Photocatalytic degradation of Acid Red 1 dye using ZnO catalyst in the presence and absence of silver

B.H. Hameed*, U.G. Akpan, K.P. Wee

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia
Tel. +60 45996422; email: chbassim@eng.usm.my

ABSTRACT

The investigation of the degradation of Acid Red 1 (AR1) dye was carried out in an aqueous suspension photoreactor. Different parameters that affect the degradation of AR1 dye such as the presence and absence of a photocatalyst, light source, air, catalyst loading, initial substrate concentration were studied. The activity of Ag-doped ZnO prepared by photoreduction of Ag^+ ion on ZnO catalyst for AR1 dye degradation was investigated. The effects of different amount of Ag^+ deposited on ZnO particles and catalysts loading on the photocatalytic degradation rate of AR1 dye were evaluated. The surface morphologies of both Ag-doped ZnO and ZnO catalysts were studied by scanning electron microscopy (SEM), while X-ray diffraction (XRD) was used to study the crystallography of the catalysts. The experimental results revealed that the presence of photocatalyst, light, and air are significant for the photodegradation process. The optimum catalyst loading was 2 g catalyst per liter solution. The presence of Ag^+ in the catalyst does not significantly enhance the photocatalytic activity of ZnO in the degradation process.

Keywords: Degradation; Acid Red 1; Activity; Photoreduction; Zinc oxide

1. Introduction

Wastewaters discharged into water channels are the major sources of environmental contaminations. When the wastewater is left untreated, a great deal of malodorous gas is noticed at the event of decomposition. It must also be noted that untreated wastewaters contain numerous pathogenic microorganisms which pose a severe threat to the existence of living organisms in water and human in particular. Certain industrial wastewater may consist of toxic compounds or potentially mutagenic or carcinogenic compounds [1]. Wastewater has the potential to affect public health, and other aquatic living organisms [2]. Amongst the industries which

discharge undesirable and specifically, colored wastewater into the environment is the textile industry.

Textile industries carry out several fiber treatments which include dyeing preliminary treatments (bleaching, desizing, mercerization), textile ennobling treatments (from dyeing to post-dyeing treatments, such as those required to increase colorant fastness, in wet and dry conditions) and then finishing, including operations such as fulling or impregnation with products giving special characteristics to fibers [3]. In this manner textile industry has contributed a large amount of effluents which caused serious environmental problems as they contain colored compounds [4,5]. Wastewater from textile industries consists of high concentration of coloring reagent (dye). Many types of dyes are inert and non-toxic at the concentration which they are discharged into the

*Corresponding author.

receiving water body such as river; but the color they impart is very undesirable to the water user for aesthetic reasons. Textile wastewater will cause an increase in biochemical oxygen demand (BOD) of the water. At the same time, some of them are highly toxic because they consist of a large amount of metal complexing dyes. Dyes usually consist of elements such as nitrogen, chlorine or sulfur. The oxidation products of these molecules may be more toxic compared to the parent molecule [6], therefore, the need for its complete degradation. The commercially used dye in textile industry is from six common dye classes; namely: acidic, basic, direct, disperse, fiber reactive and vat [7]. The effluents containing dyes are very difficult to treat since they contain many ingredients like detergents, oils, inorganic salts, heavy metals, etc.; for such effluents the BOD/COD ratio will be high, implying non-biodegradability of the dye [8]. Moreover, most organic dyes are not easily degraded by biological methods, activated carbon adsorption, ultrafiltration, reverse osmosis, coagulation, and ion exchange. None of these methods will bring about a total decomposition of the pollutant [9], but production of a secondary waste, which requires further treatment and hence making the whole exercise more expensive [10].

Recently, the advanced oxidation process has been introduced to the textile industries effluent treatment process which will bring about total mineralization of organic pollutants to carbon dioxide and water [4]. Among the advanced oxidation processes, heterogeneous photocatalysis has proved to be effective for both aquatic and atmospheric organic contaminants degradation [11,12]. Photocatalysis may be termed as a photo-induced reaction which is accelerated by the presence of a catalyst [13,14]. These types of reactions are activated by absorption of a photon with sufficient energy (equals or higher than the band-gap energy (E_{bg}) of the catalyst) [15]. The absorption leads to a charge separation due to promotion of an electron (e^-) from the valence band of the semi-conductor catalyst to the conduction band, thus generating a hole (h^+) in the valence band. The activated electrons will then react with an oxidant to produce a reduced product, and also the generated holes will react with a reductant to produce an oxidized product; and as such brings about a total mineralization of the target pollutant.

Though titanium dioxide, TiO_2, is more popularly used as a photocatalyst for a wide range of organic compounds' degradation, ZnO is found to have similar photodegradation mechanism as TiO_2. Under several conditions, ZnO catalyst has higher photocatalytic efficiency compared to TiO_2 catalyst [16]. The use of ZnO has attracted attention for the degradation of a wide range of pollutants with relatively cheap, stable and high photocatalytic activities [17]. This work was therefore targeted at the degradation of an azo dye, Acid Red 1, by heterogeneous photocatalysis using ZnO-base photocatalysts as semiconductors and this will bring about a complete mineralization of the targeted dye.

2. Experimental

2.1. Photoreduction of silver ions on ZnO

Appropriate amount of silver nitrate was dissolved in 200 ml of 1.25% ethanol. The ethanoic solution was prepared by diluting 6.6 ml 95% pure ethanol (laboratory R&M Chemical, Essek, UK) in water in 500 ml volumetric flask, and made up to the mark with double distilled water. Then, 5 g of ZnO (Merck KGaA, 64271 Darmstadt, Germany, purity ≥ 99.0%), without further purification was added to the ethanoic solution in a 250 ml volumetric flask and ultrasonicated for 20 min. Thereafter, the mixture was transferred into a photoreduction reactor for the reduction of silver ions on ZnO surface. It was then subjected to a photoreduction process under UV light irradiation with constant stirring using magnetic stirrer. After 6 h of the process, the mixture solution was filtered using Whatman filter paper, and the catalyst was dried in an oven at a temperature of 60 °C until a constant weight was achieved. The resultant dry sample was stored in a sample bottle for further use in the photodegradation process.

2.2. Catalysts characterization

Powder X-ray diffraction (XRD) patterns of the catalysts were measured by D8 Advanced X-ray solution; while the microstructure and morphology of the prepared catalysts were observed using Philips XL30S model scanning electron microscopy.

2.3. Photocatalytic degradation process

Two hundred and fifty milliliter of the desired concentration of AR1 dye solution was poured into a jacketed photocatalytic reactor, and the catalyst was added. Agitation of the reaction mixture was provided by magnetic stirrer which operated at 600 rpm. The dye and the catalyst were left in the dark to allow the adsorption of the dye on the catalyst. Samples were taken from the system to analyze until the dye concentration becomes constant (which indicated a completion of the adsorption process). After the dye concentration becomes constant, the UV light and air pump were simultaneously switched on. Samples were withdrawn at certain preset time intervals to analyze for the dye concentration using computer software attached to UV-Vis Spectrophotometer, UV-1700 PharmaSpec, Shimadzu. Prior to the

spectrophotometric measurement of the samples, spectrum measurement of the AR1 dye was carried out, and two maximum peaks were obtained at wavelengths of 505 nm and 530 nm. Therefore, in all the analyses, measurements were made at a wavelength of 505 nm.

3. Results and discussion

3.1. Characterization of the photocatalysts

Scanning electron microscopy (SEM) was employed to study the morphology of the pure ZnO and the Ag-doped ZnO. Fig. 1 shows the SEM micrographs of (a) 3% Ag-ZnO and (b) ZnO. From the SEM micrographs it can be seen that Ag was uniformly deposited on the ZnO. Close observations of the micrographs reveals that the Ag-doped ZnO is more compacted (dense) than ZnO.

To further verify the presence of Ag in the doped ZnO, both the pure ZnO and the 3% Ag-doped ZnO were subjected to XRD analysis. Fig. 2 shows the spectra of ZnO and 3% Ag–ZnO, both possessed hexagonal structures. The presence of silver in the doped sample is identified at $2\theta = 38.46°$ and $44.58°$. Though relatively low peaks (which are not present in the pure ZnO spectrum),
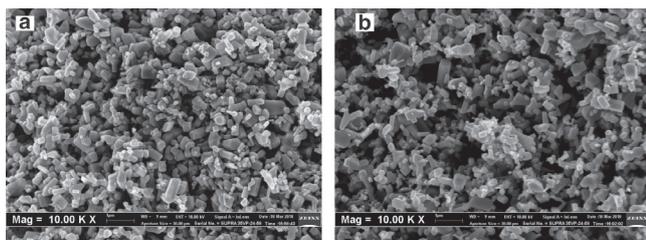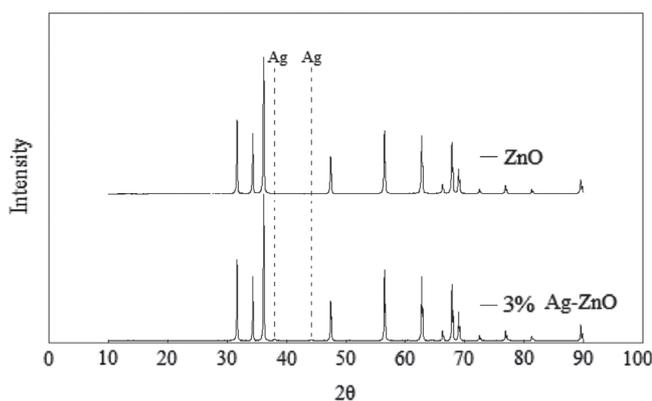
peaks at these points are evidences of the presence of Ag in the doped sample. Height et al. [18] reported a similar trend in their XRD analysis of Ag-doped ZnO, where silver peaks were dictated at $2\theta = 38.4°$, $44.5°$, and $64.6°$. A close examination of the present spectra also shows that at $2\theta = 64.4°$, there is an indication of a peak which further strengthens the claim that Ag is present in the doped sample.

The doping was actually responsible for the little enhancement in the photocatalytic ability of ZnO as illustrated by 3% Ag-doped ZnO in Fig. 8.

3.2. Zinc oxide, ZnO photocatalyst

Two identical experiments were conducted to study the effect of light on the zinc oxide photocatalyst degradation of AR1 dye. 0.1 g zinc oxide catalyst was added to 250 ml of 100 mg/l solution of AR1 in two glass wire reactors. One was irradiated with a 9 W 5 long Philips (PL-S 9W/10/2P Hg) UV bulb made in Poland, while the other was left in the dark, and both were subjected to the same operating conditions of stirring and airflow into the reactors. Evaluation of the concentrations of the content of each of the reactors revealed that there was no degradation of the AR1 in the absence of light, while a complete degradation was achieved within 80 min UV light irradiation (Fig. 3).

Preliminary investigations revealed that there was equally no degradation of AR1 during photoloysis. Furthermore, to study the effect of air on the photocatalytic degradation of AR1, two identical experiments were also set up; one with airflow into the reactor and the other without airflow into it. The importance of
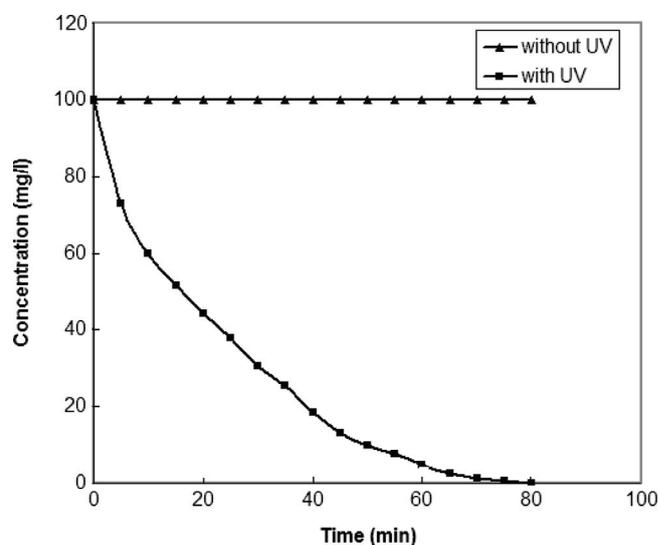

Fig. 1. SEM micrographs of (a) Ag–ZnO and (b) ZnO.

Fig. 2. XRD spectra for ZnO and 3% Ag–ZnO.

Fig. 3. Effect of UV light on the degradation of AR1 dye by 0.1 g ZnO.
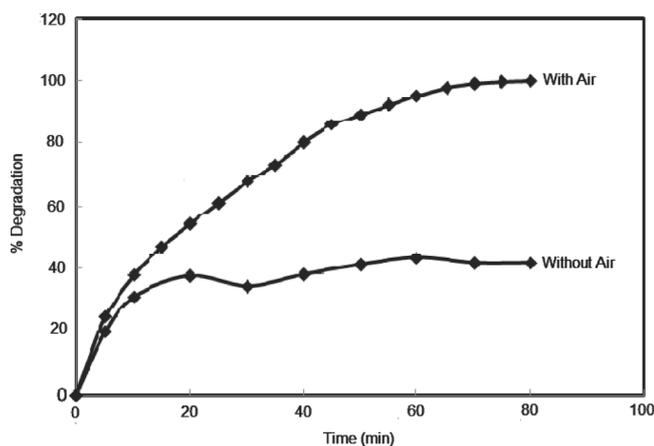
Fig. 4. Effect of air on the percentage degradation of AR1 dye by 0.1 g ZnO.

Fig. 5. Percentage degradation of AR1 dye as affected by ZnO catalyst loading.

molecular oxygen cannot be overemphasized as it can be reduced to superoxide anion; and this is a powerful oxidizing agent that attacks the organic compounds and intermediates are formed. These intermediates react with hydroxyl radicals to produce final products (P) with the major part being carbon dioxide and other compounds depending on the organic molecule composition. The results showed that at the first 10 min of irradiation, both systems with and without air supply had almost equal degradation rate. This is likely due to the oxygen trapped in the dye solution. Some moments after, the trapped oxygen must have been consumed and the degradation slope becomes less in the system without air, compared to the air-supplied system. Some small fluctuations were observed and the degradation brought to a halt after the trapped air was fully consumed (Fig. 4). This illustrate that air supply is crucial for the photocatalytic degradation process of AR1.

3.3. Effect of ZnO catalyst loading

Theoretically, the degradation of acid dye will increase with an increase in catalyst loading; this is due to the increase of the number of active sites available in the system. But the over dosage of the catalyst will reduce the degradation rate of the system as the excess catalysts may screen it from light and hence reduce the photocatalytic potentiality of the catalyst. Therefore, the determination of the optimum catalyst loading is very important. From the results (Fig. 5), it can be seen that 0.1 g ZnO greatly enhanced the degradation of AR1 dye.

When the catalyst loading was increased from 0.1 g to 0.25 g and 0.5 g ZnO, there was a significant increment in the degradation rate. Further increment in the
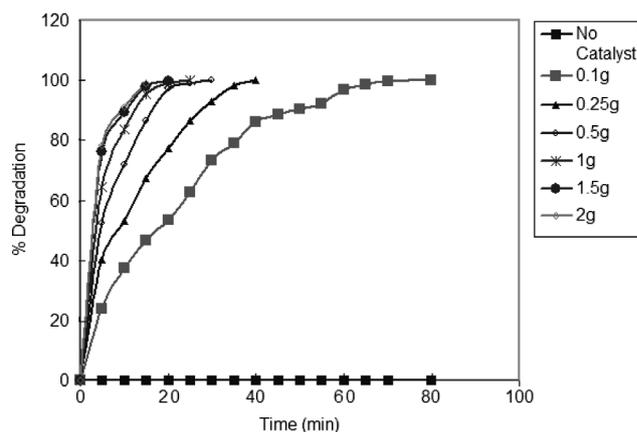
catalyst loading from 0.5 g to 1.0 g, 1.5 g and 2.0 g did not show any significant increase in the degradation rate of the dye. The initial increase in the degradation rate may be due to the increase of the active sites in the system, and as it tends to saturation, the excess catalysts in the system screened the catalyst from the light source and hence could no more greatly enhance its activity. The foregone leads to a conclusion that 0.5 g in 250 ml (or 2.0 g/l) of ZnO photocatalyst is the optimum for the degradation of AR1 under the set conditions.

3.4. Effect of substrate concentration

The initial concentration plays an important role in the degradation of the dye. High initial organic concentration will increase the probability at which the organic molecule binds itself to the photocatalyst surface and "closes" the active site that leads to the production of the hydroxyl radical on the catalyst surface and, hence decreased the photocatalytic activities of the photocatalyst [19]. The high dye concentration will also reduce the light penetration which will affect the UV light permeability into the dye solution, part of the light energy will be absorb by the dye molecules and, hence reduce the energy that reaches the catalyst which is necessary for the photocatalytic process [20].

Fig. 6 shows the effect of substrate's initial concentrations on the degradation of AR1. A close observation of the figure revealed that, though the percentage degradation appears to be lower at higher initial substrate concentrations, the amount of dye degraded at each irradiation time from dye substrate of higher initial concentrations is higher than those of lower initial concentrations. This, therefore, suggests that concentration on its own exerts some great deal of influence on the photodegradation of AR1.
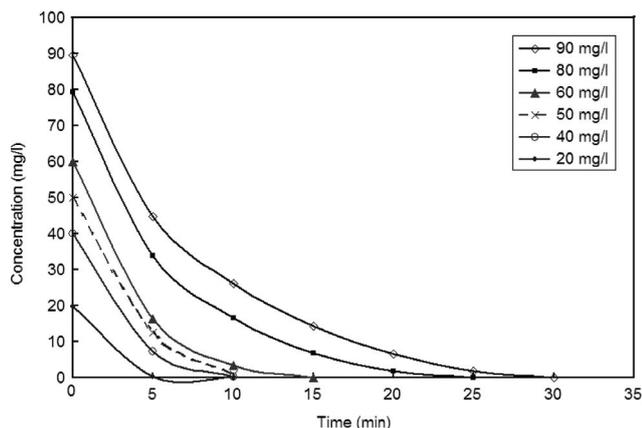
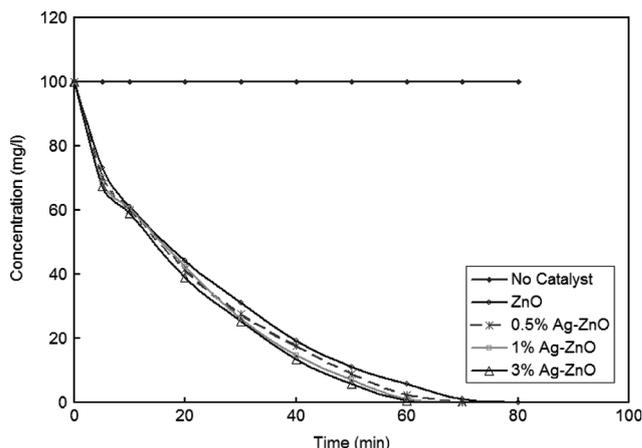Fig. 6. Effect of substrate concentration on the degradation of AR1 dye.

Fig. 8. Effect of silver doped ZnO on the degradation of AR1 dye.
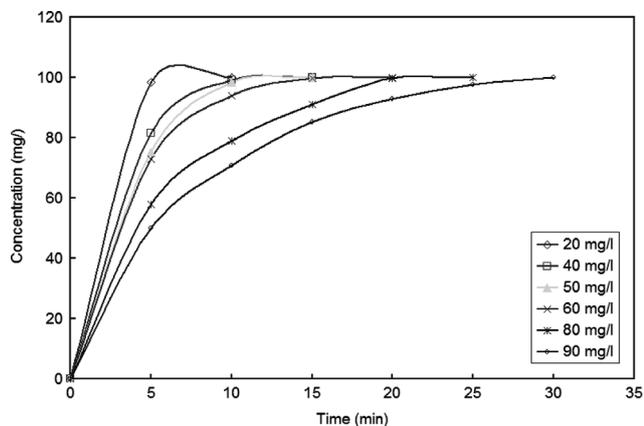

Fig. 7. Percentage degradation of AR1 dye as affected by substrate's initial concentration.

On the other hand, when percentage degradation is followed as a measure of the degradation, dye of low initial concentrations have higher percentage degradation at each irradiation times than those of higher initial concentrations (Fig. 7), and appears to be faster than the other.

3.5. Effect of silver on ZnO photocatalyst

Noble metal is believed, can improve the charge transfer and consequently the degradation process. The amount of silver doped on the ZnO surface will directly affect the performance of the degradation of the organic compounds [21]. If small amount of noble metal was doped on ZnO surface, it will only slightly reduce the energy gaps between the oxygen and the electron, but when too much of the noble metal is doped on ZnO, it will decrease the electron energy band below oxygen energy band which will increase the difficulties to

capture the photo-induced electron. In the present study, the effect of silver ions on ZnO photocatalyst was investigated. The results obtained depicted that doping ZnO with silver ions did not show much enhancement on the photocatalytic activity of the ZnO catalyst as there was a very minute increase in its activity in comparison with the undoped ZnO (Fig. 8). It is clear from Fig. 8 that there was a very minimal increase in the activity of the ZnO-photocatalyst doped with as high as 3% Ag+.

The results of this investigation are not in isolation from the findings of other researchers. In the studies of Colmenares et al. [22], Ag+ did not significantly enhance the photocatalytic efficiency of TiO_2. Though TiO_2 is a different semiconductor from ZnO, other metals ions are reported to have influenced its activity positively. Therefore, bringing together the results obtained in the present study with that of Colmenares et al. [22], it is clear that Ag+ does not significantly enhance the photocatalytic efficiency of these semiconductors.

4. Conclusion

Photocatalytic degradation of AR1 dye has been studied under the presence of photocatalyst ZnO by varying several other parameters such as present and absent of photocatalyst, UV light, air, catalyst loading, initial substrate concentration, and effect of silver doping. To have any degradation at all, air, photocatalyst, light and agitation must be provided to the photoreactor. From the results obtained, zinc oxide proved to be a very good photocatalyst in the degradation of AR1 dye. Doping ZnO with Ag+ does not significantly enhance the photocatalytic potentials of the pure ZnO in the degradation of AR1.

Acknowledgement

References

[1] E. Metcalf, Wastewater Engineering, Treatment and Reuse, McGraw Hill, 4th ed., 2004.

[2] G. Hamer, Solid waste treatment and disposal: effects on public health and environmental safety. Biotechnol. Adv. 22 (2003) 71–79.

[3] C. Lubello and R. Gori, Membrane bio-reactor for textile wastewater treatment plant upgrading. Water Sci. Technol., 52(4) (2005) 91–98.

[4] M.S.C. Leda, J.A. Helton, A.A.d.S. Onelia and M.M.C. Creusa, Discoloration And Degradation of Textile Dye Aqueous Solutions with Titanium Oxide Catalysts Obtained by The Sol gel Method. Dyes Pigments, 76 (2008) 525–529.

[5] F. Banat, S. Al-Asheh, R. Zomaout, B. Qtaishat, T. Alateat and S. Almayta, Photodegradation of methylene blue dye using bentonite as a catalyst. Desalin. Water Treat., 5 (2009) 283–289.

[6] C.C. Chen, A.J. Chaudhary and S.M. Grimes, The Effect Of Sodium Hydroxide In Photolytic And Photocatalytic Degradation of Acid Blue 29 and Ethyl Violet. Dyes Pigments, 73 (2007) 55–58.

[7] K.L. Karen and L. Michael, Textile Process Wastewater Permits: An Update and Strategies, American Dyestuff Reporter, 1994.

[8] L.G. Devi, S.G. Kumar, K.M. Reddy and C. Munikrishnappa, Effect of various inorganic anions on the degradation of Congo Red, a di azo dye, by the photo-assisted Fenton process using zero-valent metallic iron as a catalyst. Desalin. Water Treat., 4 (2009) 294–305.

[9] B. Pare, S.B. Jonnalagadda, H. Tomar, P. Singh and V.W. Bhagwat, ZnO Assisted Photocatalytic Degradation Of Acridine Orange in Aqueous solution using visible irradiation. Desalination, 232 (2008) 80–90.

[10] C.H. Wu, H.W. Chang and J.M. Chern, Basic Dye Decomposition Kinetics in A Photocatalytic Slurry Reactor. J. Hazard. Mater., 137 (2006) 336–343.

[11] C. Guillard, J. Disdiera, J.M. Herrmanna, C. Lehautb, T. Chopinb, S. Malatoc and J. Blancoc, Comparison of various titania samples of industrial origin in the solar photocatalytic detoxification of water containing 4-chlorophenol. Catal. Today, 54 (1999) 217–228.

[12] N.M. Mahmoodi, M. Arami and K. Gharanjig, Laboratory studies and CFD modeling of photocatalytic degradation of colored textile wastewater by titania nanoparticles. Desalin. Water Treat., 1 (2009) 312–317.

[13] A. Mills and L. Hunte, An overview of semiconductor photocatalysis. J. Photochem. Photobiol. A: Chem., 108 (1997) 1–35.

[14] U.G. Akpan and B.H. Hameed, Parameters affecting the photocatalytic degradation of dyes using TiO_2-based photocatalysts: A review. J. Hazard. Mater., 170 (2009) 520–529.

[15] O. Carp, C.L. Huisman and A. Reller, Photoinduced reactivity of titanium oxide photoinduced reactivity of titanium oxide. Solid State Chem., 32 (2004) 33–177.

[16] N. Sobana and M. Swaminathan, Nano-Ag Particles Doped TiO_2 for Efficient Photodegradation of Direct Azo Dyes. Sep. Purif. Technol., 56 (2007) 101–107.

[17] G. Zhou, J.C. Deng, Preparation of Ag/ZnO nano-composites. Mater. Sci. Semiconduct. Proc., 10 (2007) 90–96.

[18] M.J. Height, S.E. Pratsinis, O. Mekasuwandumrong and P. Praserthdam, Ag-ZnO catalysts for UV-photodegradation of methylene blue, Appl. Catal. B: Environ., 63 (2006) 305–312.

[19] M.A. Behnajady, N. Modirshahla and R. Hamzavi, Kinetic study on photocatalytic degradation of C.I. Acid Yellow 23 by ZnO photocatalyst. J. Hazard. Mater., B133 (2006) 226–232.

[20] M. Saquib, T.M. Abu, M.M. Haque and M. Muneer, Photocatalytic Degradation of Disperse Blue 1 Using $UV/TiO_2/H_2O_2$ process. J. Environ. Manag., 88 (2008) 300–306.

[21] L.Q. Jing, D.J. Wang, B.Q. Wang, S.D. Li, B.F. Xin, H.G. Fu and J.Z. Sun, Effects of noble metal modification on surface oxygen composition, charge separation and photocatalytic activity of ZnO nanoparticles. J. Mol. Catal. A: Chem., 244 (2006) 193–200.

[22] J.C. Colmenares, M.A. Aramendia, A. Marinas, J.M. Marinas and F.J. Urbano, Synthesis, characterization and photocatalytic activity of different metal-doped titania systems. Appl. Catal. A: Gen., 306 (2006) 120–127.