



Investigation on the Relative Degradation of Methylene Blue (MB) and Rhodamine-B (RB) Dyes under UV-Visible Light using Thermally Treated Commercial and Doped TiO₂/ZnO Photocatalysts

M. M. Rahman³, D. Roy², and M. S. H. Mukit^{1*}

*Department of Chemical Engineering and Polymer Science,
Shahjalal University of Science and Technology, Sylhet - 3114, Bangladesh.*

Abstract

The effluent from the textile, paper and food industries containing dye is strongly colored and reveals very harmful effects on living things. Semiconductor photo catalysis are propitious one for treating industrial polluted water. Upon irradiation with UV/visible light, semiconductors catalyze redox reactions in the presence of air/O₂ and water. In this work, photocatalytic degradation efficiencies of thermally treated doped and undoped commercial TiO₂ and ZnO photo catalysts have been studied for the methylene blue (MB) and Rhodamine-B (RB) dyes under UV and visible light source. The effects of operating parameters such as catalyst dosage and calcination temperature were also studied in a defined condition. The results from the above investigations concluded that thermally treated ZnO catalyst is more active on dye degradation than that of undoped and doped TiO₂. The obtained experimental data were fitted into different kinetic models and found that Modified Freundlich model fit the kinetic data well.

Keywords: Titanium dioxide, Zinc Oxide, Calcination temperature, Doping agents, Kinetic models.

1. Introduction

Water pollution by dyes is an important environmental problem. Currently available water treatment technologies merely concentrates the pollutants present by transferring them to other phases without destroying them and most of these involve high operating costs and waste disposal problem along with a generation of toxic secondary pollutants into the ecosystem [1]. Due to these drawbacks of conventional processes, the semiconductor photocatalysis has appeared to be a promising technology. Among the metal oxide semiconductors, TiO₂ and ZnO have been investigated extensively due to their chemical stability and efficient photocatalytic properties [2]. However, TiO₂ can be activated only under UV light irradiation due to its large band gap of 3.2 eV [3]. In addition, ZnO is a n-type semiconductor that possesses suitable band gap (3.17 eV). So, TiO₂ and ZnO which are the benchmarks of UV photocatalysis are inactive under visible light due to their wide band gaps [4]. Therefore, it is of great interest to improve

the photo-excited charge separation and to enhance the photocatalytic activity by modifying the surface or bulk properties of a photocatalyst [2]. In this regard, an interesting approach to deal with the issue is carried out by a coupled semiconductor technique. These coupled semiconductor photocatalysts may increase the photocatalytic efficiency by increasing the charge separation and extending the photo-responding range [5]. The aim of this work is to investigate the photocatalytic activities of thermally treated commercial and doped TiO₂ and ZnO photocatalysts on methylene blue and rhodamine-B dyes under UV and visible light and their degradation kinetics.

2. Materials and Method

2.1 Materials

Titanium (IV) Oxide (TiO₂) (SIGMA-ALDRICH, Germany), Zinc Oxide (ZnO) (LOBA CHEMIE, India), Zinc Chloride (ZnCl₂ .2H₂O) (Merck, India), Zinc Nitrate (Zn(NO₃)₂.6H₂O) (Merck, India), Tin (II) Chloride (SnCl₂.2H₂O) (E. Merck (India) Limited), Methylene Blue (MB) (Loba Chemie, India) and Rhodamine-B (RB) (Techno pharmchem,

Corresponding author:

E-mail : enr.mukit@gmail.com

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India), Absolute Ethanol were used as received. Distilled water was prepared in our laboratory and used.

2.2 Method

Commercial ZnO doped commercial TiO₂ catalyst was prepared by simple mixing. All others doped catalysts were prepared using wet impregnation method [6], maintaining catalyst/dopant ratio of 5:1 by weight. In a two neck conical flask, commercial TiO₂ powder was mixed with solutions of Zn salts in absolute ethanol. The mixture was continuously stirred for 15 minutes and then heated in the temperature range of 338-345K to get a solid mass. The obtained ZnO doped TiO₂ sample was cooled, followed by grinding to get it in powder form. The same procedure was followed to prepare SnO₂ (coming from SnCl₂.2H₂O) doped TiO₂, ZnO/SnO₂ (coming from SnCl₂.2H₂O) doped TiO₂ (5:0.5:0.5 weight ratio) and SnO₂ (coming from SnCl₂.2H₂O) doped Commercial ZnO catalysts. Then the prepared catalysts were thermally treated in a muffle furnace (JSMF-30T, Korea) for 2 hours at 450°C. Besides, TiO₂, ZnO and commercial ZnO doped TiO₂ photocatalysts were calcined at 150°C, 250°C, 350°C, 450°C, 550°C and 650°C to study the thermal effect. After that the catalyst samples were cooled to room temperature and ground and stored. All photocatalytic reactions were performed in reactor made of mirror glass for 90 minutes. In each experiment, 0.16g of catalyst was dispersed in 20ppm of dye solution. UV lamp (230Volt, 50Hz) and visible light (100W, 220V) were used to run the experiments. Samples were withdrawn at appropriate time intervals and the concentration of dye in the solution was determined by UV-spectrophotometer (UV-1650, SHIMADJU, Japan).

3. Results and Discussion

3.1 Catalyst dosage

It is essential to determine the minimum amount of catalyst required to decolorize the maximum amount of dye at our experimental condition. Optimal concentration of the catalyst depends on working conditions and the incident radiation reflux [7-8]. To get the optimum catalyst loading, the bare TiO₂ from 0.04 to 0.20 g in 200 ml of 20 ppm MB solution was taken in a photocatalytic reactor for 90 minutes and final concentration was measured. Finally, degradation of MB vs. catalyst dosage is plotted and it was found that 0.16 g/200ml as optimum catalyst dosage for dye degradation in our reactor condition [9-10].

3.2 Thermal effects

The calcination temperature of photocatalysts has a significant effect on its activity. In order to find out the optimum condition, the photocatalysts TiO₂, ZnO and commercial ZnO doped TiO₂ were calcined at different temperature (150-650°C) and used to degrade MB and RB dye solutions (**Fig.1 (a-b)**). TiO₂ exists in four mineral forms [11] viz: anatase, rutile, Brookite and titanium dioxide (B) or TiO₂ (B). Among them, anatase shows maximum photo reactivity because of its slightly higher Fermi level, lower capacity to absorb oxygen and higher degree of hydroxylation [10]. Studies show that at lower calcination temperatures anatase phase predominates, but with increasing calcination temperature the phase transfer from anatase to rutile occurs, showing lower efficiency. But a combination of rutile and anatase phase shows much greater efficiency [12]. A good phase transfer is occurred for commercial TiO₂ treated at 450°C. Above this temperature, the grain size increased and the specific surface area decreased, which can depress the photocatalytic activity of TiO₂ [10, 13]. In the case of ZnO catalysts, as the calcination temperature increases, the particle morphology changes from rod to irregular shape. This anisotropic growth of ZnO particles could be caused by higher temperature [14]. It is found that 450°C is the optimum calcination temperature for these kinds of catalysts.

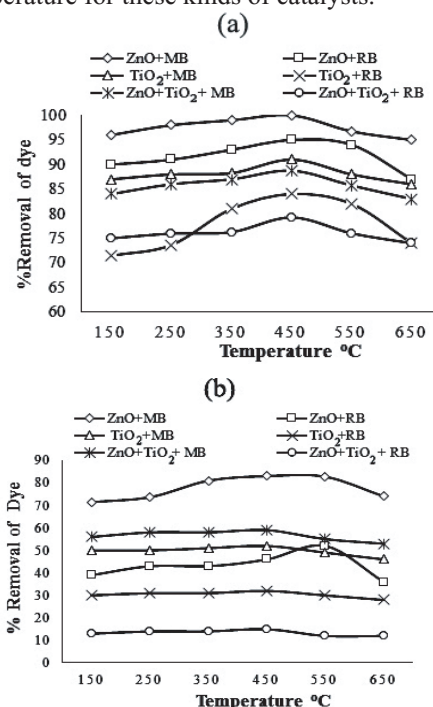


Fig.1: Effects of calcination temperature on photocatalytic degradation of MB and RB dyes under UV (a), and visible (b), light.

3.3 Relative photocatalytic degradation under UV light

Synthesized SnO_2 and commercial ZnO doped TiO_2 photocatalysts calcined at 450°C give 13% higher efficiency for MB degradation than that of commercial TiO_2 shown in Fig. 2. (a). The reason behind it is metal oxide doping enhances the photocatalytic activity of TiO_2 as doped metal atoms suppress the recombination of photo-induced electron-hole pairs [1]. Besides this, ZnO photocatalyst calcined at 450°C , shows better MB degradation (Fig.2. (a)). On the other hand, synthesized SnO_2 doped TiO_2 and commercial ZnO calcined at 450°C give higher efficiency than that of commercial TiO_2 for RB degradation (Fig. 2. (b)). The reason for greater activity of ZnO is due to the absorption of more light quanta. Since the band gap of ZnO is 3.17 eV, the quantum efficiency of ZnO is significantly larger than that of TiO_2 .

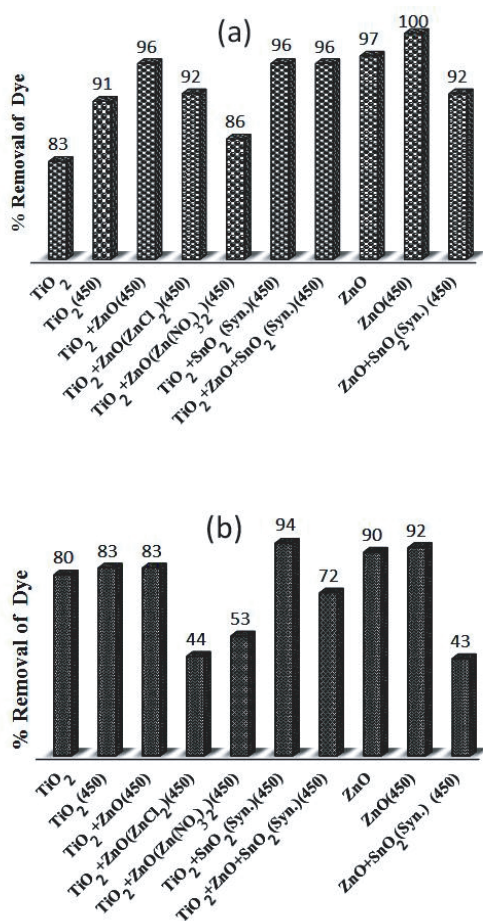


Fig.2: Photo degradation of MB (a), and RB (b), dyes using different catalysts under UV light.

3.4 Relative photocatalytic degradation under visible light

Among all doped catalysts, commercial ZnO doped TiO_2 calcined at 450°C , show 26% better result than commercial TiO_2 alone (Fig 3(a)). For effectiveness of catalysts under visible light, the conduction band of coupled semiconductor should be higher and its valence band needs to be lower than that of host semiconductor. But the conduction band of both the ZnO and SnO_2 are lower than that of TiO_2 along with large band gap (3.6 eV) of SnO_2 . In addition, doping generates impurity levels in the band gap of semiconductors. If these states lie close to the band edges, they can overlap with band states and can narrow the band gap. However, if they are present deep in the band gap they may act as recombination centers for the photogenerated carriers [4]. So, catalytic activities did not increase much and even lower for some coupled catalysts. The results obtained show that ZnO calcined at 450°C degrades most efficiently both of the MB and RB dyes (Fig.3 (a-b)). It is well known that ZnO, a direct wide band gap semiconductor, cannot be stimulated by visible light. So, the degradation may be caused by the photosensitization effect of dyes. As, visible light is absorbed by both of the Rhodamine B (in the range of 460-600 nm) and methylene blue dyes [4,15].

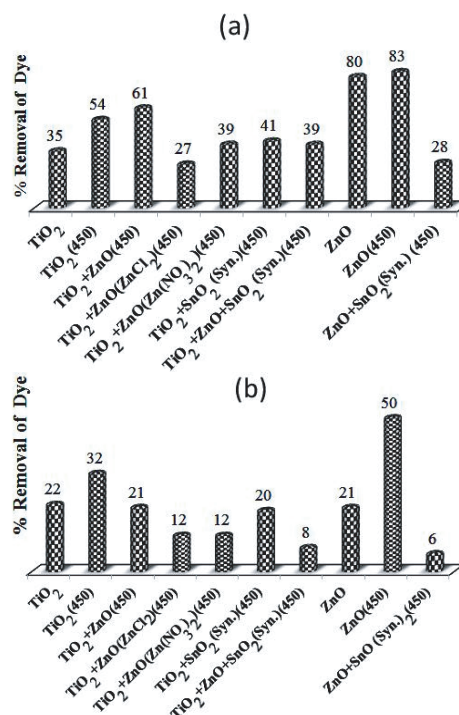


Fig.3: Photo degradation of MB (a), and RB (b), dyes using different catalysts under visible light.

3.5 Kinetic models

To study the kinetics phenomena, the whole procedure done in batch mode is repeated in continuous mode. Then all obtained experimental data are fitted into four different kinetic models, such as Zero order, Pseudo first order, Parabolic diffusion and Modified Freundlich models investigate the mechanism of successive adsorption and degradation process. The model parameter k as well as the correlation coefficient (R^2) is shown in Tables 1-4. The kinetic data of the MB and RB adsorption

simultaneous photo degradation on using catalyst are well described by the Modified Freundlich and Pseudo first order models. The Modified Freundlich model fits the kinetic data with a linear correlation coefficient of $R^2 = \sim 0.99$ (Table 1,2) for MB and $R^2 = \sim 0.99$ (Table 3,4) for RB photocatalytic degradation using different catalysts. The Modified Freundlich model, in fact, describes heterogeneous diffusion from the flat surface via molecular ion exchange. Moreover, the kinetic model prediction suggests similarities in the photocatalytic activity.

Table-1: Linear correlation coefficients (R^2) and photocatalytic degradation rate constant (k) of dissolution diffusion kinetic models for MB dye degradation by using different catalysts under UV irradiation.

Catalysts	Kinetic Models							
	Zero order		Pseudo First Order		Parabolic Diffusion		Modified Freundlich	
	R^2	K	R^2	K	R^2	K	R^2	K
TiO ₂	0.3789	0.2332	0.8564	0.0091	0.995	0.147	0.9976	0.494
TiO ₂ (450°C)	0.3269	0.2391	0.9194	0.0118	0.983	0.172	0.9903	0.5366
TiO ₂ +ZnO(450°C)	0.4234	0.2594	0.9787	0.0151	0.925	0.170	0.9954	0.4417
TiO ₂ +ZnO+SnO ₂ (Syn.)(450°C)	0.6712	0.2588	0.9751	0.0139	0.998	0.134	0.9977	0.4417
TiO ₂ +SnO ₂ (Syn.)(450°C)	0.5655	0.2381	0.9396	0.0132	0.981	0.142	0.9989	0.4646
ZnO	0.8292	0.2434	0.9555	0.0143	0.988	0.089	0.9914	0.3382
ZnO(450°C)	0.5355	0.0286	0.8404	0.0215	0.982	0.162	0.9893	0.4881
TiO ₂ +ZnO(ZnCl ₂)(450°C)	0.5538	0.2515	0.9788	0.0121	0.984	0.143	0.9951	0.4626
TiO ₂ +ZnO(Zn(NO ₃) ₂)(450°C)	0.7289	0.2034	0.9458	0.0085	0.968	0.118	0.9942	0.4007
ZnO+SnO ₂ (Syn.)(450°C)	0.7787	0.2434	0.9932	0.0115	0.990	0.090	0.9882	0.3555

Table-2: Linear correlation coefficients (R^2) and photocatalytic degradation rate constant (k) of dissolution diffusion kinetic models for MB dye degradation by using different catalysts under Visible light irradiation.

Catalysts	Kinetic Models							
	Zero order		Pseudo First Order		Parabolic Diffusion		Modified Freundlich	
	R^2	K	R^2	K	R^2	K	R^2	K
TiO ₂	0.7128	0.079	0.813	0.0022	0.959	0.049	0.9982	0.2783
TiO ₂ (450°C)	0.9013	0.1341	0.9726	0.0038	0.978	0.046	0.9923	0.2474
TiO ₂ +ZnO(450°C)	0.8428	0.1548	0.9666	0.0053	0.968	0.054	0.9982	0.2741
TiO ₂ +ZnO+SnO ₂ (Syn.)(450°C)	0.6371	0.1042	0.6254	0.0031	0.993	0.054	0.9903	0.2989
TiO ₂ +SnO ₂ (Syn.)(450°C)	0.4693	0.1067	0.7712	0.0027	0.967	0.062	0.9962	0.3293
ZnO	0.8071	0.2104	0.9817	0.0079	0.988	0.089	0.9857	0.3439
ZnO(450°C)	0.8233	0.212	0.9819	0.0083	0.985	0.083	0.9961	0.3333
TiO ₂ +ZnO(ZnCl ₂)(450°C)	0.9491	0.0692	0.9733	0.0016	0.952	0.016	0.9966	0.1527
TiO ₂ +ZnO(Zn(NO ₃) ₂)(450°C)	0.8148	0.0959	0.9003	0.0026	0.957	0.049	0.9815	0.1519
ZnO+SnO ₂ (Syn.)(450°C)	0.9315	0.0649	0.962	0.0016	0.991	0.015	0.9956	0.2627

Table-3: Linear correlation coefficients (R^2) and photocatalytic degradation rate constant (k) of dissolution diffusion kinetic models for RB dye degradation by using different catalysts under UV irradiation.

Catalysts	Kinetic Models							
	Zero order		Pseudo First Order		Parabolic Diffusion		Modified Freundlich	
	R^2	K	R^2	K	R^2	K	R^2	K
TiO ₂	0.6945	0.2172	0.9832	0.0072	0.964	0.105	0.9961	0.3881
TiO ₂ (450°C)	0.6915	0.2471	0.9841	0.0081	0.988	0.105	0.9935	0.3938
ZnO	0.6432	0.2284	0.9954	0.0111	0.982	0.112	0.9963	0.3942
ZnO(450°C)	0.7519	0.2521	0.9969	0.0124	0.986	0.094	0.9891	0.3579
TiO ₂ +SnO ₂ (Syn.)(450°C)	0.6706	0.6706	0.9945	0.0134	0.983	0.993	0.9979	0.4167

Table-4: Linear correlation coefficients (R^2) and photocatalytic degradation rate constant (k) of dissolution diffusion kinetic models for RB dye degradation by using different catalysts under Visible light irradiation.

Catalysts	Kinetic Models							
	Zero order		Pseudo First Order		Parabolic Diffusion		Modified Freundlich	
	R^2	k	R^2	K	R^2	K	R^2	K
TiO ₂	0.9482	0.0548	0.9692	0.0013	0.979	0.011	0.9938	0.1334
TiO ₂ (450°C)	0.8482	0.0787	0.9088	0.0022	0.976	0.031	0.9945	0.2159
ZnO	0.8132	0.0559	0.8579	0.0013	0.981	0.019	0.9942	0.1769
ZnO(450°C)	0.6739	0.136	0.8352	0.0039	0.958	0.061	0.9931	0.3072

4. Conclusion

The catalyst dosage 0.16 gm is efficient for 200 ml dye solution. The commercial TiO₂, ZnO and commercial ZnO doped TiO₂ photocatalysts calcined at 450°C showed higher MB and RB degradation under both UV and visible light in the defined condition. The relative study revealed that thermally treated commercial ZnO, synthesized ZnO and synthesized SnO₂ doped TiO₂ showed satisfactory MB degradation under UV light. Though the degradation by synthesized ZnO and synthesized SnO₂ doped TiO₂ under visible light is not satisfactory, commercial ZnO doped TiO₂ showed a good result. But the degradation of MB using commercial ZnO is higher than that of both doped and undoped TiO₂. On the other hand, for the degradation of RB it was observed that synthesized SnO₂ doped TiO₂ is also a promising one under UV light. The results from the above investigations conclude that thermally treated ZnO catalyst is more active than that of other photocatalysts. The obtained experimental data were fitted in kinetic models to describe the dependency of degradation rate as a function of the parameters. In this study it was observed that the Modified Freundlich model fits the kinetic data well.

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