

Cu-ZnO nanoparticles for photocatalytic degradation of methyl orange

Raviraj M. Kulkarni, Ramesh S. Malladi*, Manjunath S. Hanagadakar

Department of Chemistry, KLS Gogte Institute of Technology (Autonomous) Affiliated to Visvesvaraya Technological University, Belagavi-590 008, Karnataka, India.

*Corresponding author

DOI: 10.5185/amp.2018/7016

www.vbripress.com/amp

Abstract

Photocatalytic degradation of textile dye derivative Methyl Orange (M.O) has been studied in aqueous medium using 2% copper doped zinc oxide (2% Cu-ZnO) nanoparticles under UV irradiation. Simple inexpensive chemical precipitation method was used for synthesis of pure and copper doped zinc oxide nanoparticles. The prepared nanoparticles pure and copper doped zinc oxide was characterized by X-ray Diffraction Technique (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analysis. The prepared nanoparticles were hexagonal wurzite structure. Photocatalytic efficiency of 2% Cu-ZnO were evaluated by studying mineralization of methyl orange (M.O.) as a model compound. The M.O. kinetics degradation was investigated under different parameters such as pH of the medium, catalyst dosage, M.O concentration, intensity of light etc. In addition reusability aspects of nanoparticles were also studied, which reveals that reused nanoparticles exhibited same results as that of virgin particles. Copyright © 2018 VBRI Press.

Keywords: Photocatalysis, degradation, methyl orange, ZnO, doping.

Introduction

Air and Water contamination are the two major problems affecting the environment. Due to waste pollutants released by households and industries. Detoxification and cleansing of water and air has become the main centre of today's scientific study. The major origin of air and ground-water contamination is the industrial pollutants (minute quantity), excessive disposal of pesticides, domestic waste, landfills and fertilizers (agrochemicals). These non-degradable organic contaminants are not efficiently treated by biological treatment methods or conventional treatment methods [1].

Textile industries generate huge amount of color recalcitrant which are hazardous and non-biodegradable. These coloring matters generate several ecological problems by discharging waste materials into the water system [2].

Advanced Oxidation Processes (AOPs) are most widely used to treat toxic persistent organic pollutants present in aqueous environment. The conventional and biological methods are not efficient in the treatment of persistent organic contaminants and may produce hazardous byproducts. AOPs involve direct formation of hydroxyl (OH·) radical, that degrade a plenty of organic pollutants present in water [3] using chemical or light energy.

Heterogeneous photocatalysis believed to have considerable potential for appliances relating the degradation of untreated recalcitrant's. In this method, when a photocatalyst particle is exposed by suitably

energetic illumination (< 388 nm) $e^- - h^+$ couple are generated. This $e^- - h^+$ couple transfers to the photocatalyst surface and react with adsorbed dye molecules to give CO_2 , H_2O , [4]. However the major disadvantage of the heterogeneous photocatalysis is quick recombination of the $e^- - h^+$ couple. To avoid recombination of $e^- - h^+$ couple the metal oxides are doped with d-block elements such as Ru, Pt, Ag, Cu etc., which decrease the band gap as well as enhance the charge-separation of photocatalyst [5].

The ZnO nanoparticle has been widely used photocatalyst. ZnO is believed to be an appropriate substitute to TiO_2 (3.2eV), due to their broad energy gap (3.3eV), low cost, greater efficiency, stability with a high excitation binding energy, sufficient in environment and eco-friendly and the above characteristics makes the material to attract and potentially useful for a wide range of applications[6]. Its photo-degradation mechanism similar to that of titanium dioxide has been confirmed. In recent years, ZnO or doped ZnO nanoparticles were synthesized by various methods.

Decorating ZnO with impurity/dopant (transition metal ions) improves the optical, electrical, magnetic properties by changing its electronic structure and showing other enhancement in the different application like photoreaction and photocatalytic activity. These transition metal ions not only served as trapping sites, it also reduces charge re-combination and to facilitate interfacial electron transfer process that in turn enhance the surface reactivity. Doping also induce the widening of wavelength from UV to the visible-range [7-8].

In this paper we report, photocatalytic degradation of reactive synthetic dye methyl orange (M.O.) using 2% Cu doped ZnO photocatalyst synthesized by inexpensive simple precipitation method. Synthesized nano-crystals were analysed by analytical techniques such as XRD, SEM, and EDX. The photo-degradation efficiency, kinetics as well as rate constants related to the catalyst concentration, pH, substrate variation, and intensity variation on 2% Cu-ZnO were investigated.

Experimental

Chemicals and methods

Analar grade CLP was procured from Sigma-Aldrich, Bangalore. It is used as received without additional purification. A stock solution of M.O. was prepared by dissolving a known quantity of powder in deionized water. The $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, NaOH and $\text{Cu}(\text{NO}_3)_2$ procured from HIMEDIA. The acetate, phosphate, and borate buffers were prepared to maintain pH during reaction condition, all reagents and chemicals were used are analytical grade.

Instruments used

1. A CARY 50 Bio UV-Vis Spectrophotometer (Varian BV, The Netherlands) was used for kinetic study.
2. A photo-reactor with mercury lamp (PHILIPS, TUV 8W T5, $E_{\text{max}} = 254 \text{ nm}$) was used for degradation study.
3. An optical power meter (Newport 2936 – C) was used for measurements of UV light intensity.
4. Elico pH meter (LI 120) was used for pH measurements.
5. For characterization of nanoparticles, a Siemens X-ray Diffractometer (Cu source) (XRD) AXS D5005 was used to identify the particle size of the doped TiO_2 .
6. The surface morphologies were examined using a Scanning electron microscope (SEM) JEOL JSM 6360.

Photo catalyst preparation

For synthesizing undoped and copper doped ZnO, 0.1M zinc nitrate salt was dissolved in deionized water and 10 mg l^{-1} of sodium dodecyl sulphate (surfactant) was added to control particle size, and serves as a capping agent during preparation of zinc nitrate solution [15]. 0.1 M NaOH solution is prepared separately in deionized water. NaOH was added drop wise with steady stirring thoroughly (2000 RPM) to zinc nitrate solution for 3 hrs. The resultant mixture was allowed to settle for overnight then suspension was decanted carefully, the residual solution was washed and filtered several time with distilled water then with ethanol to treat the impurities which are adhere to the nanoparticles. Then the suspension was dehydrated in an oven at 120°C for 3 hrs then powder is grounded in a mortar then calcined at 500°C for about 1 hr in a muffle furnace (with a heating rate about 10°C per minute).

During the drying process, complete transformation of zinc hydroxide to Zinc oxide takes place. The same procedure was followed to synthesize 2% Cu doped ZnO nanoparticles the only difference was the addition of 0.1 M copper nitrate solution in zinc nitrate solution. The copper concentration was 1 and 2 (% mole ratio). The copper when doped with ZnO nanoparticles it enters in to the interstitial position of ZnO lattice. Similar literatures were earlier reported [9].

Photocatalysis study

A known concentration of M.O and buffer mixture was kept in a pyrex beaker. A dosage of 0.1 gl^{-1} of 2% Cu-ZnO nanoparticles was added. Before illumination, the suspensions were stirred for 1hr in dark place to reach adsorption and desorption equilibrium between M.O and photocatalyst. Then, it was taken in to the photo-reactor and then kept beneath 8 W UV lamps (Philips) with a wavelength peak at 254 nm and of $4\text{mW}/\text{cm}^2$ intensity with continuous magnetic stirring. After every 10 minutes interval the solution was taken out and centrifuged at 2000 rpm for 5 min. The decrease in the concentration of M.O was monitored at 464 nm ($\epsilon = 29933 \text{ l mol}^{-1} \text{ cm}^{-1}$) using visible spectrophotometer (a CARY 50 Bio UV-Visible Spectrophotometer) and the degree of mineralization was studied.

Results and discussion

Comparison of different photocatalysts

The degree of mineralization of M.O with UV, UV/ZnO, UV/1% Cu-ZnO and UV/2% Cu-ZnO was studied. It was seen that the mineralization efficiency of M.O with UV/2% Cu-ZnO was more potential than UV, UV/ZnO and UV/1% Cu-ZnO

Influence of copper doping on ZnO was examined by using 2% (mole ratio) of copper, higher content of copper may favours separating charge-carriers effectively and hindered the re-combination of $e^- - h^+$ pairs. Hence, enhances the photocatalytic activity. The photo-degradation rate was maximum with 2% Cu-ZnO compared with UV and UV-ZnO, and UV/1% Cu-ZnO hence, further studies were carried out with UV/2% Cu-ZnO.

The % degradation efficiency of M.O was examined under similar environment by UV, UV-ZnO, UV/1% Cu-ZnO and UV/2% Cu-ZnO and % adsorption in dark was also investigated. The % degradation activity of M.O was found to be 40%, 50%, 63.5%, and 90% with UV, UV/ZnO, UV/1% Cu-ZnO and UV/2% Cu-ZnO respectively within 100 minute.

Characterization of ZnO and 1% and 2% Cu-ZnO

X-ray diffraction studies

XRD spectra of pure and copper doped zinc oxide nanoparticles at 600°C temperature as shown in Fig.1. The intense sharp peak confirmed that the synthesized samples were crystalline in nature with hexagonal wurtzite structure. It can be confirmed by the

appearance of [100] [002] [101] [102] [110] [103] [200] and [112] diffraction peaks from different lattices at angles 2θ ($10-90^\circ$). The intense peak of [101] indicates that the expansion of nanocrystal has taken place along the easy route of crystallization of zinc oxide. No additional peaks were observed which implies that the wurzite structure is not disturbed by Cu-doped ZnO. This indicates that prepared zinc oxide nanoparticles were hexagonal wurzite structure.

The mean particle sizes of synthesized nanoparticles were calculated by Debye Scherrer equation (1) taking full width half-maxima of A (101) intense line.

$$D = k \lambda / \beta \cos \theta \quad (1)$$

where “k = dimension less shape factor (0.94), Cu ($K\alpha$) = wavelength radiation of X-ray (0.154 nm). β = full width at half max. $\theta = 1/2$ diffraction angle”. The particle size of ZnO, 1% Cu-ZnO, and 2% Cu-ZnO was found to be 18.76, 38.45 and 41.12 nm respectively.

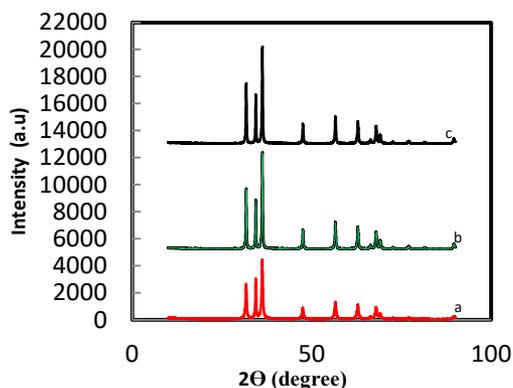


Fig. 1. XRD patterns of (a) Undoped ZnO, (b) 1% and (c) 2% Cu-ZnO.

Scanning electron microscope

To study the morphology of prepared samples, the SEM analysis of pure ZnO, 1% and 2% Cu-ZnO nanoparticles are carried out at similar magnifications (15000). These images show that the non-uniform distribution agglomerated cluster to form a pointer as shown in Figs. 2a, 2b, 2c.

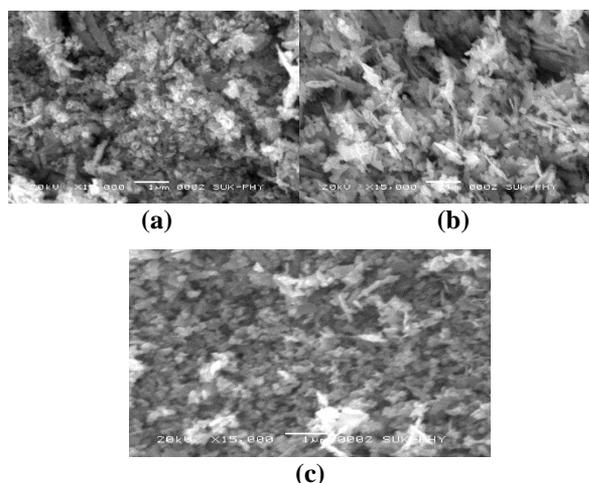


Fig.2. SEM Images of (a) Undoped ZnO, (b) 1% and (c) 2% Cu-ZnO.

Energy dispersive X-ray spectroscopy

To study the composition of prepared nanoparticles of 1% and 2 % Cu-ZnO, EDX analysis was done. Spectra shows that the existence of only three distinct X-ray spectral lines which are related with O $K\alpha$, Cu $K\alpha$, and Zn $K\alpha$. The atomic % of 1% Cu-ZnO Ti = 30.17, O = 68.76 and Cu = 1.07 and for 2% Cu-ZnO Ti = 26.71, O = 71.32 and Cu = 1.97 respectively. The spectral peaks suggest that presence of Zn, O, and Cu in the prepared nano-crystals indicating no other impurity in prepared samples by the simple precipitation method as shown in Fig. 3a and 3b.

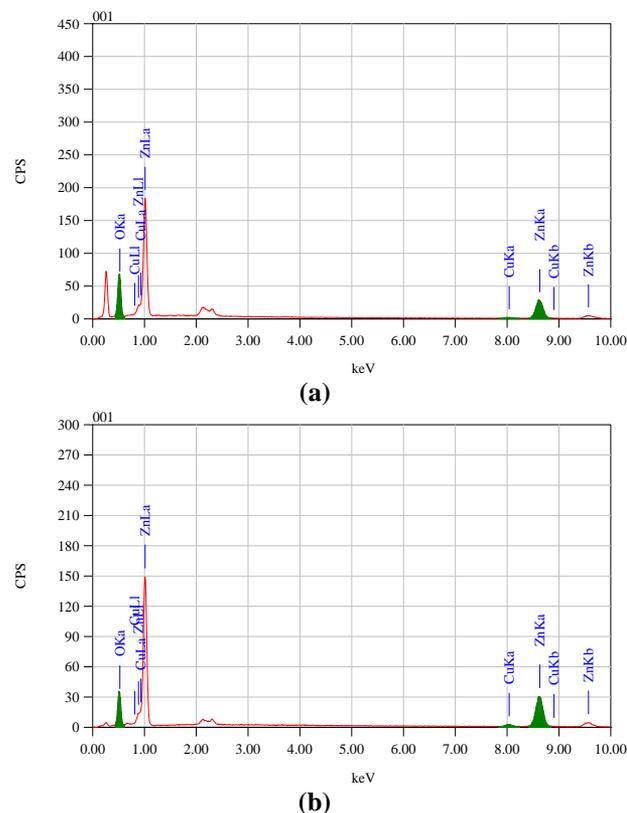


Fig. 3. EDX of (a) 1% and (b) 2% Cu-ZnO.

Effect of photocatalyst dosage

The degree of photocatalytic mineralization was investigated taking various amounts of 2% Cu-ZnO (0.025 g l^{-1} to 0.250 g l^{-1}) and keeping [M.O.] constant at $2 \times 10^{-5} \text{ mol dm}^{-3}$. The result shows that initially when amount of catalyst increased, the rate of photo-degradation also increases as shown in Fig. 4. But, when the amount of photocatalyst catalyst exceeds the optimum amount (0.1 g l^{-1}) the photo-degradation efficiency decreases. This behavior may be due to, increase in the amount of active centers on photocatalyst. In turn the rate of radical formation increases. Hence, photocatalytic rate of reaction increases initially. Whereas, at higher amount of photocatalyst above 0.1 g l^{-1} , led to increase in the turbidity of the M.O. solution, as a result the light can't reach the photocatalyst surface due to masking effect.

Hence, decrease in the rate of photo-degradation was observed [8].

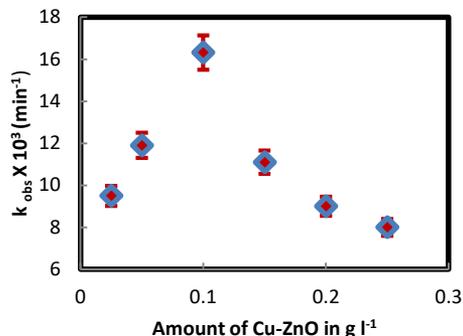


Fig. 4. Effect of different amounts of 2% Cu-ZnO photocatalyst on the degradation of M.O. at [M.O.] = 3×10^{-5} mol dm⁻³, at pH=4, light intensity = 4mW/cm².

Effect of [M.O.]

The degree of mineralization of M.O. was investigated by changing the [M.O.] from 0.5×10^{-5} to 5.0×10^{-5} mol dm⁻³ and keeping amount of photocatalyst constant (i.e. Cu-ZnO = 0.1 g l⁻¹). The degradation rate of M.O. was initially increases with increase in the [M.O.]. After 2×10^{-5} mol dm⁻³ limiting value increase in [M.O.] leads to decline in the rate constant (Fig. 5). It is due to fact that the more number of active centers on the semiconductor photocatalyst existing initially for reaction which is incredibly vital for the degradation of M.O., but as the M.O concentration increased above 2×10^{-5} mol dm⁻³ the suspension became more turbid and covers the photocatalyst surface. Hence, the light entering the solution decreased there by only less number of photons strikes the surface of photocatalyst. Hence, the formation of OH· and O₂⁻ radicals were limited. Even at higher [M.O.] the path length was further condensed and the photo-degradation was insignificant [10].

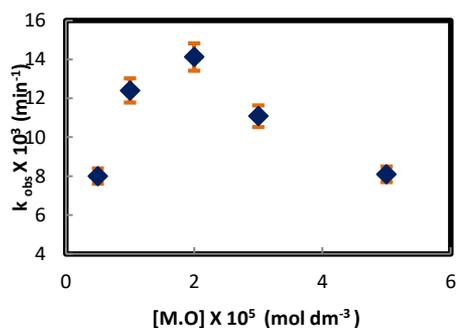


Fig. 5. Effect of of [M.O.] on photo-catalytic rate constants with 2% Cu-ZnO at 25 °C, [2% Cu-ZnO] = 0.1 g l⁻¹, at pH=4, light intensity = 4mW/cm²

Effect of pH

The degree of photocatalytic reaction rate was examined, by changing pH 4 to 9, by keeping other reaction conditions constant. Initially, when the pH of the medium increased the rate of reaction also increases. Further, increase in pH, (pH > 6) the rate of photocatalytic degradation starts decreasing as shown in

Fig. 6. This behavior may be explained on the basis of surface properties of adsorbent and adsorbate. In acidic medium the surface of a photocatalyst acts as a positive surface whereas dye molecule act as a negative ion, hence strong electrostatic force of attraction leads to strong adsorption and consequent degradation takes place hence the rate of photocatalytic degradation increases. Where as in alkaline medium photocatalyst surface acts as a negative surface and dye molecule also acts as negatively charged. Hence, the repulsion between two negatively charged species takes place. Thus, the rate of degradation of M.O decreases at higher pH value [11].

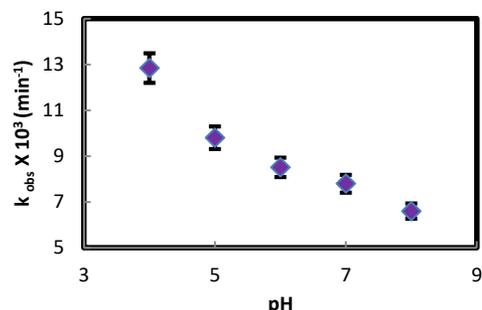


Fig. 6. Effect of pH on the rate constant of photo catalytic degradation of M.O. with 2% Cu-ZnO at 25 °C, [Cu-ZnO] = 0.1 g l⁻¹, [M.O.] = 3×10^{-5} mol dm⁻³, light intensity = 4mW/cm².

Effect of intensity of UV light

Effect of intensity of light on the degradation of rate constant of M.O. was studied by varying UV lamp distance from the target. It shows that, when UV intensity of light increases the rate of photocatalytic degradation of M.O. also increases as shown in Fig. 7. It is due to fact that, when UV- light intensity increases; the amount of photons hitting per unit area of the photocatalyst (2% Cu-ZnO) also increases. Subsequently, plenty of e⁻ – h⁺ pairs are generated; consequently the h⁺ mineralize the M.O. molecules adsorbed on the photocatalyst surface and oxidize to water. This results in effective degradation of MO [12].

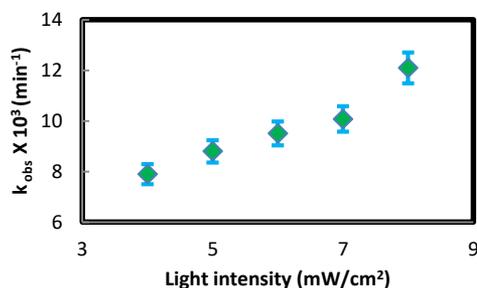


Fig. 7. M.O. degradation under different UV intensities M.O. with 2% Cu-ZnO at 25 °C, [Cu-ZnO] = 0.1 g l⁻¹, [M.O.] = 3×10^{-5} mol dm⁻³, at pH = 4.

Efficacy of reusable catalyst

The 2% Cu-ZnO nano-crystals used in the photocatalytic degradation was taken out and centrifuged at 2000 RPM, then it is washed a number of

times with deionized water and followed by ethanol, then evaporated moisture in a hot oven (30-40 °C) then taken out the white solid crushed in a mortar. Then, photocatalyst was used for next succeeding photocatalytic treatment, the marginal change after repetitive use of photo-degradation efficiency was observed [13].

Conclusion

Chemical precipitation method was used to prepare pure and Cu-ZnO nanoparticles. The XRD patterns and SEM topography shows that prepared nanoparticles were wurzite structure. The EDX analysis shows that presence of Cu in ZnO. The average particle size of 2% Cu-ZnO (20.0 to 35.0 nm) exhibited excellent achievable photo-catalytic degradation of M.O. in the acidic condition (pH 4). It was found that 2% Cu-ZnO shows the highest potential for degradation of methyl orange compare to ZnO and 1% Cu-ZnO.

Acknowledgements

We thank VGST, Bangalore for financial support under young scientist research grants scheme

References

1. Malatoa, S.; Fernández-Ibáñez, P.; Maldonado, M.I; Blanco, J.; Gernjak, W; *Catal. Today.*, **2009**, *147*, 59.
DOI: [10.1016/j.cattod.2009.06.018](https://doi.org/10.1016/j.cattod.2009.06.018)
2. Kansal, S. K., Singh M., Sud, D; *J. Hazard. Mater.*, **2007**, *141*, 581.
DOI: [10.1016/j.jhazmat.2006.07.035](https://doi.org/10.1016/j.jhazmat.2006.07.035)
3. Hoffman, M.; Martin, S.; Choi, W.; Bahnemann, D; *Chem. Rev.*, **1995**, *95*, 69.
DOI: [10.1021/cr00033a004](https://doi.org/10.1021/cr00033a004)
4. Beydoun, D.; Amal, R.; Low G.; McEvoy, S; *J. Nano. Res.* **1999**, *1*, 439.
DOI: [10.1023/A:1010044830871](https://doi.org/10.1023/A:1010044830871)
5. Dong, Y.; Zhan, S.; Wang, P.; *Journal of Wuhan University of Technology-Mater, Sci. Ed.*, **2012**, *27*, 615.
DOI: [10.1007/s11595-012-0515-2](https://doi.org/10.1007/s11595-012-0515-2)
6. Zhang, D.F; *Russ. J. Phys. Chem. A.* **2011**, *85*, 1416.
DOI: [10.1134/S0036024411080073](https://doi.org/10.1134/S0036024411080073)
7. Zhang, D.F.; Zeng, F.B; *Russ. J. Phys. Chem. A.* **2011**, *85*, 1825.
DOI: [10.1134/S0036024411100347](https://doi.org/10.1134/S0036024411100347)
8. Justicia, I.; Ordejón, P.; Canto, G.; Mozos, J.L.; Fraxedas, J.; Battistoni, G.A.; Gerbasí, R.; Figueras, A; *Adv. Mater.* **2002**, *14*, 1399.
DOI: [10.1002/1521-4095\(20021002\)14:19<1399::AID-MA1399>3.0.CO;2-C](https://doi.org/10.1002/1521-4095(20021002)14:19<1399::AID-MA1399>3.0.CO;2-C)
9. Gallino, F.; Valentin, C.D.; Pacchioni, G.; Chiesa, M.; Giamello, E; *J. Mater. Chem.*, **2010**, *20*, 689.
DOI: [10.1039/B915578C](https://doi.org/10.1039/B915578C)
10. Pourtedal, H.R.; Eskandari, H.; Keshavarza, M.H.; Semnani, A; *Acta Chim. Slov.*, **2009**, *56*, 353.
11. Moghaddam, M.B.; Yangjeh, A.H; *J. Iran. Chem. Soc.*, **2011**, *8*, 169.
12. Peill, N.J.; Hoffmann, M.R; *Env. Sci. Technol.*, **1996**, *30*, 2806.
DOI: [10.1021/es960047d](https://doi.org/10.1021/es960047d)
13. Fernández-Ibáñez, P.; Blanco, J.; Malato, S.; Delas-Nieves F.; *Water Res.*, **2003**, *37*, 3180.
DOI: [10.1016/S0043-1354\(03\)00157-X](https://doi.org/10.1016/S0043-1354(03)00157-X)