

PHOTOCATALYTIC DEGRADATION OF PROCIAN YELLOW IN AQUEOUS SUSPENSION OF ZnO BY VISIBLE LIGHT

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Abstract

The present work focused on the detailed investigation of photocatalytic degradation of Procion Yellow (PY). The degradation has been carried out in aqueous heterogeneous medium containing ZnO as photocatalyst in a batch reactor. The disappearance of color of the dye, monitored spectrophotometrically. Degradation experiments were carried out to optimize the amount of catalyst, effect of dye concentration, effect of pH etc. The degradation rate was strongly influenced by the initial concentrations of dye and catalyst. More than 91% color of 5.0×10^{-5} M PY in 50mL suspension containing 0.9 g ZnO vanishes within an hour of illumination. ZnO has been found experimentally to be a highly efficient photocatalyst for the degradation of Procion Yellow (PY) dye and hence there is a great potential in the treatment of organic pollutants such as dyes.

Keywords and phrases: Procion yellow, Photocatalytic degradation, ZnO mediated degradation, Langmuir-Hinshelwood model

Introduction

A dye can generally be described as a colored substance that has an affinity to the substrate to which it is being applied. Dyes are now classified according to their chemical and dyeing properties however, the release of these dye compounds into the environment can be detrimental, not only because of their color, but also because some dyes and their breakdown products are toxic. About one-half of the dyes used in textile industry include acid, reactive, azo and direct dye.

Versatile classes of colored compounds are azo dyes that have extensively been used in industry for applications such as textiles, foodstuffs, paper, leathers, ball-point pen factories, additives and analytical chemistry (Dakiky, 2000). During dye production and textile manufacturing processes, a large quantity of waste water containing dye and dye intermediates with intensive color and toxicity are introduced into the aquatic environment (Brown, 1993). In such cases, removing color from wastes is urgent, because the presence of even small amounts of dyes (below 1 ppm) is clearly visible and influences water environment considerably. It is necessary to find an effective method of wastewater treatment in order to remove color from effluents. Dyes can be removed from textile wastewaters through conventional treatment such as coagulation, adsorption on activated carbon, ultra filtration and reverse osmosis. However, these processes are considered as nondestructive since they simply transfer the dye from liquid to solid wastes. Consequently, the regeneration of the adsorbent material and post-treatment of solid wastes, which are expensive operations, are needed (Kang, 1997; Sheng, 1999).

Advanced oxidation processes (AOPs) are alternative techniques based on the intermediary of hydroxyl and other radicals to oxidize recalcitrant, toxic and non-biodegradable compounds to various by products and eventually to inert end-products. These processes generally include UV/H₂O₂, UV/O₃ or UV/Fenton's reagent, chlorination, bleaching, photocatalytic oxidation and wet-air oxidation (Oussi, 1997; Robinson, 2001) for the oxidative degradation of contaminants. Among the various AOPs, semiconductor-mediated photocatalysis has been given great credit over the past few years due to its potential to destroy a wide range of organic and inorganic pollutants at ambient temperatures and pressures, with no harmful by-products (Fox, 1993). The most commonly studied catalysts are TiO₂, ZnO, Fe₂O₃, ZnS, WO₃ and CdS. Several works have shown a superior degradation efficiency of photocatalytic systems mediated by ZnO (Palominos, 2009; Sakthivel, 2003). In general, the photo-activated chemical reactions are characterized by a free radical mechanism initiated by the interaction of photons of a proper energy level with the molecules of chemical species present in the solution, with or without the presence of the catalyst. As part of our goal of photodegradation of organic pollutants mediated by various semiconducting oxides, here we report one such study using ZnO, having the same band gap energy as that of P25 TiO₂, to degrade Procian Yellow (Fig. 1) by visible light.

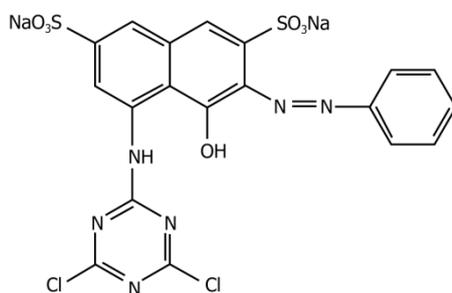


Fig. 1: The structure of Procian Yellow (PY)

Materials and Methods

Materials: Procian Yellow (PY) was obtained from local dye suppliers and ZnO was used as received without further purification; other chemicals were of analytical grade. Deionized water was used in making solutions. All the experiments were performed at the usual pH~6.10 of PY solution.

Analysis of PY: UV-1601PC spectrophotometer (Shimadzu) was used for spectrophotometric analysis of PY solutions. PY in aqueous solution has only one peak in the visible region ($\lambda_{\text{max}} = 428 \text{ nm}$) and it obeys Beer-Lambert law ($\epsilon = 8.11 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 26°C) within the concentration range used in this study. Solutions containing photocatalyst suspensions were adequately centrifuged before measuring the absorbance (A).

Photochemical reactor and light source: A Beaker (inside diameter 3.84 cm and height 5.36 cm), made of Pyrex glass, was used as the reactor for all experiments. Light from the 10W Fluorescent lamp was focused on the reactor surface horizontally which was arranged in a wooden box with Al-foil inside lining. The reactor was placed on a magnetically stirred plate and the distance of the solution surface from the lower part of

the lamp was fixed. The Total system was enclosed in a wooden box called lamp house. A thermometer was installed inside the lamp-house to serve the purpose of observing the inside temperature. The temperature inside the box remained at $27 \pm 1^\circ\text{C}$ during the experiment. A fixed volume of suspension was taken into the reactor, which was maintained at a 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.

Photodegradation: A typical experiment was carried out in the following way: 0.90 g finely ground ZnO powder was taken in a beaker. 50.0 mL PY of a 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 tubes at every five minutes and centrifuged. The clear solutions from the centrifuge tubes were taken to measure the concentration spectrophotometrically. Photodegradation of dyes was studied with different initial concentration of RNB, with different amount of ZnO at the usual pH (~6.10) of the solution and different initial pH of the medium. Fig. 2 shows the pattern of the change of absorbance with time. The change in absorbance represents decolorization of the dye.

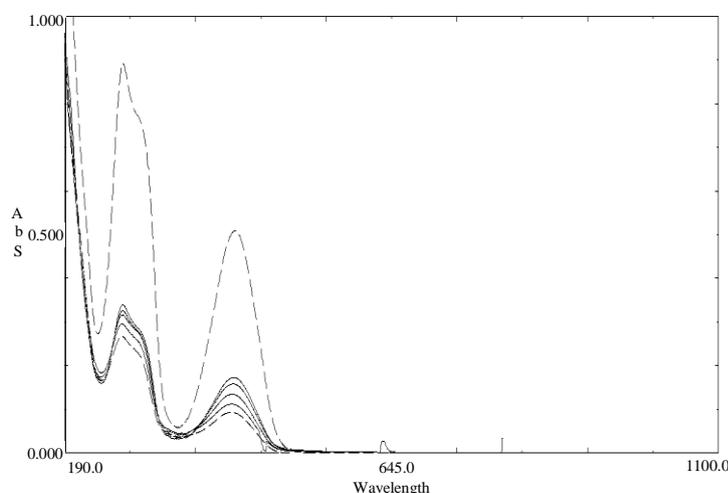


Fig. 2: The pattern of degradation of PY (Reference water)

Measurement of initial rate: The concentration of PY at zero time, $[\text{PY}]_0$, was determined by measuring the absorbance (A) of this solution. The solution is then illuminated and the samples were withdrawn at regular intervals for measuring the absorbance. $\ln A$ was plotted against time and the slope of the straight line drawn through the first few points was found out. The slope is the apparent rate constant (k'). Thus, the initial rate of degradation, R_i , is

$$R_i = k'[\text{PY}]_0 \quad (1)$$

Results and Discussion

In absence of ZnO, when PY solution was illuminated under adequate experimental conditions the change in absorbance was quite insignificant (Fig.3). However, the

significant amount of absorbance change was obtained when PY solution was illuminated in the presence of ZnO.

The PY solution can completely be decolorized if it is illuminated for sufficiently long time in the presence of ZnO. For an example, more than 91% color of 5.0×10^{-5} M PY in 50.0 mL suspension containing 0.90g ZnO disappears within 60 minutes of illumination. The decrease in the absorbance does not indicate that mineralization occurs immediately. Mineralization means the formation of CO_2 , H_2O and other inorganic anions. The heteroatoms present in the organic substrate are generally converted to anions in which they are in their highest oxidation states. Fragmentation of the dye molecules precedes mineralization and at the onset of fragmentation, decolourization of the solution begins. Accordingly, the rate of change of absorbance with time at the beginning of photolysis will be a measure of the initial rate of photodegradation.

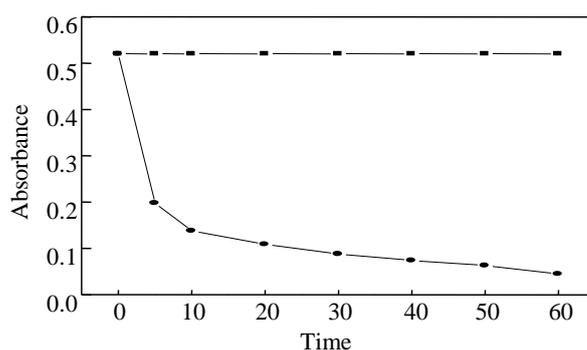


Fig. 3: Effect of light on PY solution on absence (upper plot) and in presence of ZnO (lower plot) [PY] = 5.0×10^{-5} M, ZnO = 0.90g

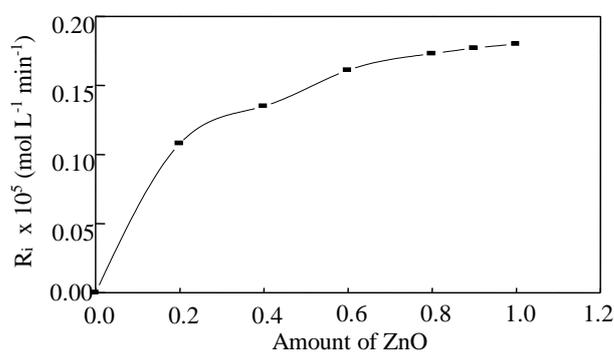


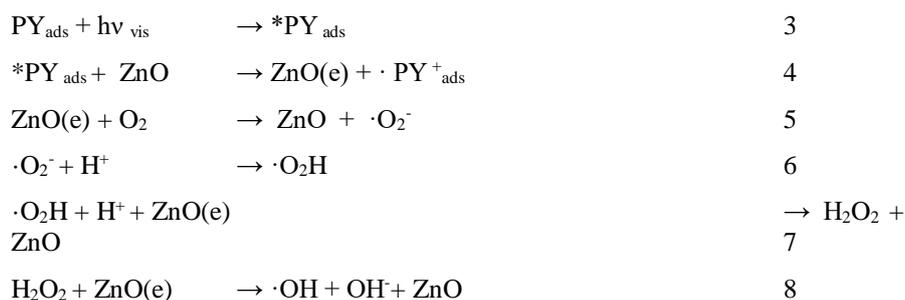
Fig. 4: Initial rate vs amount of ZnO

A plot of R_i with a fixed initial concentration of PY, $[\text{PY}]_0$ (5.0×10^{-5} M) against the amount of ZnO is shown in Fig.4. With the increase in the amount of ZnO, the initial rate of degradation of the dye increases. The percent degradation also increases with the increase of irradiation time for different concentration of ZnO suspension. The initial increase of degradation may be due to the increase of total active surface area as the

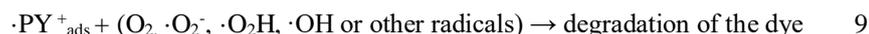
catalysts dosage increases. It facilitates the active sites on catalyst surface. So the increased amount of ZnO accommodates more dye molecules on its surface and the adsorbed dye molecules predominantly undergo fragmentation in the presence of light.

The mechanism of ZnO-photocatalyzed reactions has been a subject of extensive research (Domenech, 1986). It has been widely recognized that hydroxyl radical $\cdot\text{OH}$ acts as active substance for the mineralization of organic compounds.

ZnO (band gap energy 3.2 eV) may not be excited by visible light, but dye molecules, PY adsorbed on ZnO surface and gets excited (*PY). The excited dye, *PY can subsequently inject an electron to the conduction band of ZnO. Assuming this, we suggest the following steps that may involve for the photodegradation of PY on ZnO as has been previously done (Mahmood, 2003).



Finally,



PY_{ads} is the dye adsorbed on the surface of ZnO, $\text{ZnO}(e)$ indicates an electron trapped in the ZnO particle. Since photolysis was carried out in an open reactor there was generous involvement of aerial oxygen in the process. The step 9 is the significant step that degrades PY adsorbed on the surface of the mediator. However, there could be reactions in the bulk producing PY^+ , which can participate in the reactions with radicals, oxygen, etc.

Solution pH is an important parameter in the evaluation of aqueous-phase mediated photocatalytic reaction. Experiments were carried out at different pH values, ranging from 2.05-9.05 using 5.00×10^{-5} M concentration of PY in 0.9 g/50mL concentration of ZnO suspension. The results indicate, the pH of the medium does not have spectacular influence on the photodegradation.

A plot of R_i for different initial concentrations, $[\text{PY}]_0$, with a fixed quantity of ZnO (0.9g/50.0mL solution) against these concentrations is shown in Fig.5. The increased concentration of PY increases the initial rate of photodegradation. The percent degradation of PY solution was increasing upto the concentration of $[\text{PY}]$ was 7.1×10^{-5} M however decreases with further increase of PY concentration Fig. 6. The reason for increase in % of degradation with concentration might be due to the increased initial adsorption of PY molecules on catalyst surface.

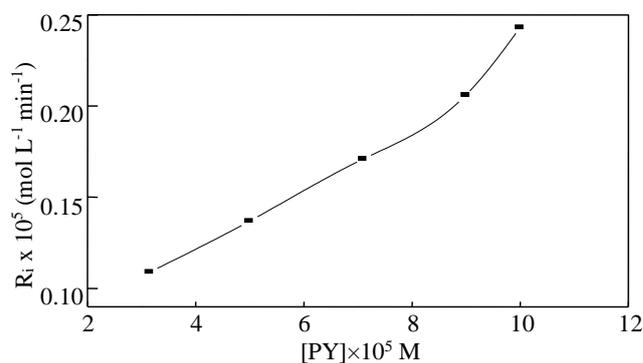


Fig. 5: Initial rate vs PY concentration

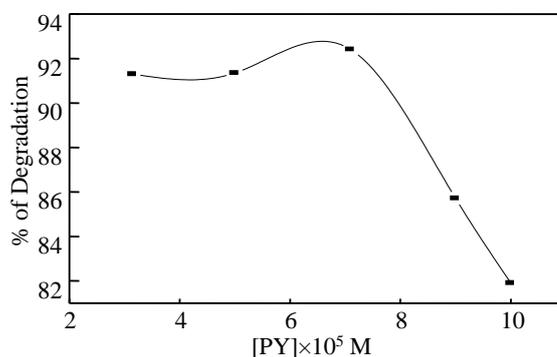


Fig. 6: % of degradation vs PY concentration

With further increase of PY concentration, the equilibrium adsorption of PY on the catalyst surface sites increased hence competitive adsorption of $\cdot\text{OH}$ in same sites decreased, meaning a lower rate of formation of $\cdot\text{OH}$ radical which is the principle oxidant necessary for high degradation efficiency. On the other hand, considering the Beer-Lambert law, as the initial PY concentration increased, the path length of photon entering the solution decreased, resulting in lower photon adsorption on catalyst particles and, consequently, a lower photodegradation rate.

The initial rate (R_i) of mediated photodegradation of substrates in aqueous solution matches Langmuir-Hinshelwood kinetic model. This model has been applied to photodegradation of PY as

$$\frac{1}{R_i} = \frac{1}{k_{LH}} + \frac{1}{k_{LH} K_{LH} [PY]_0} \quad (2)$$

Where R_i is the initial disappearance rate of color of PY. $[dye]_0$ is the initial concentration of PY. K_{LH} is the Langmuir adsorption coefficient of the PY on the ZnO surface. k_{LH} is the proportionality constant suggesting a measure of the intrinsic reactivity of the photoactivated surface with the dye. The Langmuir-Hinshelwood plot for this system is

shown in Fig. 6.

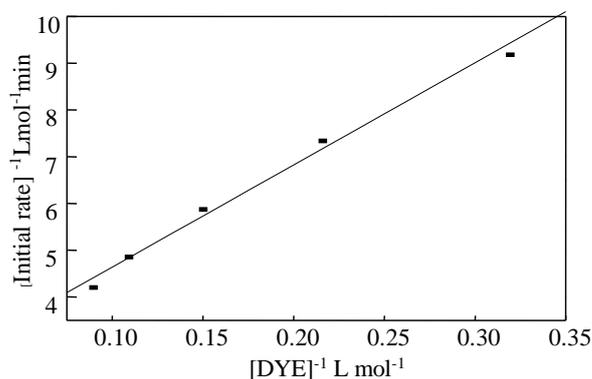


Fig. 6: $[\text{DYE}]^{-1}$ vs $[\text{initial rate}]^{-1}$ plot for photodegradation of PY in presence of ZnO

Table. 1 Effects of various parameters on the degradation of PY.

[PY] $\times 10^5$ M	Catalyst (g/50mL)	pH	(%) Degradation After 60 min
3.15	0.9	6.10	91.30
5.0			91.35
7.10			92.41
9.0			81.71
10.0			81.90
5.0	0.2	6.10	75.77
	0.4		82.89
	0.6		84.42
	0.8		88.65
	0.9		91.35
	1.0		89.62

Products from degradation of PY

The final products of mineralization (Saqib, 2002; Lachheb, 2002) of a molecule like PY (Fig. 1) should be CO_2 , H_2O , SO_4^{2-} , NO_3^- , Cl^- and N_2 . If photolysis is continued for more than one hour and the spectrum of the solution is recorded nothing significant, except a peak near about 200nm, could be observed in the spectrum indicating that NO_3^- is present in the solution after mineralization (Mahmood, 2003). This suggests that the PY has been completely mineralized.

PY has two $-\text{SO}_3^-$ group linked to aromatic ring. During heterogeneous photodegradation attack on these groups will be favored if the molecule is adsorbed with its $-\text{SO}_3^-$ group oriented to the surface and the initial mineralization product will be SO_4^{2-} . The outcome of nitrogen in the molecule strongly depends on its initial oxidation state (Quddus, 1999). The nitrogen in $>\text{NH}$, with -3 oxidation state, is likely to be initially converted to NH_4^+ followed by its slow oxidation to NO_3^- . The nitrogens in the azoic group will be

converted to dinitrogen, N_2 (Liu, 2000). CO_2 formation is a relatively later phenomenon (Lachheb, 2002). Photocatalytic method is known to mineralize the dyes completely. The findings of the present study can be optimized for mineralization of dyes in the effluents from the fabric dyeing factories.

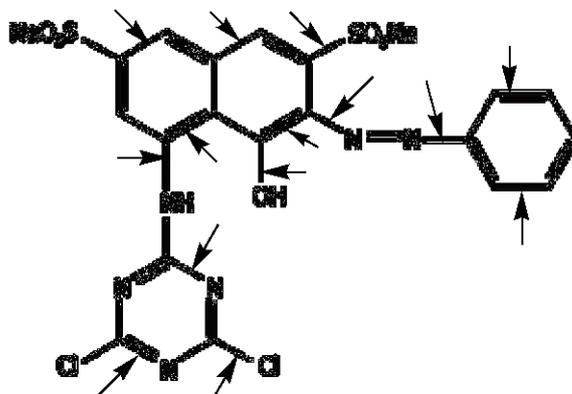


Fig. 7: Possible breaking positions of PY

Conclusion

In the presence of visible light, ZnO can efficiently catalyze the decolorization of PY in the aqueous solution. Photodecolorization of PY is unaffected by the initial pH of its solution in the range of 2.05 to 9.05. With increasing the concentration of PY initial rate of photodegradation increases. The percent degradation of PY solution was increases first however decreases with further increase of PY concentration. So the photodegradation degree of dye was obviously affected by the initial dye concentration. Finally, it can be concluded that ZnO is an efficient recoverable photocatalyst in PY degradation whose nature does not change even if it is used as a photocatalyst.

The heterogeneous photo-catalysis is a prominent method for degradation of dyes and dye intermediates contained industrial wastewaters, in aqueous system under simple handling with no specific technical equipments is necessary, and also in-expensive with less investment, less energy demand and produce harmless byproducts.

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