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## Photocatalytic Activity under Solar Irradiation of Silver and Copper Doped Zincoxide: Photodeposition Versus Liquid Impregnation Methods

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**Abstract:** In this study, silver and copper doped zinc oxide photocatalysts were synthesized simply by Liquid Impregnation (LI) and Photo Deposition (PD) methods. The photocatalytic activities under solar irradiation for commercial azo dye degradation were observed. The photocatalysts with 0.5, 1.0, 1.5 2.0 and 2.5 % (mole ratio) metal versus ZnO was prepared. The photodegradation rates of the dye were estimated from the residual concentration at variable time detected by UV-Vis spectrophotometer. The experimental result shows that the Ag doped ZnO synthesized by PD method possess the highest photocatalytic activity while Cu doped ZnO synthesized by LI method has the reverse. The catalyst synthesized by PD method possesses more activity than another. The metal ion ( $\text{Ag}^+/\text{Cu}^{2+}$ ) doped on ZnO acting as electron consumer leading to the lowering photocatalytic activity of the LI metal doped ZnO. The photocatalytic activity of all metal doped ZnO is in similar trend which increasing from 0.5-1.5 % mole ratio and decreasing afterward.

**Key words:** Photocatalytic degradation, textile dye, metal doped ZnO, photodeposition, liquid impregnation

### INTRODUCTION

To now, environmental problems such as air, soil and water pollution have provided the motivation for research in the area of environmental treatment. One of the most serious cause of water problem is from textile industries where produced a large volume of colored dye effluents. Most of the dyes used in dyeing are synthetic, toxic and non-biodegradable. Both physical and chemical processes such as precipitation, adsorption, flocculation, reverse osmosis and ultra-filtration were applied to remove these toxic substances in wastewater from production process before releasing to environment. However, these techniques are non-destructive process which the toxic substances are only removed and transferred. So, the new type of pollution is rise and further treatment has also provided (Arslan *et al.*, 2000; Chaudhuri and Sur, 2000; Stock *et al.*, 2000).

Recently, photocatalytic techniques have been attracted much attention to be one of the most interesting processes for wastewater treatment because of many advantages over other traditional techniques such as convenient handle, quick and low concentration (ppb level) oxidation and none of high toxic products i.e., polycyclic aromatic compound are observed after photocatalytic process has reached. The photocatalytic treatment for wastewater has been widely reported (Qaradawi and Salman, 2002; Wang *et al.*, 2004; Liu *et al.*, 2005, 2006; Baiocchi *et al.*, 2002; Kansal *et al.*, 2007;

Bianco Prevot *et al.*, 2004; Rizzo *et al.*, 2009; Giraldo *et al.*, 2010; Lin and Lee, 2010; Selli *et al.*, 2008; Sanchez *et al.*, 2011; Son *et al.*, 2009; Petrik and Kimmel, 2010; Elmolla and Chaudhuri, 2010; Yang *et al.*, 2008).

$\text{TiO}_2$  as well as ZnO have been considered as the promising photocatalyst due to their high photocatalytic activity, photo-stability, wide-band gap and less toxic. The quantum efficiency of ZnO is significantly higher than that of  $\text{TiO}_2$  (Mai *et al.*, 2008). The better activity of ZnO than  $\text{TiO}_2$  was reported in some cases (Chen, 2007). The ZnO-mediated photocatalytic process has been successfully used to organic pollutant degradation (Height *et al.*, 2006; Akyol *et al.*, 2004). Due to it is available at low cost and absorbs over larger fraction of the solar spectrum than  $\text{TiO}_2$  (Christoskova and Stoyanova, 2001), thus ZnO is considered as suitable material for photocatalytic degradation of organic pollutants than  $\text{TiO}_2$ . However, many studies have been reported the photocatalytic activity of  $\text{TiO}_2$  photocatalyst for either dye degradation or antimicrobial activity (Fatimah *et al.*, 2009; Zulfakar *et al.*, 2011; Qourzal *et al.*, 2006; Tchatchueng *et al.*, 2009; Desai and Kowshik, 2009). Previous studies have reported the photodegradation of organic pollutants by ZnO (Mansilla *et al.*, 1994; Ohnishi *et al.*, 1989; Peralta-Zamora *et al.*, 1998; Richard *et al.*, 1997) and removal of color from landfill by solar photocatalytic system by using ZnO photocatalyst was also reported (Makhtar *et al.*, 2010).

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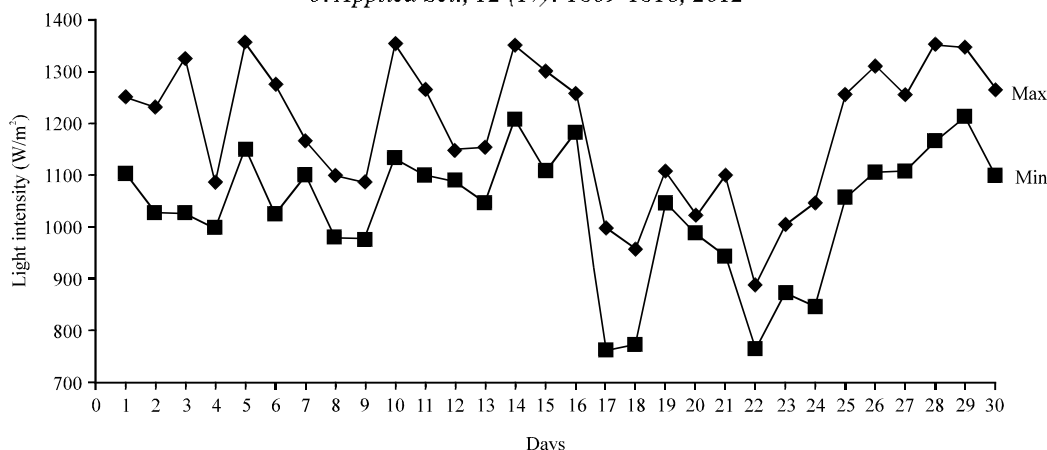


Fig. 1: Solar irradiation pattern of the month of December 2011

However, the main problem for the photocatalytic process is due to the fast recombination of the electron-hole pairs. This situation is a cause of decreasing of photocatalytic activity of the photocatalyst. Doping of transition metals on the photocatalyst surface (Wood *et al.*, 2001; Stroyuk *et al.*, 2005) as well as coupling of two photocatalysts can improve the charge-transfer and photocatalytic activity. In this study, the photocatalytic degradation of reactive synthetic dye using Ag and Cu doped ZnO photocatalysts synthesized by convenient photodeposition and liquid impregnation methods were reported. The photodegradation efficiency, kinetics as well as rate constants related to the loading contents of metals on ZnO were reported.

### MATERIALS AND METHODS

**Materials:** The commercial azo anionic dye, C.I acid red 142 (C.I. No. 6406-66-2) is a model of organic dye pollutant for textile industry. ZnO powder (analytical grade) was purchased from RFCL limited, the analytical grade AgNO<sub>3</sub> and Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O were purchased from Merck and QR&C companies, respectively.

#### Preparation of silver doped ZnO photocatalyst

**Liquid impregnation method:** The silver doping on ZnO by LI method was prepared in this following step. Firstly, 3 g of ZnO was added to 100 mL deionized water. The amount of AgNO<sub>3</sub>/Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O with 0.5, 1.0, 1.5 2.0 and 2.5% (mole ratio) versus ZnO was required to add into ZnO slurry. The slurry was stirred well and rest for 24 h (performed in darkness) and then dried in an air oven at 100°C for 12 h. the dried solids were grounded in an agate mortar and calcined at 600°C for 6 h in a furnace.

**Photodeposition method:** For PD method, 3 g of ZnO was added to 100 mL deionized water. The amount of AgNO<sub>3</sub>/Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O with 0.5, 1.0, 1.5, 2.0 and 2.5%

(mole ratio) versus ZnO was required to added into ZnO slurry. The slurry was stirred well under solar irradiation for 3 h and then dried in an air oven at 100°C for 12 h. The dried solids were grounded in an agate mortar and calcined at 600°C for 6 h in a furnace.

**Photocatalytic activity under solar radiation:** For the photocatalytic degradation of acid red 142 dye, a 1 ppm dye solution containing 1 g of different types of metal doped and undoped ZnO were prepared and agitated for 30 min in darkness. A 100 mL of the solution mixture was transferred into the batch reactor. The reaction was initiated when the solution mixture was exposed to the solar irradiation. The solution was stirred well during the reaction progress. The residual of the dye in solution was measured by the absorption at 620 nm by UV-Vis spectrophotometer (T80+model UV-Vis spectrophotometer, PG Instruments Ltd). The degradation efficiency is calculated using the following equation:

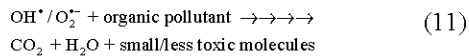
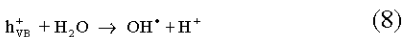
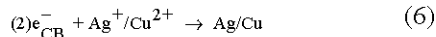
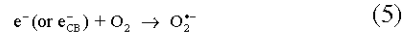
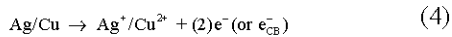
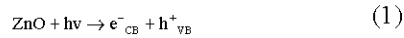
$$\text{Degradation rate (\%)} = \frac{C_0 - C}{C_0} \times 100 = \frac{A_0 - A}{A_0} \times 100$$

where, C<sub>0</sub> and C represent the initial and variable concentrations while A<sub>0</sub> and A are initial and variable absorbance, respectively. Concentration of the dye remaining in solution was received from the standard curve.

**Solar irradiation condition:** Due to performing under solar condition, the solar irradiation pattern was monitored in the month of December 2011 from 10.00 a.m. to 3.00 p.m. The solar light intensity was measured by Lux-UV-IR meter (LX-72, DIGICON). The solar light intensity was recorded on every reaction time during experiment performed as shown in Fig. 1. The radiation of more than 1000 W m<sup>-2</sup> was recorded on all the experimental days. The experiments were not carried out on the days with solar intensity of less than 1000 W m<sup>-2</sup>.

**RESULTS AND DISCUSSION**

The photocatalytic process of the metal doped (Ag/Cu) ZnO is represented in Fig. 2. The photocatalytic mechanism of Ag/Cu doped ZnO can be proposed as follows (Chen *et al.*, 2008; Zheng *et al.*, 2007; Wang *et al.*, 2007):



The basis of photocatalytic activity of Ag/Cu doped ZnO can be summarized that; (1) ZnO acts as an electron and hole sources (Eq. 1) for degradation of dye. The electron in Valence Band (VB) was excited to conduction band by UV light with equal or higher energy than energy band gap of ZnO leading to simultaneous generation of a hole (h<sup>+</sup>) in VB, (2) oxygen vacancy defects (V<sup>\*</sup><sub>o</sub> and V<sup>\*</sup><sub>o</sub> in Eq. 2, 3) and Ag/Cu nanoparticles on the ZnO surface act as a sink for electron and improve of the electron-hole pair separation generated in Eq. 1, (3) photoelectron can be easily trapped by acceptors such as molecular oxygen forming superoxide radical anion (O<sup>·-</sup><sub>2</sub>) as shown in Eq. 5, (4) The photoinduced hole can be easily trapped by OH<sup>-</sup> as well as H<sub>2</sub>O to produce OH<sup>·</sup> (Eq. 7, 8), (5) The generated O<sup>·-</sup><sub>2</sub> can react with H<sub>2</sub>O forming H<sub>2</sub>O<sub>2</sub> and then reacts with forming OH<sup>·</sup> (Eq. 9, 10) and (6) The overall photocatalytic reaction is due to the oxidation reaction between these generated reactive oxygen species

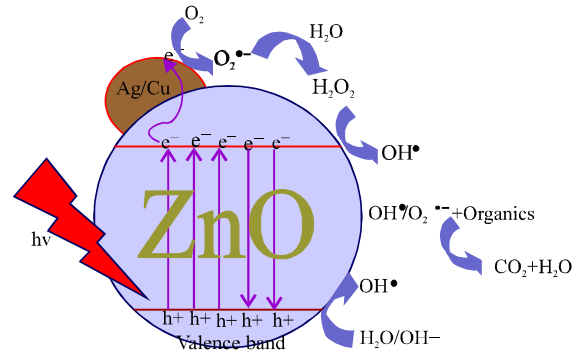


Fig. 2: Mechanism of photocatalytic process of Ag/Cu doped ZnO under solar irradiation

(O<sup>·-</sup><sub>2</sub> and OH<sup>·</sup>) and pollutant i.e., synthetic dye (Eq.11). The enhancement of photocatalytic activity based on metal doping ZnO is depend upon the additional rate of O<sup>·-</sup><sub>2</sub> and OH<sup>·</sup> formations (Eq. 3, 5,1 0). In addition, the rate of electron transfer from VB of ZnO to deposited Ag/Cu should also be faster than those of electron-hole pair recombination. The photocatalytic activity as well as key mechanism concerning to the photocatalytic process of Ag doped ZnO has been observed and proposed (Zhang, 2011). It has been concluded that Ag particle deposited on ZnO surface acting as electron traps to effectively separate the excited electron-hole pairs. This can be supported the mechanisms presented above.

**Effect of Ag and Cu doping on photocatalytic activity of ZnO:** The photocatalytic activity of undoped and metal doped ZnO was carried out without adjustment of pH. The photodegradation of acid red 142 in the presence of undoped and metal doped ZnO powder under solar radiation versus irradiation time was shown in Fig. 3. As can be seen, the Ag doped ZnO synthesized with both PD and LI methods are generally more efficient in photodegradation of the dye than Cu doped ZnO. The metal doped ZnO with PD is more effective than those of LI method. In a period of initial to 1 h, all metal doped ZnO showed percentage photodegradation of the dye higher than those of the undoped one except for 1.5:1 and 2:1 LI Cu dope ZnO but in a reverse afterward except for PD Ag doped ZnO. It can be noted that the metal doping can accelerate the photocatalytic activity of ZnO within 1 h of photocatalytic experiment. The different photocatalytic activity of the metal doped ZnO synthesized by the two methods can be ascribed in term of oxidation state of the metals. During the preparation process by PD method, the Ag<sup>+</sup> and Cu<sup>2+</sup> were reduced to Ag and Cu but on the other

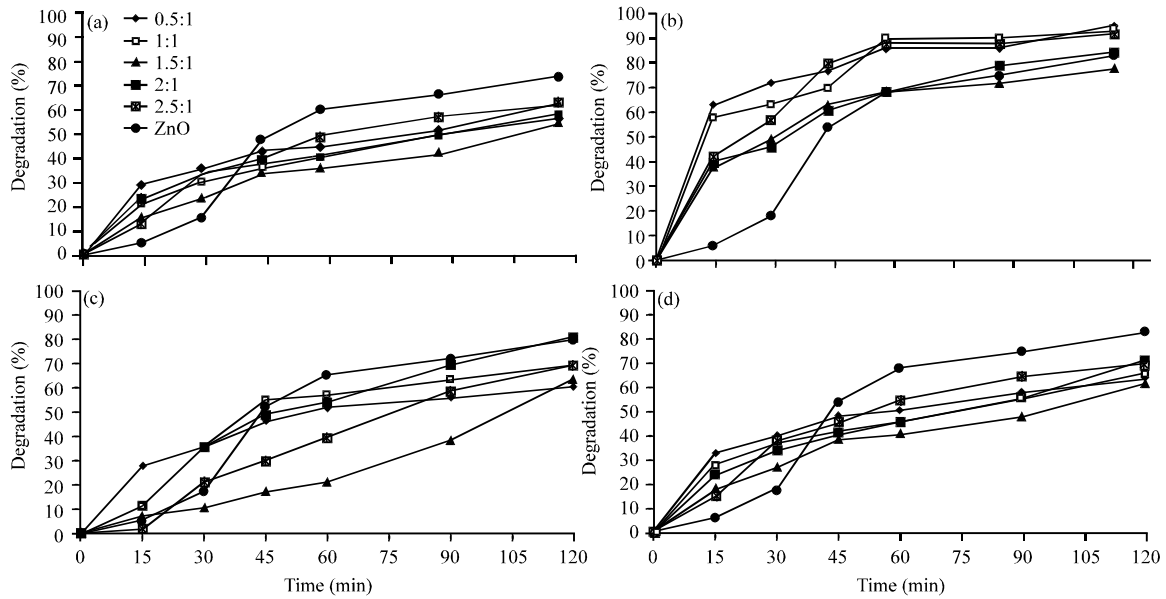


Fig. 3: Percent degradation of acid red 142 by, (a) LI Ag doped, (b) PD Ag doped, (c) LI Cu doped and, (d) PD Cu doped ZnO

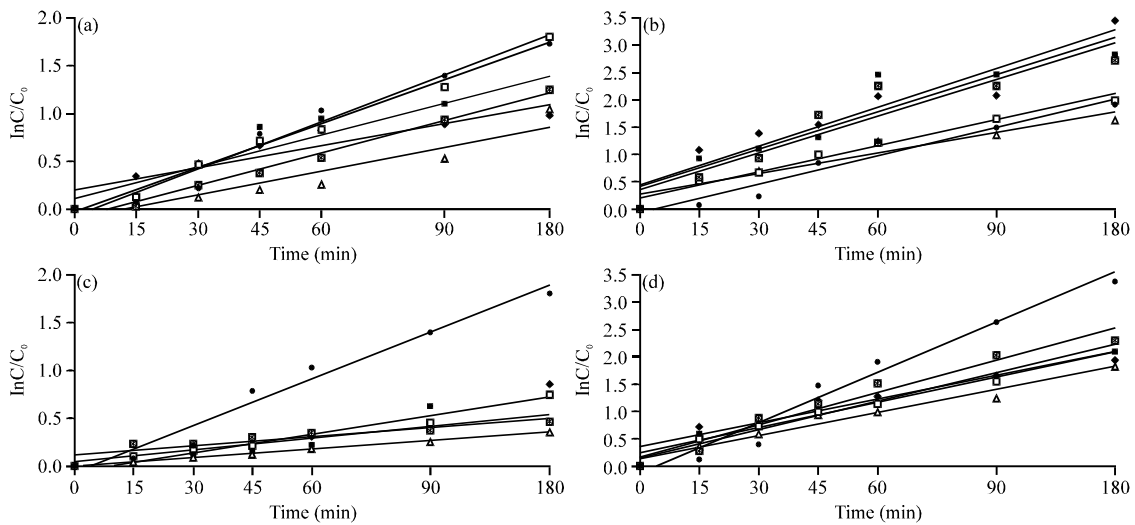


Fig. 4: Pseudo-first-order kinetics for photodegradation of acid red 142 by (a) LI Ag doped (b) PD Ag doped (c) LI Cu doped and (d) PD Cu doped ZnO.

hand,  $\text{Ag}^+$  and  $\text{Cu}^{2+}$  were deposited directly on the ZnO surface by LI method. The deposited  $\text{Ag}^+$  and  $\text{Cu}^{2+}$  consumes electron during the photocatalytic process leading to the decreasing of photocatalytic activity of metal doped LI ZnO. This can be stated that the electron transfers from ZnO to  $\text{Ag}^+$  or  $\text{Cu}^{2+}$  is rather fast regarded to the electron transfer to the dissolved oxygen molecules, so therefore the formation of  $\text{O}^{\cdot -}_2$  is reduced (Szabo-Bardos *et al.*, 2003).

Based on the Ag doped PD method, the best photocatalytic activity in comparison to undoped ZnO

was found. This indicated that the electron-hole pair charge recombination was competed with the electron transfer for ZnO to Ag atom. In case of Cu doping, both PD and LI Cu doped ZnO powders possess a little bit higher photocatalytic activity in comparison to undoped one. Consider of the standard reduction potential,  $\text{Cu}^{2+}$  requires 0.15 V while  $\text{Ag}^+$  requires only 0.80 V to form their zero oxidation states. The doping of Cu based on PD method is lesser completed than those of Ag, therefore  $\text{Cu}^+$  may be mostly deposited instead of Cu atom leading to decreasing of photocatalytic activity. It can be noted

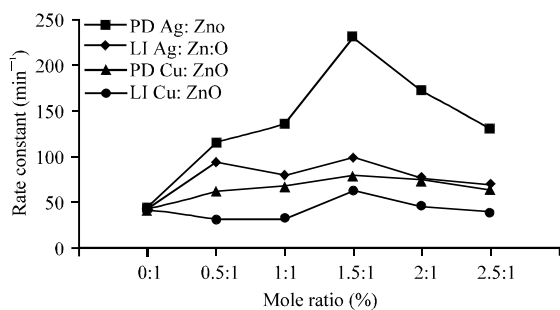


Fig. 5: The rate constants based on pseudo-first-order kinetics for photodegradation of acid red 142 by metal doped ZnO versus mole ratio of metal loading

that the deposition of metal ion ( $\text{Ag}^+/\text{Cu}^{2+}$ ; LI method) affected negatively to the photocatalytic activity of ZnO compared to another one ( $\text{Ag}/\text{Cu}$ ; PD method) because the ions act as electron consumer instead of electron donor.

**Kinetics of photodegradation:** Kinetics of photodegradation of the dye by all metal doped and undoped ZnO assumed to be pseudo-first-order reaction indicated by the strength line of the plot between  $\ln C_0/C$  and irradiation time as shown in Fig. 4. Based on the strength line, rate constant can be calculated and the relationship between rate constants and mole ratio of metal doping are plotted in Fig 5. It was found that all metal doped ZnO has pseudo-first-order kinetic rate constant generally higher than those of the undoped ZnO. The low rate constant  $43 \text{ min}^{-1}$  was found for undoped ZnO due to its slowly initial reaction. It can be seen that Ag and Cu contents loading on ZnO surface have the maximum value of 1.5% for both Ag and Cu doped ZnO. The rate constant of photodegradation of the dye by Ag and Cu doped ZnO is increasing up to 1.5:1 mole ratio then decreasing afterward. The highest rate constant ( $\sim 250 \text{ min}^{-1}$ ) was found in PD 1.5:1 Ag doped ZnO. Based on 1.5:1 mole ratio metal: ZnO, the kinetic rate ( $\text{min}^{-1}$ ) for all metal doped ZnO are in decreasing order: PD Ag (246) > LI Ag (98) > PD Cu (78) > LI Cu (54). The effect of Ag and Cu doping on ZnO photocatalytic activity may be caused from several reasons as previously discussed for Ag doped  $\text{TiO}_2$  (Behnajady *et al.*, 2008), Excessive coverage of metals on ZnO limits the light reaching to ZnO surface, reducing the number of photogenerated electron-hole pairs, leading to the decreasing of ZnO photocatalytic activity (Carp *et al.*, 2004). Negatively charge metal sites have attracted holes and subsequently recombined with electrons, therefore the negatively charge Ag/Cu sites are the charge

recombination center (Carp *et al.*, 2004). Metals may occupy the active site on ZnO surface for a desired photocatalytic reaction, causing of losing photocatalytic activity of metal doped ZnO (Coleman *et al.*, 2005). The probability of the hole capture is increased by a large number of metal particles at high content loading, in this case the probability of holes reacting with the adsorbed species i.e.  $\text{H}_2\text{O}$  or  $\text{H}_2\text{O}_2$  is decreased (Sobana *et al.*, 2006).

Previously, porous Ag doped ZnO microrods were synthesized and photocatalytic activity over methyl orange degradation observed (Jia *et al.*, 2012). It was found that 3% (mole fraction) of Ag loaded on ZnO reached the highest activity. Similarly, photodegradation of methyl orange by Ag doped ZnO with 65% dye removal achieved within 100 min was observed (Zhang and Zeng, 2010). The Ag loaded ZnO photocatalyst with 3% Ag loading was observed and possessed the highest rate of rhodamine 6G degradation (Geofgekutty *et al.*, 2008). The 0.5% Ag loaded ZnO possessed the highest rate of photocatalytic activity for AR88 textile dyes degradation has been observed (Behnajady *et al.*, 2009). Ag doped ZnO with precursor zinc nitrate hexahydrate by applying hybrid induction and laser heating techniques has been synthesized and determined its activity for DBP degradation (Qi *et al.*, 2011). Thus, it can be noted that the photocatalytic activities of various% Ag doped ZnO is depended upon the methods of synthesis and starting reagents. In addition, Ag doped ZnO- $\text{SnO}_2$  co-catalyst has been also shown the better photocatalytic activity than those of the undoped ZnO- $\text{SnO}_2$  at photocatalytic degradation of AR27 dyes (Behnajady *et al.*, 2010).

## CONCLUSION

The Ag and Cu doped ZnO powders were synthesized simply by two methods; photodeposition and liquid impregnation with 0.5, 1.0, 1.5 2.0 and 2.5% mole ratio (metal:ZnO). The metal doped ZnO synthesized by PD method possesses more photocatalytic activity than those by LI method. The decreasing photocatalytic activity of the LI metal doped ZnO due to the consumption of electron by the deposited metal ions during the photocatalytic process. However, generally, all metal doped ZnO shows the pseudo-first-order kinetic rate of photocatalytic degradation higher than those undoped ZnO except for 0.5:1 and 1:1 LI Cu doped ZnO. The photocatalytic activity of metal doped ZnO is increased from 0.5 to 1.5% mole ratio and decreased afterward. It can be stated by several reasons as described in the results and discussion part.

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