

## Photocatalytic degradation of some organic dyes under solar light irradiation using TiO<sub>2</sub> and ZnO nanoparticles

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**ABSTRACT:** Nanoparticles of the ZnO and TiO<sub>2</sub> were synthesized and the physicochemical properties of the compounds were characterized by IR, X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The XRD patterns of the ZnO and TiO<sub>2</sub> nanoparticles could be indexed to hexagonal and rutile phase, respectively. Aggregated nanoparticles of ZnO and TiO<sub>2</sub> with spherical-like shapes were observed with particle diameter in the range of 80-100 nm. These nanoparticles were used for photocatalytic degradation of various dyes, Rhodamine B (RhB), Methylene blue (MB) and Acridine orange (AO) under solar light irradiation at room temperature. Effect of the amount of catalyst on the rate of photodegradation was investigated. In general, because ZnO is unstable, due to incongruous dissolution to yield Zn(OH)<sub>2</sub> on the ZnO particle surfaces and thus leading to catalyst inactivation, the catalytic activity of the system for photodegradation of dyes decreased dramatically when TiO<sub>2</sub> was replaced by ZnO.

**Keywords:** Nanoparticles; Photocatalytic degradation; ZnO; TiO<sub>2</sub>

### INTRODUCTION

With the development of the textile industry, intense concerns were focused on the contamination of the environment caused by dye pollutants, which caused severe environmental pollution and health problems due to the variety, toxicity and persistence characteristics [1-6]. Most of dyes are characterized by complicated constitution and high chemical stability, hence persist for long distances in flowing water, retards photosynthetic activity, inhibit the growth of aquatic biota by blocking out sunlight and utilizing dissolved oxygen and also decrease the recreation value of stream [7]. Therefore degradation of the dyes in industrial wastewaters has generated considerable attention due to their huge volume of production, slow biodegradation, low decoloration and high toxicity [8-11].

Metal oxides can adopt a vast number of structural geometries with an electronic structure that can exhibit metallic, semiconductor or insulator character and therefore play a very important role in many areas of chemistry,

physics and materials science [12-16]. In recent years, an enormous interest has been devoted to heterogeneous photocatalysis using metal oxides owing to its potential applications to both environmental applications and organic synthesis [17-21]. Many attempts have been made to study photocatalytic activity of different metal oxides such as SnO<sub>2</sub>, ZrO<sub>2</sub>, CdS [22,23].

Titanium dioxide (TiO<sub>2</sub>) and zinc oxide (ZnO) that are characterized by chemical stability, environmentally friendly, no toxicity and cheap production cost, are used in a large variety of different fields of photochemistry ranging from large-scale products to more advanced applications, for example, in environmental remediation, photo-electrolysis of water and dye-sensitized solar cells [24-27].

Sunlight is abundantly available natural source of energy which can be conveniently exploited for the irradiation of semiconductors in the photodegradation of pollutants and can make the process economically more viable [28,29]. Dyes can be degraded in the presence of photocatalyst upon irradiation with visible light because of their absorption in the visible region.

In the present study the degradation of the three dyes

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Rhodamine B (RB), Methylene blue (MB) and Acridine orange (AO) were investigated using solar light irradiation and the efficiencies of various metal oxide catalysts were compared (Scheme 1). With using TiO<sub>2</sub> and ZnO nanoparticles as a photocatalyst under solar irradiation, the effects of different operational parameters on the degradation of dyes were studied.

## EXPERIMENTAL

### Materials

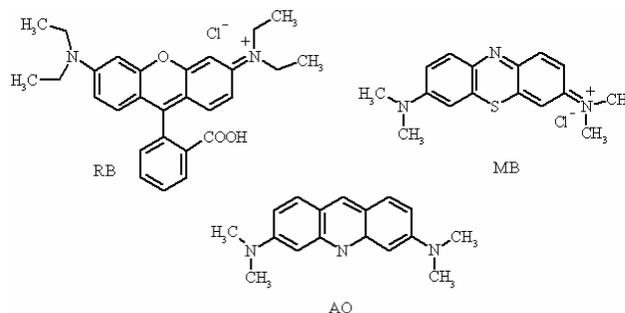
Chemicals and solvents were purchased from *Merck* and *Sigma-Aldrich* and were used without further purification.

### Characterization

Transmission electron microscopy (TEM) was conducted on carbon-coated copper grids using a FEI Technai G2 F20 Field Emission scanning transmission electron microscope (STEM) at 200 kV (point-to-point resolution <0.25 nm, line-to-line resolution <0.10 nm). TEM samples were prepared by placing 2-3 drops of dilute ethanol solutions of the nanomaterials onto carbon coated copper grids. Composition was characterized by energy dispersive spectroscopy (EDS) line scans in STEM mode, and by energy-filtered (EF) imaging spectroscopy (EF-TEM). SEM was carried out with Philips CM120 and LEO 1430VP instruments. The X-ray powder patterns were recorded with a Bruker D8 ADVANCE (Germany) diffractometer (Cu-K $\alpha$  radiation). Absorption spectra were recorded by a CARY 100 Bio VARIAN UV-Vis spectrophotometer. FT-IR spectrum was obtained by using a Unicam Matson 1000 FT-IR spectrophotometer using KBr disks at room temperature.

### Synthesis of ZnO Nanoparticles

Nanoparticles of ZnO were prepared using a polyethylene glycol (PEG) sol-gel method. Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, ethanol, and PEG (Mw = 1000) were used as starting raw materials. 1.0 g of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was dissolved in the transparent solution of PEG (1.5 g) and ethanol (20 ml) with constant stirring at 150 °C until a viscous gel was formed. Viscous gel was dried at 350 °C for 30 min. To obtain ZnO nanoparticles, the resulting dried porous precursors were ground into powder and calcined in air at 600 °C for 6 h.



*Scheme 1.* Structure of Rhodamine B (RB), Methylene blue (MB) and Acridine orange (AO)

### Synthesis of TiO<sub>2</sub> Nanoparticles

The controlled hydrolysis of titanium isopropoxide under ice-cold (0 °C) condition with vigorous stirring gives white precipitate of TiO(OH)<sub>2</sub>. The precipitate was washed several times in distilled water and then dissolved in nitric acid to get a clear, transparent titanyl nitrate [TiO(NO<sub>3</sub>)<sub>2</sub>] solution [30]. Aqueous solution of 1:1 molar ratio of titanyl nitrate and urea were taken in a 250 ml beaker and introduced into a muffle furnace maintained at 673 K. Solid products were obtained within 2 h of total preparation time.

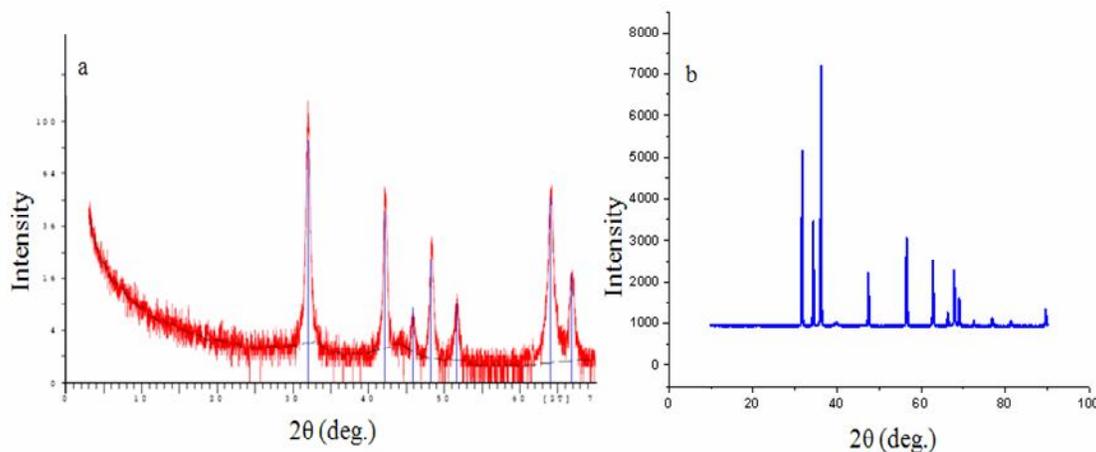
### Photocatalytic Degradation of the Dye under Solar Irradiation

Experiments were carried out under solar light. To 50 ml of dye solution (10 mg l<sup>-1</sup>), 10 mg of catalyst was added and suspension was subjected to solar light irradiation. The aqueous suspension was magnetically stirred throughout the experiment. For a given time interval, a small quantity of the mixture solution was pipetted into a quartz cell, and its absorption spectrum was measured using an UV-Vis spectrophotometer.

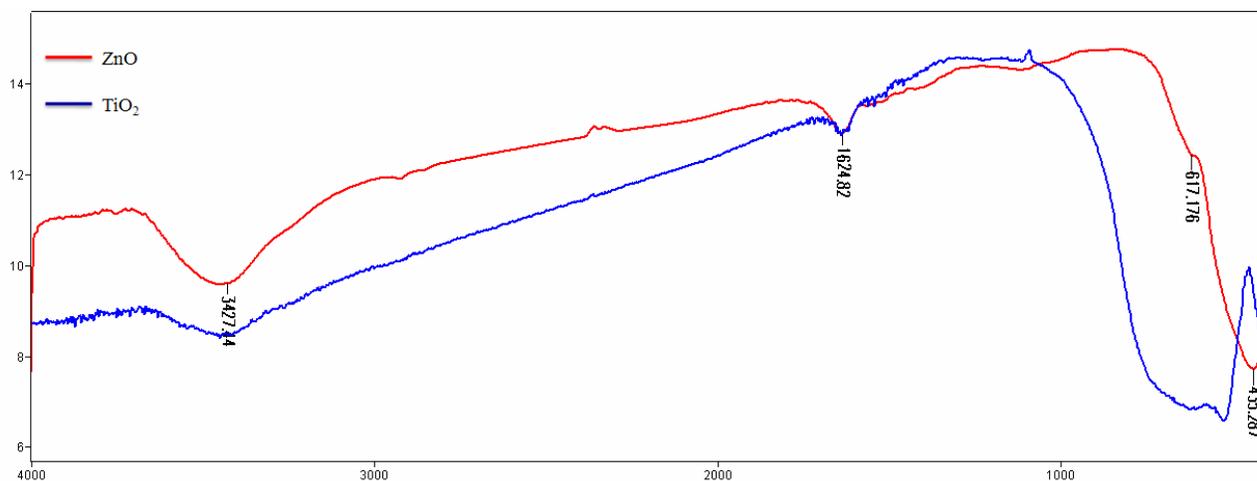
## RESULTS AND DISCUSSION

### Catalyst Characterization

XRD patterns were recorded for nanoparticles to determine structure and phase formation of ZnO and TiO<sub>2</sub> photocatalysts (Fig. 1). XRD patterns of the ZnO show peaks at the positions of 31.75°, 34.38°, 36.21°, 47.44°, 56.35°, 62.73°, 66.27°, 67.79° and 69.10°, which are in



**Fig. 1.** XRD pattern of a) TiO<sub>2</sub>; b) ZnO nanoparticles.



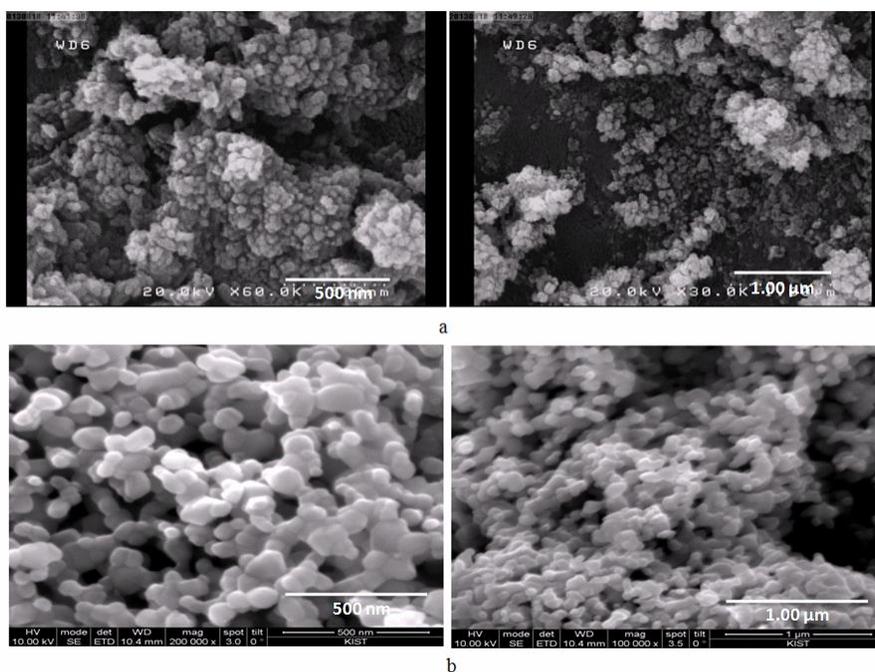
**Fig. 2.** IR spectra of TiO<sub>2</sub> and ZnO nanoparticles.

good agreement with the standard JCPDS file for ZnO (JCPDS 36-1451,  $a = b = 3.249 \text{ \AA}$ ,  $c = 5.206 \text{ \AA}$ ,  $\alpha = \beta = 90^\circ$  and  $\gamma = 120^\circ$ ) and can be indexed as the hexagonal wurtzite structure of ZnO having space group P63mc [31]. The structure of ZnO is characterized by two interconnecting sublattices of Zn<sup>2+</sup> and O<sup>2-</sup>, and each Zn ion is surrounded by a tetrahedral of O ions, and *vice versa*. Also XRD pattern of TiO<sub>2</sub> nanoparticles could be indexed to rutile phase of titania. The samples consisted of a pure ZnO and TiO<sub>2</sub> phases with no possible impurities.

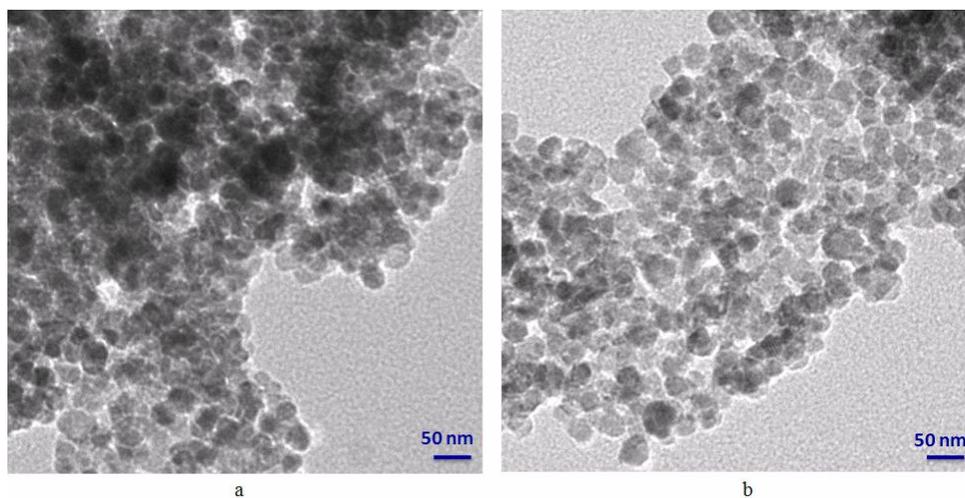
Figure 2 shows the FT-IR spectra of the synthesized

ZnO and TiO<sub>2</sub> nanoparticles. The peaks at  $\nu = 617 \text{ cm}^{-1}$  and  $435 \text{ cm}^{-1}$  are related to the stretching vibrations of Zn-O bonds [32]. Also, TiO<sub>2</sub> nanoparticles show broad band in the region of  $400\text{-}900 \text{ cm}^{-1}$  due to unresolved stretching vibrations of Ti-O-Ti. The weak peak at  $1620 \text{ cm}^{-1}$  corresponds to the bending vibrations of O-H, and the broad band at around  $3427 \text{ cm}^{-1}$  are attributed to the surface adsorbed water and hydroxyl groups [33].

Particle morphology and textural properties of ZnO and TiO<sub>2</sub> catalysts were also studied carefully by SEM and TEM. Representative SEM and TEM images recorded for



**Fig. 3.** SEM images of a) TiO<sub>2</sub>; b) ZnO nanoparticles.



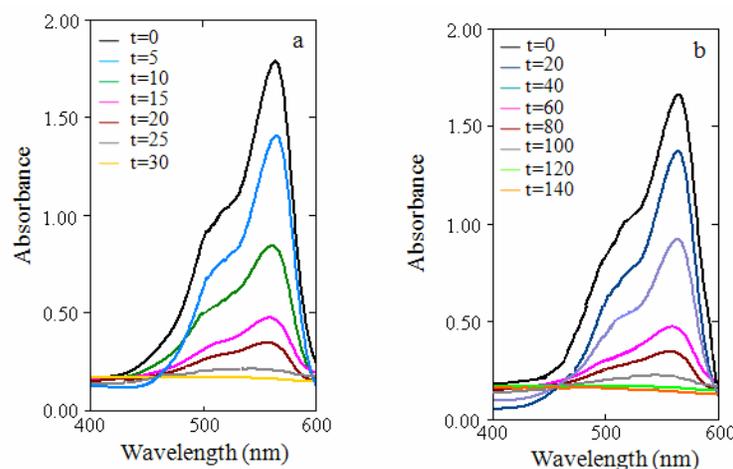
**Fig. 4.** TEM images of (a) TiO<sub>2</sub>; b) ZnO nanoparticles.

ZnO and TiO<sub>2</sub> materials are shown, respectively, in Figs. 3 and 4. Aggregated nanoparticles of ZnO and TiO<sub>2</sub> with spherical-like shapes are observed with particle diameter in the range of 80-100 nm.

### Catalytic Performance

Photodegradation experiments were carried out under

irradiation of the dye solution under solar light ( $\sim 400 \text{ W m}^{-2}$ ). The extent of dye degradation was monitored using UV-Vis spectroscopic techniques. The first photodegradation of Rhodamine B (RB) by various metal oxides as a photocatalyst was investigated. In the absence of a photocatalyst, the photodegradation of RhB under solar light irradiation was very slow, and almost no degradation



**Fig. 5.** Changes of UV-Vis spectra during the degradation of RB on a) TiO<sub>2</sub>; b) ZnO under solar light irradiation. 50 mg catalyst; 50 ml RB (10 mg l<sup>-1</sup>).

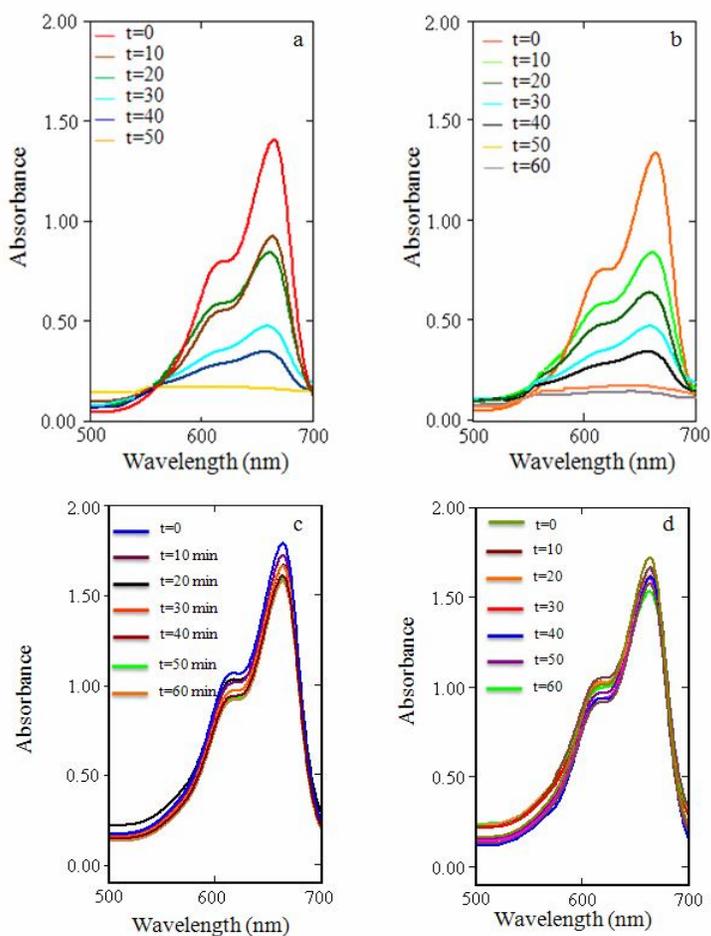
**Table 1.** Effect of the Amount of Catalyst on the Time for Complete RB Degradation

Entry	Amount of catalyst (mg)	Time for complete degradation of RB (min)	
		TiO <sub>2</sub>	ZnO
1	10	70	360
2	20	58	180
3	30	45	145
4	40	38	135
5	50	30	120

of RhB was observed after 120 min. But When the TiO<sub>2</sub> catalyst was added to the RB solution under solar irradiation, the degradation of RB was complete after 35 min, showing that TiO<sub>2</sub> facilitated the degradation of RB by solar light (Fig. 5a). The catalytic activity of the system decreased when TiO<sub>2</sub> was replaced by ZnO and loss of RB took more than 120 min (Fig. 5b). TiO<sub>2</sub> is the most promising photocatalyst as it is chemically inert and stable with respect to photocorrosion and chemical corrosion, but ZnO is unstable due to incongruous dissolution to yield Zn(OH)<sub>2</sub> on the ZnO particle surfaces and thus leading to catalyst inactivation [34]. Other catalysts, MoO<sub>3</sub>, WO<sub>3</sub>, RuO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, Mn<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> have negligible activity.

As shown in Table 1, the amount of catalysts TiO<sub>2</sub> and ZnO could also significantly affect the rate of degradation of RB. When the amount of catalysts TiO<sub>2</sub> and ZnO were increased from 0.01-0.05 g, the time for complete RB degradation was reduced from 70 min to 35 min and 360 min to 120 min, respectively.

In final, photocatalytic activity of ZnO and TiO<sub>2</sub> nanoparticles was evaluated by degrading two other dyes, MB and AO in aqueous suspensions under solar light irradiation at room temperature. In Fig. 6, UV-Vis spectra after different illumination times of a MB solution with TiO<sub>2</sub> and ZnO catalysts are shown. As can be seen from the figure, the maximum absorption peak at 663 nm gradually decreases during the illumination and the removal of MB



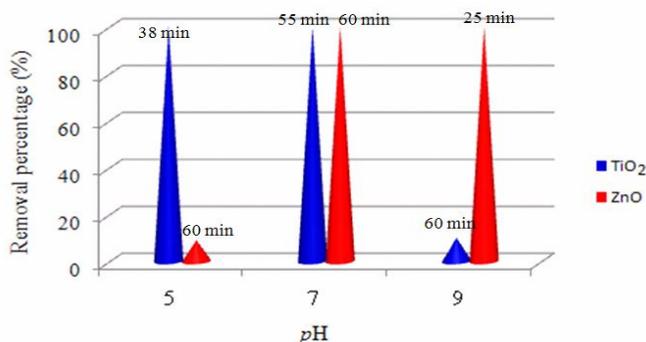
**Fig. 6.** Changes of UV-Vis spectra during the degradation of MB on a) TiO<sub>2</sub>; b) ZnO under solar light irradiation; c) TiO<sub>2</sub>; d) ZnO in the absence of solar light irradiation. 50 mg catalyst; 50 ml MB (10 mg l<sup>-1</sup>).

for two catalysts are complete after 50 min. The reaction in the absence of solar light irradiation, confirmed that adding only TiO<sub>2</sub> or ZnO catalyst into the solution within 60 min, little removal of MB (about 5%) occurred, indicating that the effect of adsorption on MB removal is not obvious (Figs. 6c, d).

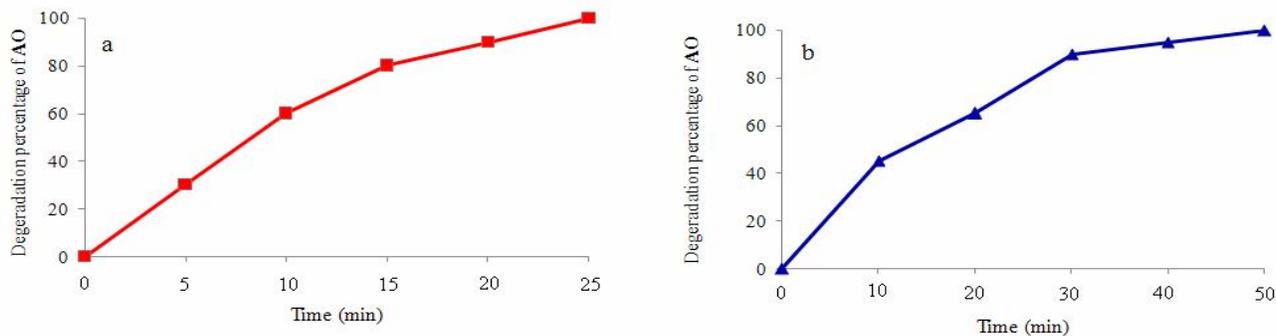
It is known that the adsorption capacity on catalyst of dye is a key factor, which the more target molecules adsorbed on catalyst, the faster or more complete these molecules decomposed. So, the adsorption experiments were carried out to study the adsorption of MB dye on TiO<sub>2</sub> and ZnO nanoparticles at various *pH*. The effect of *pH* on

the degradation efficiency of MB was examined in the range of 5-9. The initial *pH* was adjusted by addition of 1.0 M NaOH or HCl. As shown in Fig. 7, TiO<sub>2</sub> and ZnO are efficient catalysts over a wide *pH* range from 5-9, which is the range of *pH* found in most natural and polluted waters. The activity follows the order *pH* 5 > 7 > 9 and 9 > 7 > 5, respectively, for TiO<sub>2</sub> and ZnO nanoparticles.

Also when TiO<sub>2</sub> and ZnO were used as a catalyst for degradation of AO under solar light irradiation, the degradation percentage of AO increased almost linearly with time and the AO degradation was complete after 35 min and 50 min, respectively (Fig. 8). The percentage of



**Fig. 7.** Effects of pH on the degradation of MB in the presence of TiO<sub>2</sub> and ZnO.



**Fig. 8.** Percentage degradation of AO with a) TiO<sub>2</sub>; b) ZnO under solar light irradiation. 50 mg catalyst; 50 ml AO(10 mg l<sup>-1</sup>).

removal efficiency was calculated by using  $(I_0 - I) \times 100/I_0$ .

## CONCLUSIONS

Nanoparticles of ZnO and TiO<sub>2</sub> were successfully synthesized and characterized by XRD, IR, SEM, EDX and TEM. These new materials were found to be an effective catalyst for the destruction of industrial dyes Rhodamine B (RB), Methylene blue (MB) and Acridine orange (AO) under solar irradiation at room temperature.

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## REFERENCES

- [1] M.M. Alnuaimi, M.A. Rauf, S.S. Ashraf, *Dyes Pigm.* 72 (2007) 367.
- [2] J.H. Sun, S.P. Sun, G.L. Wang, L.P. Qiao, *Dyes Pigm.* 74 (2007) 647.
- [3] D.H. Bremner, R. Molina, F. Martinez, J.A. Melero, Y. Segura, *Appl. Catal. B: Environ.* 90 (2009) 380.
- [4] G. Moussavi, M. Mahmoudi, *Chem. Eng. J.* 152 (2009) 1.
- [5] S. Ameen, M. Shaheer Akhtar, Y. Soon Kim, O-Bong Yang, H. Shik Shin, *Colloid Polym. Sci.* 289 (2011) 415.
- [6] S. Caudo, G. Centi, C. Genovese, S. Perathoner, *Top. Catal.* 40 (2006) 207.

- [7] P. Bautista, A.F. Mohedano, J.A. Casas, J.A. Zazo, J.J. Rodriguez, *J. Chem. Technol. Biotechnol.* 83 (2008) 1323.
- [8] A. Xu, X. Li, S. Ye, G. Yin, Q. Zeng, *Appl. Catal. B: Environ.* 102 (2011) 37.
- [9] H. Habazaki, Y. Hayashi, H. Konno, *Electrochim. Acta* 47 (2012) 4181.
- [10] S. Caudo, G. Centi, C. Genovese, S. Perathoner, *Top. Catal.* 40 (2006) 207.
- [11] M. Amini, B. Pourbadiei, T. Purnima A. Ruberu, L. Keith Woo, *New J. Chem.* 38 (2014) 1250.
- [12] J. Cao, Y. Zhu, L. Shi, L. Zhu, K. Bao, S. Liu, Y. Qian, *Eur. J. Inorg. Chem.* 2010 (2010) 1172.
- [13] J. Zhao, Z. Tao, J. Liang, J. Chen, *Cryst. Growth Des.* 8 (2008) 2799.
- [14] T. Yu, J. Moon, J. Park, Y.I. Park, H.B. Na, B.H. Kim, I.C. Song, W.K. Moon, T. Hyeon, *Chem. Mater.* 21 (2009) 2272.
- [15] Y. Ding, C. Hou, B. Li, Y. Lei, *Electroanalysis* 23 (2011) 1245.
- [16] M. Amini, H. Naslhajian, S.M.F. Farnia, *New J. Chem.* 38 (2014) 1581.
- [17] S.S. Shinde, P.S. Shinde, C.H. Bhosale, K.Y. Rajpure, *J. Photochem. Photobiol. B: Biol.* 104 (2011) 425.
- [18] S.S. Shinde, C.H. Bhosale, K.Y. Rajpure, *J. Photochem. Photobiol. B: Biol.* 103 (2011) 111.
- [19] P. Amornpitoksuk, S. Suwanboon, S. Sangkanu, A. Sukhoom, J. Wudtipan, K. Srijan, S. Kaewtaro, *Power Tech.* 212 (2011) 432.
- [20] W.S. Chiua, P.S. Khiewa, M. Clokea, D. Isaa, T.K. Tana, S. Radimanb, R. Abd-Shukorb, M.A. Abd-Hamidb, N.M. Huangc, H.N. Limd, C.H. Chiac, *Chem. Eng. J.* 158 (2010) 345.
- [21] J.H. Sun, S.Y. Dong, Y.K. Wang, S.P. Sun, *J. Hazard. Mater.* 172 (2009) 1520.
- [22] A.A. Khodja, T. Sehili, J.F. Pilichowski, P. Boule, *J. Photochem. Photobiol. A: Chem.* 141 (2001) 231.
- [23] K. Vinod Gopal, P.V. Kamat, *Environ. Sci. Technol.* 29 (1995) 841.
- [24] J. Bao, M.A. Zimmler, F. Capasso, *Nano Lett.* 6 (2006) 1719.
- [25] X.D. Bai, P.X. Gao, Z.L. Wang, E.G. Wang, *Appl. Phys. Lett.* 82 (2003) 4806.
- [26] H.F. Lin, S.C. Liao, S.W. Hung, *J. Photochem. Photobiol. A* 174 (2005) 82.
- [27] M.A. Mahadik, S.S. Shinde, H.M. Pathan, K.Y. Rajpure, C.H. Bhosale, *J. Photochem. Photobiol. B: Biol.* 142 (2014) 43.
- [28] Y. Wang, L. Liu, L. Xu, X. Cao, X. Li, Y. Huang, C. Meng, Z. Wang, W. Zhu, *Nanoscale* 6 (2014) 6790.
- [29] J. Wang, J. Wang, Q. Sun, W. Wang, Z. Yan, W. Gong, L. Min, *J. Mater. Chem.* 19 (2009) 6597.
- [30] K. Nagaveni, M.S. Hegde, N. Ravishankar, G.N. Subbanna, G. Madras, *Langmuir* 20 (2004) 2900.
- [31] S. Labuayai, V. Promarak, S. Maensiri, *Appl. Phys. A Mater. Sci. Process* 94 (2009) 755.
- [32] H.M. Ismail, *J. Anal. Appl. Pyrolysis* 21(1991) 315.
- [33] A. Becheri, M. Durr, P.L. Nostro, P. Baglioni, *J. Nanopart. Res.* 10 (2008) 679.
- [34] D.W. Bahnemann, C. Kormann, M.R. Hoffmann, *J. Phys. Chem.* 91 (1987) 3789.