

$$PDE\,(\%) = 100 \times (C_0 - C_t)/C_0 \qquad (1)$$

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

Where, C0 and C_t are the initial and photolyzed concentration (mg/L), respectively, PDE (photo catalytic 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 decolonization efficiency, a series of experiments were carried out by varying the catalyst from 0.5 to 5.0 g/L in the solution with 50 mg/L dye concentration, reaction temperature = 30 °C, time = 2 h. . The profile

behavior of photo catalytic degradation is illustrated in Fig. 2.

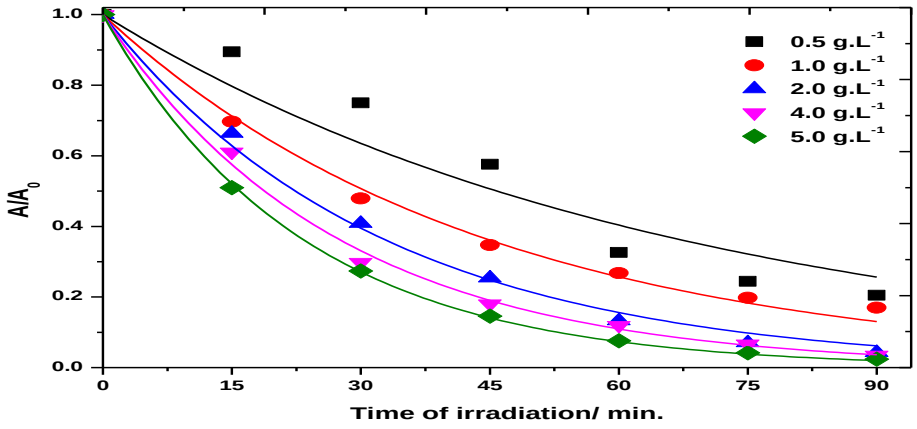

Figure.2: Photo catalytic degradation of CV dye at different mass dosage. Experimental Conditions: Initial conc. 50 mg.L^{-1}, Temp. 30 ^{o}C, and L.I. 2.42 mW.cm^{-2}

Fig. 3 shows the relationship between the catalyst loading and the degradation rate, and the photo catalytic 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 1.0 g/L, the degradation rate not change. It is probably due to the aggregation of the free catalyst particles and the "screening" effect [12]. The result is consistent with many other researches that there are an optimal amount of catalyst loading [13].

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 photo catalytic 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 photo generated electron–hole pair, which results in an increase in number of hydroxyl radicals responsible for dye degradation [14-16].

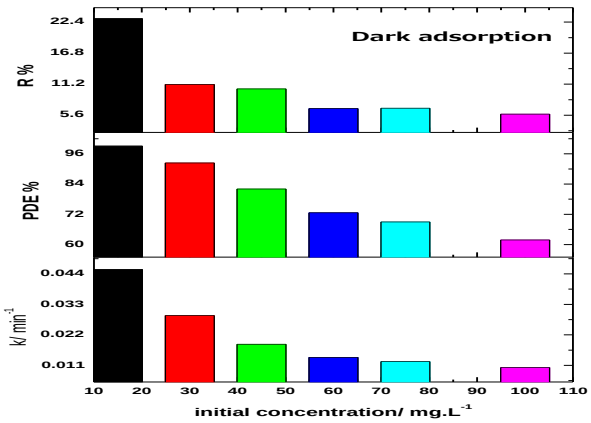

Figure 3: CV: a) removal adsorption, b) photocatalytic degradation efficiency a) degradation rate constant under different catalyst loading. Experimental Conditions: Initial conc. 50 mg.L^{-1}, Temp. 30 ^{o}C, and L.I. 2.42 mW.cm^{-2}

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 15 mg. L^{-1} to 50 mg.L^{-1} in the steps of 50 at a constant catalyst loading of 1.0 g/L. Fig. 4

shows the time dependence of photo catalytic degradation of CV dye under different concentrations.

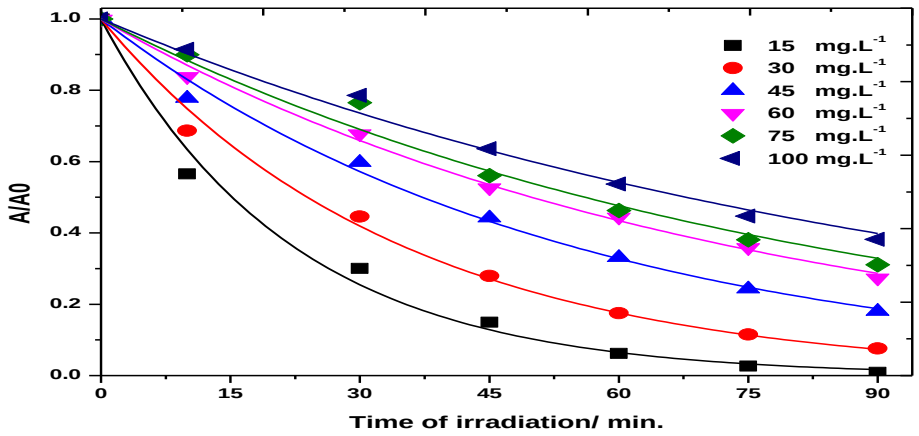

Figure4: Photo catalytic degradation of CV dye at different initial concentration. Experimental Conditions: mass amount 1.0 g.L^{-1}, Temp. 30^{o}C, and L.I. 2.42 mW.cm^{2}

Fig. 5 shows the rate of photcatalytic degradation of CV dye, it is clear from Fig. 8a that when the initial concentration of CV dye increased the rate of photo catalytic degradation decreased, in vise versa of Fig. 8b that shows demonstrates the effect of initial dye concentration on the photo catalytic degradation efficiency by varying the initial concentration from 15 to 100 mg/L with the constant ZnO catalyst loading (1.0 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 60 to 100 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 decolonization efficiency [20, 21].

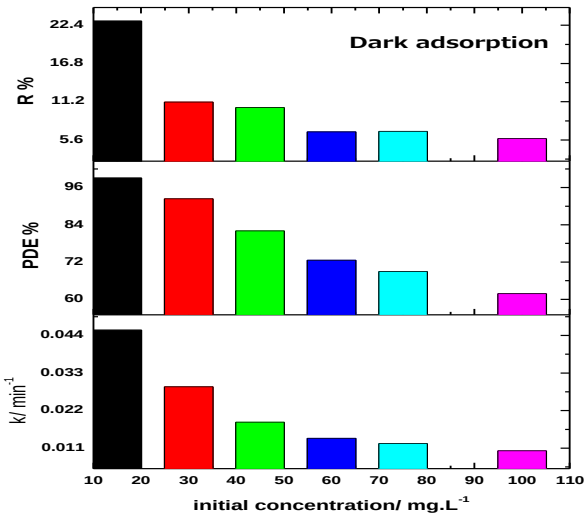

Figure 5: Effect of initial dye concentration a) rate constant, b) photo catalytic degradation efficiency on the photo catalytic degradation of CV dye. Experimental Conditions: mass amount 1.0 g.L^{-1}, Temp. 30 ^{o}C, and L.I. 2.42 mW.cm^{-2}

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 photo catalysis, electron–hole formation in the photochemical reaction is strongly dependent on the light intensity [22]. Light intensity distribution within the reactor invariably determines the overall pollutant conversion and degradation efficiency [23]. 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 variables [24]. Experiments were conducted by varying I from 7.90 to 2.05 mW cm^{-2} , the time dependence of the photo catalytic degradation on light intensity was shown in Fig. 6, the rate of photo catalytic degradation and the photo catalytic degradation efficiency were illustrated in Fig. 7. it was clear from results in Fig. 7 the rate of photo catalytic degradation and photo degradation 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 photo catalytic removal. however, the relation between the light intensity and the photo catalytic 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 flux [25].

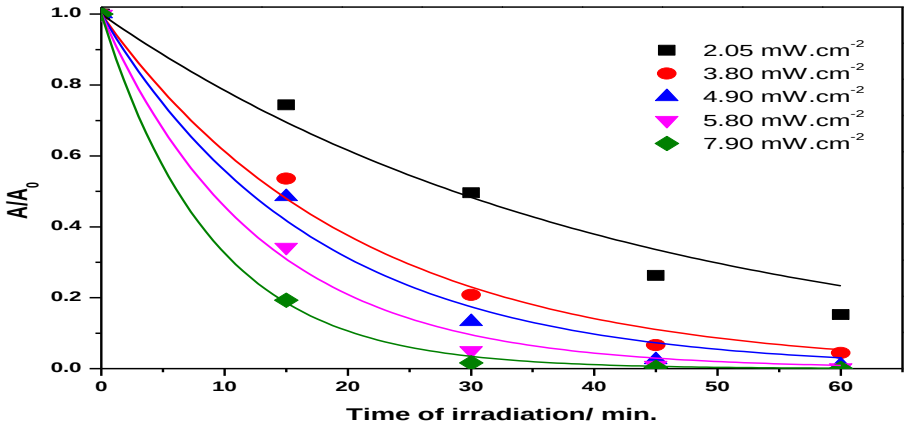

Figure 6: Photo catalytic degradation of CV dye at different light intensities. Experimental Conditions: Initial conc. 50 mg.L^{-1}, Temp. 30 °C, and mass amount 1.0 g.L^{-1}

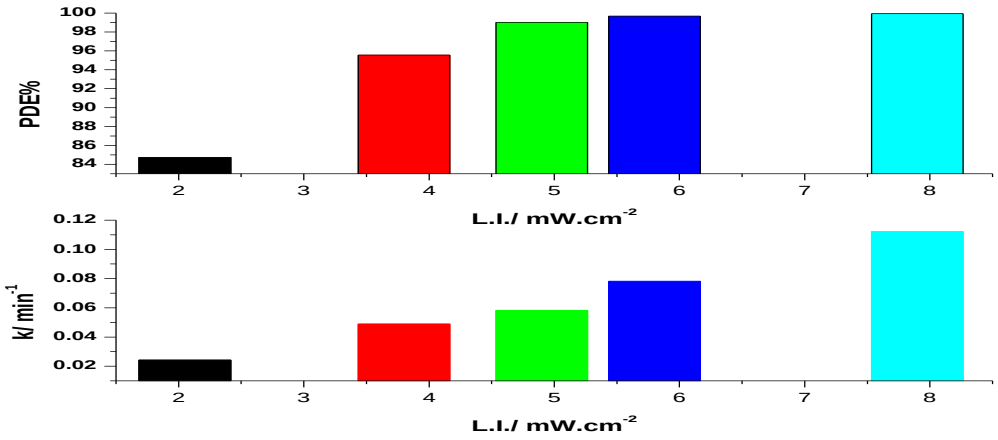

Figure 7: Effect of light intensity a) rate constant, b) photo catalytic degradation efficiency on the photo catalytic degradation of CV dye. Experimental Conditions: mass amount 1.0 g.L^{-1}, Temp. 30 °C, and initial concentration 50 mg.L^{-1}

Conclusions

The obtained results show that Crystal Violet can be easily degraded by a ZnO assisted process in aqueous dispersions under UV irradiation. The photo degradation of the dye follows first order kinetics and parameters like the ZnO concentration, light intensity and initial dye concentration affect the photo degradation 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 photo degradation 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 photo catalytic decomposition of CV dye was most efficient in the solution at lower initial concentration, and higher light intensity.

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