

A COMPARATIVE STUDY BETWEEN TiO₂ AND ZnO PHOTOCATALYSIS: PHOTOCATALYTIC DEGRADATION OF CIBACRON YELLOW FN-2R DYE

F.A. CATAÑO, S.H. VALENCIA, E.A. HINCAPIÉ, G.M. RESTREPO and J.M. MARÍN

Grupo Procesos Físicoquímicos Aplicados, Universidad de Antioquia, Sede de Investigación Universitaria, cra. 53 # 61 - 30 Medellín, Colombia.

fczapata@matematicas.udea.edu.co, hvalens@gmail.com, andresa18@gmail.com, gloma@udea.edu.co, jmmarin@udea.edu.co

Abstract— Cibacron Yellow FN-2R dye was degraded by heterogeneous photocatalysis with both titanium dioxide (TiO₂), Degussa P-25, and zinc oxide (ZnO). A 3² factorial design was used with photocatalyst amount and pH as factors and the pseudo-first-order constant as response variable. On the optimal conditions the pseudo-first order rate constant was higher when ZnO was used as catalyst. However, the evolution of total zinc (Zn) in solution indicated a significant loss of ZnO on those optimal conditions as consequence of its susceptibility to chemical dissolution and photodissolution. Due to the solubility curve of ZnO has a minimum at pH around 10 and its photodissolution does not occur at pH>10, the photodegradation experiments using ZnO were performed with a pH control near to 10. In this condition, the photocatalytic activity of ZnO was similar to that obtained with TiO₂ when it is used in its optimal conditions.

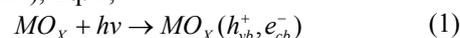
Keywords — Heterogeneous photocatalysis, TiO₂, ZnO, azo dyes, decolorization, photocatalyst.

I. INTRODUCTION

The negative impact that different industries have on water environment due to wastewater discharges is frequently a great environmental and health concern. Especially if it is considered the continuous deterioration to which rivers and marine environments are exposed (UNESCO, 2006). Among the environmental contaminants are the dyes used by the textile industries. They have some problems associated with the wastewater discharges in aquatic ecosystems like eutrophication, the decreasing of the sunlight penetration due to the dye absorption, the reducing of the photosynthesis process of aquatic plants and problems of visual pollution (Rathi *et al.*, 2003; Guillard *et al.*, 2003). Moreover, these compounds are metabolized by humans and animals producing free aromatic amines that are potentially carcinogenic and mutagenic (Alves *et al.*, 2007). Conventional methods for wastewater treatment do not seem to be alternatives to take into account for water treatment that contains those contaminants (Pandey *et al.*, 2007). Using biological treatments result questionable, because dyes are highly recalcitrant due to their xenobiotic nature. On the other hand, an incomplete mineralization is obtained, having aromatics amines as products of biodegradations, which may be more toxic than the initial

compounds (Rathi *et al.*, 2003; Pandey *et al.*, 2007).

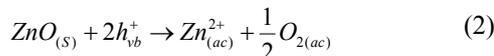
Heterogeneous photocatalysis has proved to be an effective alternative to remove organic pollutants in water (Hoffmann *et al.*, 1995). This technology is based on the absorption of photons of equal or higher energy than the semiconductor band gap, producing electron-hole pairs (e⁻/h⁺), Eq. 1,



where M represents a metal, h_{vb}^+ produced holes in the valence band (vb), e_{cb}^- electrons in the conduction band (cb). The species h_{vb}^+ and e_{cb}^- may participate in charge transfer reactions when the illuminated solid is placed in contact with an aqueous solution. The photogenerated electrons in the cb may reduce the molecular oxygen and the photogenerated hole in the vb may oxidize organic molecules. Thus the illuminated semiconductor acts as a catalyst for the reaction of oxidation of organic matter. Theoretical fundamentals of heterogeneous photocatalysis can be found elsewhere (Hoffmann *et al.*, 1995; Herrmann, 1999; Monllor-Satoca *et al.*, 2007).

A wide range of semiconductors may be used for photocatalysis, such as: ZnO, TiO₂, CeO₂, CdS, ZnS. TiO₂ semiconductor is the most used due to its good chemical and photochemical stability, it exhibits high photocatalytic activity, it is non-toxic and it is abundant and cheap (Herrmann, 1999). Nevertheless, heterogeneous photocatalysis investigations in polluted waters with substances such as: 2-phenylphenol (Khodja *et al.*, 2001), rhodamine 6G (Kansal *et al.*, 2007), pulp mill bleaching wastewater (Yeber *et al.*, 1999), reactive blue 19 (Lizama *et al.*, 2002) and some AZO dyes (Kansal *et al.*, 2007; Akyol *et al.*, 2004; Kositizi *et al.*, 2007; Sakthivel *et al.*, 2003), the degradation with ZnO presents a better photocatalytic behavior than the TiO₂. In contrast, ZnO has the disadvantage that it is susceptible to two dissolution processes during the heterogeneous photocatalytic process. The first one is the chemical dissolution with these species in solution: Zn²⁺_(ac), Zn(OH)⁺_(ac), Zn(OH)_{2(ac)}, Zn(OH)₃⁻_(ac) and Zn(OH)₄²⁻_(ac). In acid and neutral medium, Zn²⁺_(ac) predominates, in strong basic medium the Zn(OH)₄²⁻_(ac) is the principal species and pH around 10 the ZnO solubility curve has a minimum with Zn(OH)_{2(ac)} as principal species in solution (Degen and Kosec, 2000). The second dissolution process is the photochemical dissolution, where the photogenerated holes can oxidize the ZnO, Eq. 2, but this phenomenon

does not occur at $\text{pH} > 10$ (Khodja *et al.*, 2001; Schoenmakers *et al.*, 1996; Domènech and Prieto, 1986). These dissolution processes limit the use of this semiconductor in photocatalysis, but if the ZnO dissolves slowly or the degree of dissolution is small this semiconductor would be useful in practical applications.



where s is solid, ac is aqueous.

This research studies the degradation photocatalytic of the Cibacron Yellow FN-2R, an AZO dye widely used, with TiO_2 and ZnO as an alternative of TiO_2 .

II. MATERIALS AND METHODS

A. Photocatalysts and AZO dye

Degussa P-25 TiO_2 (surface area $50 \text{ m}^2/\text{g}$); ZnO from Merck (surface area $5 \text{ m}^2/\text{g}$); Cibacron Yellow FN-2R, a reactive AZO supplied by a local textile industry (its chemical structure is protected by commercial patents); deionized and distilled water.

B. Photoreactor

The samples were irradiated using a batch photoreactor of pyrex glass with 9 cm in diameter and 30 cm in height (volume: 1.5 L) with a cooling jacket using water, a magnetic stirring and an aeration system that pumps air through the suspension to a rate of 1.5 L/min to keep a saturation concentration of dissolved oxygen. The radiation source were five ultraviolet lamps (Sylvania 6W/BLB; output between 310 and 410 nm with maximum at 350 nm). They were placed vertically around the photoreactor. The irradiance which reached the photoreactor was 6 W/m^2 - 25 W/m^2 (depending on the distance from the lamps) and it was measured using a radiometer (Radiometer PMA 2200 with an UV-A detector PMA 2110. Solar Light Co).

C. Photocatalytic degradation

A Cibacron Yellow FN-2R solution of 20 ppm (1.5 L) was prepared and its pH was adjusted to a predetermined value with a concentrated solution of NaOH or HNO_3 . The solution was magnetically stirred and aerated in order to assure a dissolved oxygen saturated solution, in the photoreactor. Then the catalyst TiO_2 or ZnO was added at a specific concentration. This suspension was kept in the dark in order to guarantee the equilibrium adsorption of the dye on the surface of the semiconductor at each specific pH. Then the lamps were switched on to initiate the reaction, this time is $t=0$. At intervals of irradiation time aliquots of reaction mixture were withdrawn, filtered using a $0.15 \mu\text{m}$ membrane filters and analyzed.

D. Analytic Methods

The UV/Vis absorption of the degradation of Cibacron Yellow FN-2R was measured at 429 nm corresponding to the wavelength of maximum absorbance in the visible region with a UV-Vis spectrophotometer, Thermo Evolution 600. COD was measured by the closed reflux colorimetric method and for total Zn in solution by the zincon method (Eaton and Clesceri, 2005). The dimension of TiO_2 and ZnO particles was measured by a particle size analyzer Hydro 2000 MU.

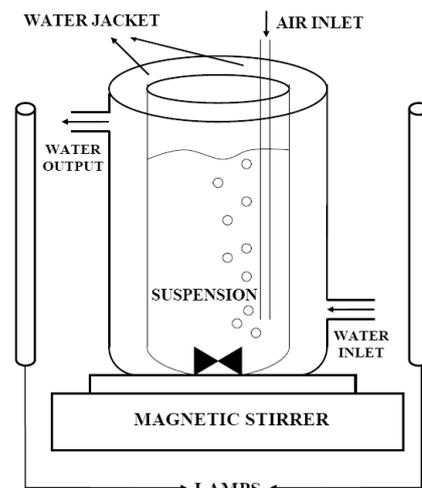


Fig. 1. Schematic of the photocatalytic reactor.

III. RESULTS AND DISCUSSION

A. Photolysis and adsorption

UV irradiation alone in the absence of photocatalysts did not produce changes in Cibacron Yellow FN-2R solution after seven hours of irradiation, due to the low-intensity UV source.

The adsorption equilibrium in the dark for both photocatalysts was reached before 1 hour, Fig. 2 and 3. These Dye adsorption percentages decrease with pH increasing. For both TiO_2 and ZnO the surface is positively charged at pH below the isoelectric point, and the Cibacron Yellow FN-2R is a dye of anionic nature, leading to higher adsorption, $\text{pH}_{\text{PZC}}=6.5$ (Matos *et al.*, 2010) and $\text{pH}_{\text{PZC}}=9\pm 0.3$ (Kansal *et al.*, 2009) for TiO_2 and ZnO respectively.

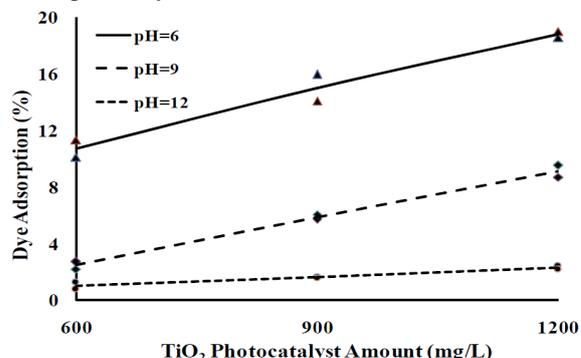


Fig. 2. Adsorption of Cibacron Yellow FN-2R in the dark as a function of pH and TiO_2 amount.

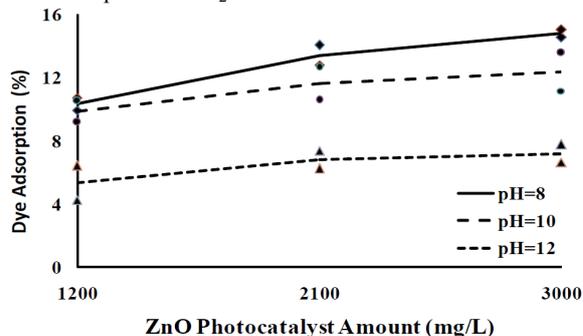


Fig. 3. Adsorption of Cibacron Yellow FN-2R in the dark as a function of pH and ZnO amount.

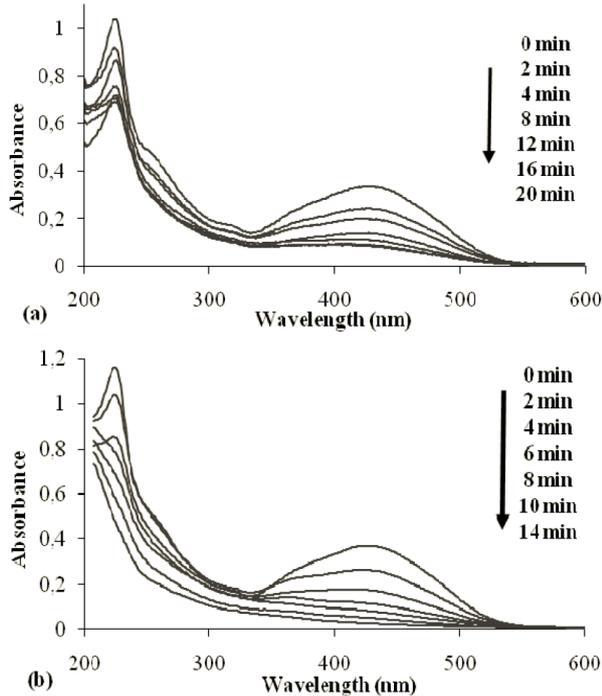


Fig. 4. Absorption spectra evolution of Cibacron Yellow FN-2R (20 ppm) solution during heterogeneous photocatalysis using: a) 900 mg/L TiO₂; pH = 6 b) 900 mg/L ZnO; pH = 8.

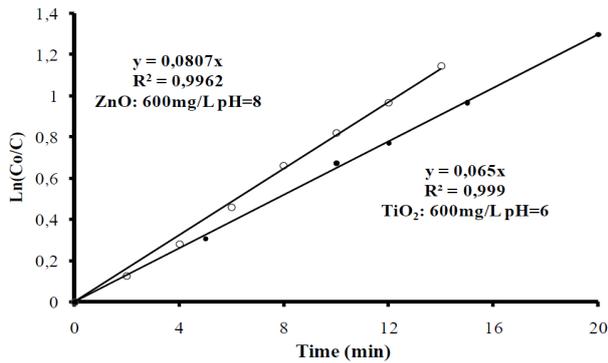


Fig. 5. Graphs of $\ln(C_0/C)$ vs t at 600 mg/L ZnO with pH = 8 and 600 mg/L TiO₂ with pH = 6.

B. Degradation experiments

Figure 4 shows the evolution for the absorption spectra of a Cibacron Yellow FN-2R solution during heterogeneous photocatalysis with both semiconductors. In both cases there is a fast decay of the peak at 429 nm, indicating that the AZO group present in the dye structure is chemically transformed.

C. Degradation kinetic

Degradation kinetics of dyes generally can be approximated by a first order kinetics (Wu, 2004) and therefore the first order rate constant is the most accurate measurements of photoactivity of the catalyst. For a degradation that follows a kinetic of first order, the Eq. 3 is used:

$$\ln\left(\frac{C_0}{C}\right) = kt \tag{3}$$

where C_0 is the concentration after adsorption in the dark at $t=0$, C corresponds to the dye concentration at any time and k (min^{-1}) is the pseudo-first order constant.

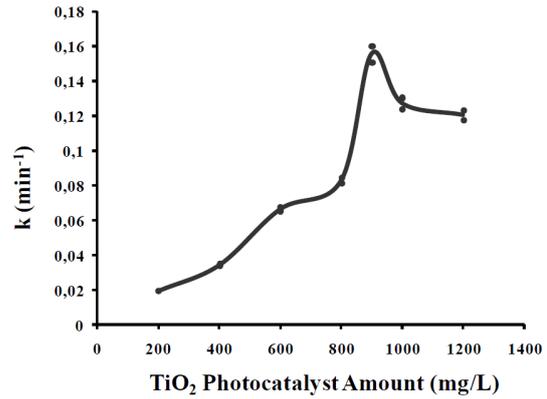


Fig. 6. Effect of TiO₂ amount on pseudo-first order rate constant of Cibacron Yellow FN-2R photodegradation at pH = 6.

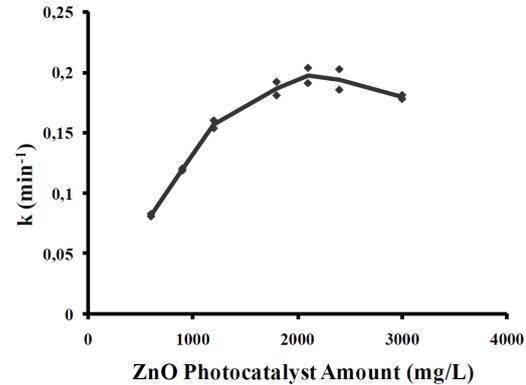


Fig. 7. Effect of ZnO amount on pseudo-first order rate constant of Cibacron Yellow FN-2R photodegradation at pH = 8.

Figure 5 shows the kinetic analysis for TiO₂ and ZnO. The graph of $\ln(C_0/C)$ vs. t is a straight line through the origin. Therefore, the rate of decolorization follows a first order law and the slope gives k (min^{-1}). This does not suggest anything about the mechanism, limiting step or another aspect of the reaction and it must be taken as a simple and quick way to analyze data. The constant k (min^{-1}) was taken as an interest variable in order to compare the performance of both semiconductors. The variable combination photocatalyst amount-pH which maximizes k (min^{-1}) was determined for each photocatalyst.

D. Effect of the photocatalyst amount

The effect of the photocatalyst amount on the k (min^{-1}) was studied with TiO₂ and ZnO, at pH=6 and pH=8, respectively. Figures 6 and 7 show that an increase in the photocatalyst amount, increasing k (min^{-1}). This tendency is kept until a point in which further increases in photocatalyst amount do not increase the k (min^{-1}).

This behaviour is due to that a low photocatalyst amount, the surface area and the kinetic processes of the interfacial charge transfer are low and as result a low kinetics of degradation were obtained. Increasing the photocatalyst amount, the surface area increases and therefore the kinetic increases. Nevertheless, increasing the photocatalyst amount increases the turbidity of the suspension, reducing the UV irradiation penetration. This leads to the generation of dark zones in the reactor where the reaction rates will be smaller or negligible

(Herrmann, 1999; Kansal *et al.*, 2007; Daneshvar *et al.*, 2004; Chen and Ray, 1999). The optimal photocatalyst amounts were 900 mg/L for TiO₂ and 2100 mg/L for ZnO. The optimal amount of ZnO is higher than for TiO₂, probably because the ZnO has a smaller specific surface area than the TiO₂, even with the agglomeration, where ZnO has a dimension of particle between 0.8-20 μm with a maximum in 4 μm and TiO₂ between 0.26-4 μm with a maximum in 0.4 μm. This particle size increases leading to a loss in the effective area and consequently a decrease in photocatalytic activity.

E. Influence of pH and photocatalyst amount

In order to study systematically the effect of pH and photocatalyst amount on the photodegradation of the dye, a 3² factorial experimental design for each semiconductor was used (Montgomery, 2005). Photocatalyst amount and initial pH were the factors and *k* (min⁻¹) was the response variable. The levels for the photocatalyst amount were: 600, 900, 1200 mg/L for TiO₂ and 1200, 2100, 3000 mg/L for ZnO. The pH levels were 6, 9, 12 for experiments with TiO₂ and 8, 10, 12 for experiments with ZnO. For the ZnO, the range pH 8-12 corresponds to a range in which its solubility can be considered low (Degen and Kosec, 2000). For the TiO₂, pH values in acidic medium were not taken because, in general, the reactive dyes are present in alkaline wastewaters (Lizama *et al.*, 2002). Figures 8 and 9 show *k* (min⁻¹) vs. photocatalyst amount-pH. Both, photocatalyst amount and initial pH have a statical effect on *k* (min⁻¹). This fact can be observed for the two photocatalysts, because a pH decreasing leads to increases in *k* (min⁻¹) for each one of the photocatalyst amounts. As a result, the optimal pH was 6 for TiO₂ and 8 for ZnO, independent of the photocatalyst amount used.

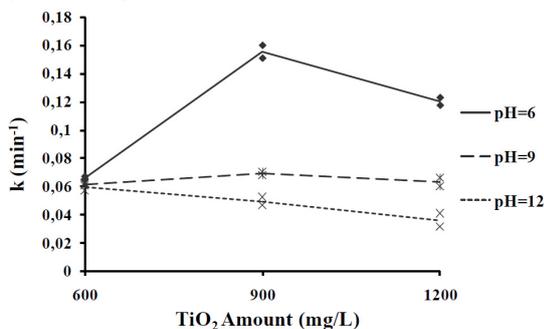


Fig. 8. Effect of TiO₂ amount-pH on the pseudo-first order degradation rate constant of Cibacron Yellow FN-2R.

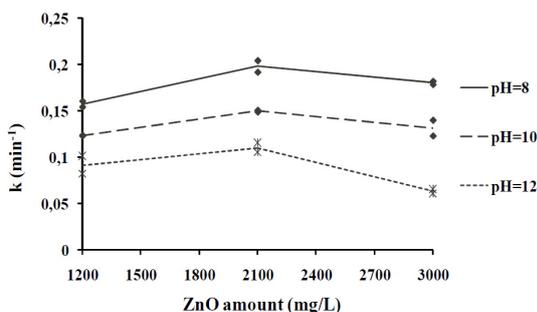
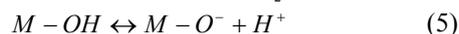
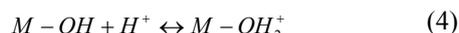


Fig. 9. Effect of ZnO amount - pH on the pseudo-first order degradation rate constant.

The dependence on pH can be explained by the superficial charge density on the photocatalyst. The metallic oxides in contact with aqueous solutions adsorb water molecules by the union between the metal of the oxide and the oxygen of the water and the water hydrolysis occurs. Consequently, a metallic hydroxide layer is formed on the oxide surface (Stumm and Morgan, 1996). This surface has two different kinds of OH, one basic and another acid, Eqs. 4 and 5, respectively; these chemical equilibriums generate a surface electric charge.



where *M* is a metal.

There is a pH at which each of the semiconductors exhibit a neutral net electrical charge, the isoelectric point. At pH below the isoelectric point, the semiconductor carry a positive net charge, at lower pHs this positive surface charge density is increased; above the isoelectric point the semiconductor carry a negative net charge and at higher pH this negative charge density is increased. The affinity of the photocatalyst for the dye is defined by the electrostatic interactions that exist between them.

The Cibacron Yellow FN-2R is a dye of anionic nature, due to the presence of sulfonic groups (-SO₃⁻Na⁺) in its structure. The TiO₂ surface is positively charged at the experimental pH=6, below the isoelectric point, p*H*_{PZC}=6.5 (Matos *et al.*, 2010) and there are favourable interactions between TiO₂ and the dye. Therefore, these interactions lead to higher *k* (min⁻¹) values. The TiO₂ surface is negatively charged at pH above the isoelectric point and the repulsions between photocatalyst and substrate lead to lower *k* (min⁻¹) values. The same behaviour is observed with the ZnO for values below and above the isoelectric point, p*H*_{PZC}=9±0.3 (Kansal *et al.*, 2009). The optimal ZnO concentration that shows the highest *k* (min⁻¹) value was 2100 mg/L and it was independent of pH, Fig 7. This behaviour does not occur with TiO₂ because the optimal TiO₂ concentration was 900 mg/L at pH=6 and 600 mg/L at pH=12, Fig 8.

This behaviour of TiO₂ can be explained taking into account the stability of the photocatalyst suspension. At high pH, the high surface charge leads to a stable suspension and a lower semiconductor agglomeration, and at pH close to the isoelectric point, the low surface charge leads to a higher agglomeration. For TiO₂ at pH=6, close to the isoelectric point, produces greater agglomeration decreasing the photocatalyst area, while at pH=12 the agglomerated TiO₂ particles are lower and there is a high photocatalyst area. Therefore, at high pH a low photocatalytic concentration is needed to generate high superficial area. With ZnO, the used pH values were close to the isoelectric point, but the effect of the agglomeration is less than with TiO₂. The same trend was also observed by Lizama *et al.* (2002). These authors carried out the photodegradation of reactive blue 19 by heterogeneous photocatalysis and they found that at high pH values the TiO₂ amount was lower than this

one at neutral pH, in order to maximize k (min^{-1}).

The pH not only determines the affinity of the surface oxide for the pollutant but also the agglomeration grade of the photocatalyst particles in suspension, although both aspects have effect in the degradation kinetic, the first one seems to be more relevant as the results suggest, because a low value of pH a high agglomeration is present which leads to a lower superficial area, nevertheless an increment in k (min^{-1}) is produced, perhaps as consequence of improved electrostatic interactions. In contrast, at high pH, electrostatic repulsions between dye and photocatalyst have a negative effect in k (min^{-1}), despite the high superficial area. For each photocatalyst there is a photocatalyst amount-pH ($\text{TiO}_2=900$ mg/L; pH=6 and $\text{ZnO}=2100$ mg/L; pH=8) couple that maximizes k , Table 1.

Under intrinsic k , it is possible to achieve a higher k (min^{-1}) using ZnO. This comparison suggests a certain potential use of ZnO as photocatalyst for practical applications.

F. Test of degradation with TiO_2 and ZnO

The oxidation of 20 mg/L Cibacron Yellow FN-2R solution using heterogeneous photocatalysis with TiO_2 and ZnO was measured by COD. Both semiconductors were used in their optimal condition. Figure 10 shows a COD removal of 69.8% in 3 hours using ZnO as photocatalyst and 41.7% in 4 hours using TiO_2 .

Despite the good results obtained with ZnO, the measurement of total Zn in aqueous phase during the photodegradation process shows that it reaches 5 mg/L when ZnO is used under the optimal conditions, Fig. 11a. The chemical and the photochemical solubilization represent economic losses and may also generate additional pollution problems. $\text{Zn}^{2+}_{(\text{aq})}$ presents toxicity to some aquatic organisms and has a strong tendency to bioaccumulate (EPA, 1995). The United Nations Food and Agriculture Organization has recommended level below 2 mg/L for Zn in irrigation waters and U.S. EPA secondary drinking water standard is 5 mg/L. For these reasons, the heterogeneous photocatalysis process with ZnO needs a strict pH control to minimize losses due to solubility. Solubility of ZnO has a minimum at pH=10 and the photodissolution does not occur at pH>10 (Degen and Kosec, 2000; Domènech and Prieto, 1986). The measure of total Zn in the solution due to losses by solubilization at pH=10 does not exceed 2 mg/L (Fig. 11b). This level is lower than the observed in Fig. 11a, so a photocatalytic test was carried out controlling the pH near to 10 in order to minimize the ZnO losses. This control was done by adding NaOH concentrated solution to maintain pH in a range of 9.3 and 10.7 approximately.

G. Test of degradation with ZnO controlling pH

Figure 12 shows the evolution of the COD with 2100 mg/L ZnO and pH=10. The COD removal obtained after 4 hour of treatment was 43.7%. This value is very similar to the obtained with the TiO_2 in its optimal conditions.

Table 1. Comparison of the pseudo-first order constants.

Photocatalyst	k (min^{-1})	Intrinsic k ($\text{min}^{-1}\text{Lm}^{-2}$)	Specific k ($\text{min}^{-1}\text{Lmg}^{-1}$)
TiO_2 ($50 \text{ m}^2\text{g}^{-1}$)	0.1555	3.455×10^{-3}	1.727×10^{-4}
ZnO ($5 \text{ m}^2\text{g}^{-1}$)	0.1979	1.885×10^{-2}	9.423×10^{-5}

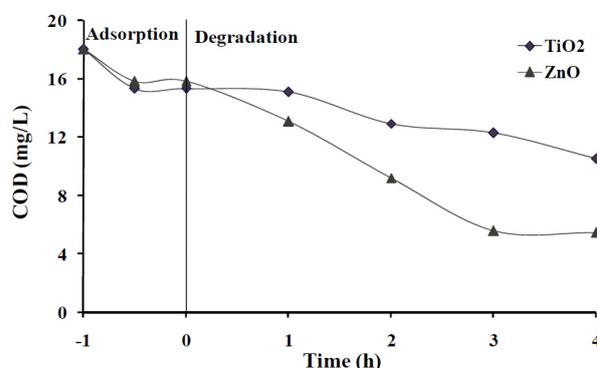


Fig. 10. Change of COD during the heterogeneous photocatalysis of Cibacron Yellow FN-2R solution: 900 mg/L and pH=6 for TiO_2 and 2100 mg/L and pH=8 for ZnO.

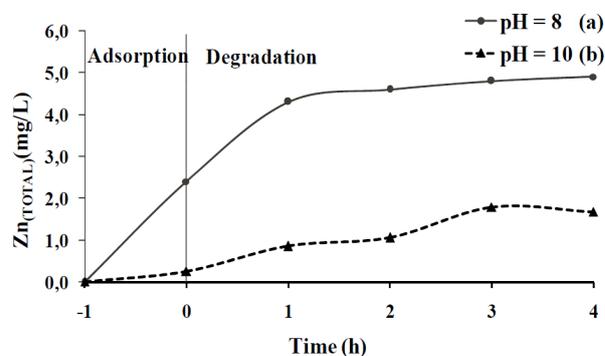


Fig. 11. Total zinc concentration during the photocatalytic degradation of Cibacron Yellow FN-2R solution using 2100 mg/L of ZnO.

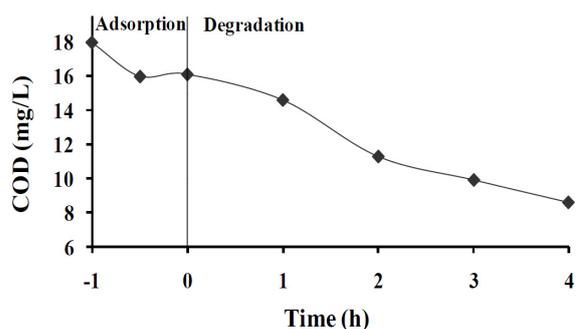


Fig. 12. Change of COD during the heterogeneous photocatalysis of Cibacron Yellow FN-2R solution using ZnO 2100 mg/L and pH=10.

IV. CONCLUSIONS

ZnO has shown to be an interesting alternative, compared with the Degussa P25 TiO_2 , for removing contaminants in water by heterogeneous photocatalysis, due to its low cost and high kinetics rate. However, the processes of dissolution and photodissolution of ZnO can limit its use because they could cause economic losses and additional pollution problems. As both dissolution phenomena depend of the pH, it suggests a strict

control of pH to minimize the ZnO losses. The optimal conditions for the Cibacron Yellow FN-2R degradation using ZnO do not correspond with those that minimize the ZnO losses by dissolution. However, with the conditions that minimize ZnO losses, the obtained photocatalytic degradation efficiency was similar to that obtained with TiO₂ when it is used in its optimal conditions (based on the intrinsic pseudo-first order constant).

ACKNOWLEDGEMENTS

The authors thank the financial support to the University of Antioquia through the program "Estrategia de Sostenibilidad de Grupos 2009-2010".

REFERENCES

- Akyol, A., H.C. Yatmaz and M. Bayramoglu. "Photocatalytic decolorization of Remazol Red RR in aqueous ZnO suspensions," *Appl. Catal. B: Environ.*, **54**, 19-24 (2004).
- Alves, R.O., A.P. Bazo, D.M. Fávero, C.M. Rech, D.P. Oliveira and G.A. Umbuzeiro. "Mutagenic and carcinogenic potential of a textile azo dye processing plant effluent that impacts a drinking water source," *Mutat. Res.*, **626**, 53-60 (2007).
- Chen, D. and A.K. Ray. "Photocatalytic kinetics of phenol and its derivatives over UV irradiated TiO₂," *J. Photochem. Photobiol. B: Env.*, **23**, 143-157 (1999).
- Daneshvar, N., D. Salari, A.R. Khataee. "Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO₂," *J. Photochem. Photobiol. A: Chem.*, **162**, 317-322 (2004).
- Degen, A. and M. Kosec. "Effect of pH and impurities on the surface charge of zinc oxide in aqueous solution," *J. Eur. Ceram. Soc.*, **20**, 667-673 (2000).
- Doménech, J. and A. Prieto. "Stability of ZnO Particles in Aqueous Suspensions under UV Illumination," *J. Phys. Chem.*, **90**, 1123-1126 (1986).
- Eaton, A.D. and L.S., Clesceri, *Standard Methods for the Examination of Water and Wastewater*, APHA-AWWA-WPCF, 21th ed. (2005).
- EPA, Environmental Protection Agency U.S. *Federal Register Environmental Documents*, **60**, Number 176. Sept. 12, <http://www.epa.gov/fedrgstr/EPA-TRI/1995/September/Day-12/pr-25.html> (1995).
- Guillard, C., H. Lachheb, A. Houas, M. Ksibi, E. Elaloui and J.M. Herrmann. "Influence of chemical structure of dyes, of pH and of inorganic salts on their photocatalytic degradation by TiO₂ comparison of the efficiency of powder and supported TiO₂," *J. Photochem. Photobiol. A: Chem.*, **158**, 27-36 (2003).
- Herrmann, J.M. "Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants," *Catal. Today.*, **53**, 115-129 (1999).
- Hoffmann, M.R., S.T. Martín, W. Choi and D.W. Bahnemann, "Environmental Applications of Semiconductor Photocatalysis," *Chem. Rev.*, **95**, 69-96 (1995).
- Kansal, S.K., M. Singh and D. Sud. "Studies on photodegradation of two commercial dyes in aqueous phase using different photocatalyst," *J. Hazard. Mater.*, **141**, 581-590 (2007).
- Kansal, S.K., N. Kaur and S. Singh. "Photocatalytic degradation of two commercial reactive dyes in an aqueous phase using nanophotocatalyst," *Nanoscale Res. Lett.*, **4**, 709-716 (2009).
- Khodja, A.A., T. Sehili, J. Pillichowski and P. Boule, "Photocatalytic degradation of 2-phenylphenol on TiO₂ and ZnO in aqueous suspensions," *J. Photochem. Photobiol. A: Chem.*, **141**, 231-239 (2001).
- Kositzki, M., I. Poullos, K. Samara, E. Tsatsaroni and E. Darakas. "Photocatalytic oxidation of Cibacron Yellow LS-R," *J. Hazard. Mater.* **146**, 680-685 (2007).
- Lizama, C., J. Freer, J. Baeza, J. Baeza and H.D. Mansilla. "Optimized photodegradation of Reactive Blue 19 on TiO₂ and ZnO suspensions," *Catal. Today.*, **76**, 235-246 (2002).
- Matos, J., E. García-Lopez, L. Palmisano, A. García and G. Maeci, "Influence of activated carbon in TiO₂ and ZnO photo-assisted degradation of 2-propano in gas-solid regime," *Appl. Catal. B: Environ.*, **99**, 170-180 (2010).
- Monllor-Satoca, D., R. Gómez, M. González-Hidalgo and P. Salvador, "The Direct-Indirect' model: An alternative kinetic approach in heterogeneous photocatalysis based on the degree of interaction of dissolved pollutant species with the semiconductor surface," *Catal. Today.*, **129**, 247-255 (2007).
- Montgomery, D.C. *Design and Analysis of Experiments*, 6th ed. (2005).
- Pandey, A., P. Singh and L. Iyenga. "Bacterial decolorization and degradation of azo dyes," *Int. Bioder. Biodegr.*, **59**, 73-84 (2007).
- Rathi, A., H.K. Rajor and R.K. Sharma. "Photodegradation of direct yellow-12 using UV/H₂O₂/Fe²⁺," *J. Hazard. Mater.*, **102**, 231-234 (2003).
- Sakthivel, S., B. Neppolian, M.V. Shankar, B. Aradindoo, M. Palanichamy and V. Murugesan. "Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO₂," *Sol. Energ. Mater. Sol. Cell.*, **77**, 65-82 (2003).
- Schoenmakers, G.H., D. Vanmaekelbergh and J.J. Kelly. "Study of Charge Carrier Dynamics at Illuminated ZnO Photoanodes," *J. Phys. Chem.*, **100**, 3215-3220 (1996).
- Stumm, W. and J.J. Morgan, *Aquatic Chemistry*, Wiley: New York, third ed. (1996).
- UNESCO, *Water a shared responsibility*, The 2nd United Nations World Water Development Report, Ciudad de México (2006).
- Wu, C. "Comparison of azo dye degradation efficiency using UV/single semiconductor and UV/coupled semiconductor systems," *Chemosphere.*, **57**, 601608 (2004).
- Yeber, M.C., J. Rodriguez, J. Freer, J. Baeza, N. Duran and H.S. Mansilla. "Advanced oxidation of a pulp mill bleaching wastewater," *Chemosphere*, **39**, 1679-1688 (1999).

Received: August 29, 2010.

Accepted: April 13, 2011.

Recommended by Subject Editor Walter Ambrosini.