

RESEARCH ARTICLE

**Langmuir-Hinshelwood Kinetic
Expression for the Photocatalytic
Degradation of Metanil Yellow
Aqueous Solutions by ZnO
Catalyst**

*Chemical Sciences
Journal, Vol. 2012:
CSJ-85*

Langmuir-Hinshelwood Kinetic Expression for the Photocatalytic Degradation of Metanil Yellow Aqueous Solutions by ZnO Catalyst

S Khezrianjoo, HD Revanasiddappa*

Department of Chemistry, University of Mysore, Mysore, Karnataka, India.

*Correspondence to: Hosakere D Revanasiddappa, hdrevanasiddappa@yahoo.com

Accepted: Nov 23, 2012; Published: Dec 07, 2012

Abstract

The kinetics studies of the adsorption and degradation phenomena involved in the photocatalytic degradation of Metanil Yellow (MY) were investigated using a batch reactor and UV light irradiation. Experiments were performed in a suspended ZnO system at natural pH of 6.93 and catalyst concentration of 1 g L^{-1} . The initial concentration of MY varied between 10-50 mg L^{-1} . The kinetic analysis of the photodecomposition of MY showed that the disappearance followed satisfactorily the pseudo first-order according to Langmuir–Hinshelwood model. From the results, the adsorption was found to be an essential factor in the photodegradability of the dye. The linear transform of the Langmuir isotherm curve was further used to determine the characteristic parameters which were: maximum absorbable dye quantity $Q_{max} = 6.802 \text{ mg g}^{-1}$ and adsorption equilibrium constant $K_{ads} = 0.168 \text{ L mg}^{-1}$. The adsorption constant calculated from the linear form of this model, $K_{LH} = 0.155 \text{ L mg}^{-1}$ was found reasonably similar to K_{ads} deduced from isotherm adsorption.

Keywords: Acid Yellow 36; dark surface adsorption; kinetic model; zinc oxide.

1. Introduction

The removal of hazardous chemicals from wastewater is presently one of the most important subjects in pollution control. These pollutants may originate from industrial applications such as textile processing. Photocatalytic oxidation (PCO) is a highly effective process for the degradation of a wide variety of priority pollutants in water and wastewater [1, 2]. PCO occurs as a result of the interaction of a semiconductor photocatalyst and UV radiation that yields highly reactive hydroxyl radicals, which are believed to be the main species responsible for the oxidation of organic substrates [1, 2]. Photocatalytic oxidation in the presence of semiconducting materials, of organic compounds with environmental concern has been studied extensively during the last 20 years and it has been demonstrated that heterogeneous photocatalysis can be an alternative to conventional methods for the removal of organic pollutants from water and wastewater [3].

The catalyst may be used either as an aqueous slurry or it may immobilize onto a supporting substrate [4]. Suspension or slurry type reactors have been reported to be efficient due to the large surface area of catalyst available for reaction and the efficient mass transfer within such systems [5]. However, due to the small particle size of the ZnO particles, a post-treatment catalyst recovery stage is necessary.

In the last decade, the mechanism of heterogeneous photocatalysis has been investigated by many researchers [6, 7]. A photocatalytic reaction proceeds on the surface of semiconductors via several steps: (i) production of electron–hole pairs by irradiating the semiconductor with light having an energy content higher than the band gap energy of the semiconductor; (ii) separation of the photogenerated electrons and holes due to trapping by species that are adsorbed on the semiconductor; (iii) redox reactions between the trapped electrons and holes and the adsorbents; (iv) desorption of reaction products and reconstruction of the surface [6, 7].

PCO kinetics of many organic substrates has been analyzed in terms of Langmuir–Hinshelwood (L–H) rate equations [8-10]. Langmuir–Hinshelwood rate expression has been successfully used for heterogeneous photocatalytic degradation to determine the relationship between the initial degradation rate and the initial concentration of the organic substrate [8-10].

$$\frac{1}{k_{obs}} = \frac{1}{k_c K_{LH}} + \frac{[MY]_0}{k_c} \quad (1)$$

where $[MY]_0$ is the initial concentration of organic compound (mg L^{-1}), K_{LH} the Langmuir–Hinshelwood adsorption equilibrium constant (L mg^{-1}) and k_c the rate constant of surface reaction ($\text{mg L}^{-1} \text{ min}^{-1}$). The fitting of experimental data with L–H type kinetic models has so far only been demonstrated for the PCO of organic substrates in single-component systems [8-10]. Another point to check is adequate use of the dark adsorption

measurement; if the kinetically obtained K_{LH} is different from that obtained in dark adsorption measurement, the L–H mechanism cannot be adopted [11]. Therefore, dark adsorption measurement is always required.

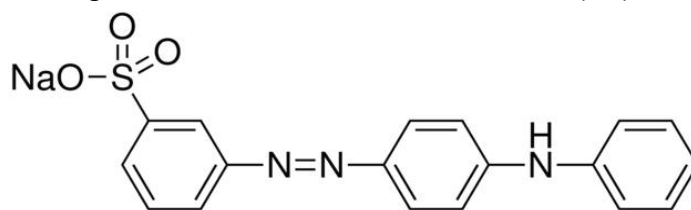
In the present work, an evaluation of the binding constants of a mono azo dye, “Metanil Yellow”, color index name “Acid Yellow 36” calculated under dark adsorption and under irradiation with UV light was performed to support the validity of the L–H reaction mechanism. MY is a water soluble substantive dye and has a vast amount of applications in several industries [12].

2. Methods

2.1. Reagents

All reagents were used as received without more purification. The Metanil Yellow dye $C_{18}H_{14}N_3NaO_3S$ (CI No. 13065, CAS No. 587-98-4, MW=375.38) was provided by SD Fine Chem company. The molecular structure of this dye is shown in Figure 1. ZnO catalyst was Loba Chemie product. Distilled water was used to prepare the solutions.

Figure 1: Chemical structure of Metanil Yellow (MY).



2.2. Reactor

A circulating photo-reactor with a cube body shape and a capacity of about one liter was used. The 18 watt UV lamp (Philips TUV PL-L) was positioned on top of the reactor with 15 cm distance from the surface of solution. A pump was circulating the solution. In this way, both the well-mixing and fluidizing of catalyst particles were provided. The whole reactor body was covered with reflectors of polished aluminum thin layer. Since the photocatalysis is sustained by a ready supply of dissolved oxygen, air was supplied to the reaction system at constant flow-rate using a micro air compressor.

2.3. Photocatalytic experimental procedure

To perform the experiments, one liter of solution containing 50 mg L^{-1} of MY (1.33×10^{-4} M), which is within the range of typical concentration in textile wastewaters [13] and a known amount of ZnO concentration was prepared. To start the degradation, the solution was transferred to the reactor, and the lamp was switched on. During each experiment, circulation of suspension was maintained to keep suspension homogeneous. The experiments were done in ambient temperature and natural pH of solution (pH = 6.93). Samples (5 mL) were taken at regular time intervals and then centrifuged, to separate the ZnO particles from the samples. Analyses were performed with UV-Vis spectrophotometer (Systronics 166) provided with 1 cm matched quartz cells.

3. Results and Discussion

3.1. Effect of catalyst concentration

In slurry photocatalytic processes, catalyst dosage is an important parameter that can affect the degradation rate. The optimal catalyst concentration depends on the nature of the compounds and the photoreactor geometry [14]. Figure 2 shows a plot of the reaction rate constant (k_{obs}) as a function of the catalyst concentration at the fixed MY concentration ($50 \text{ mg } L^{-1}$). With catalyst concentrations up to about $1 \text{ g } L^{-1}$, the degradation rate increases; while it decreases mildly above this concentration. Increasing the concentration of the catalyst causes an increase in the reaction rate because of an increase of the active site of the catalyst which causes more hydroxyl radical generation; meanwhile, more dye molecules can be adsorbed on the catalyst surface [8]. On the other hand, the additional higher quantities of it would increase opacity of the suspension which in turn would provide reductions in the light intensity throughout the solution [8].

An empirical relationship between the initial decolorization rate and catalyst concentration has been reported by Galindo *et al.* ($r_0 \alpha [catalyst]^n [dye]$) [3], where n is an exponent less than 1 for all the dyes studied [3, 15], relative to low concentration of catalyst. As it can be seen in Figure 3, the dependence of the ZnO concentration on the initial decolorization rate of MY follows a similar relationship ($r_0 \alpha [ZnO]^{0.87} [MY]$), when the ZnO concentration is less than $1 \text{ g } L^{-1}$.

Figure 2: Effect of ZnO concentration (g L^{-1}) on the degradation rate constant k_{obs} during the photocatalytic oxidation.

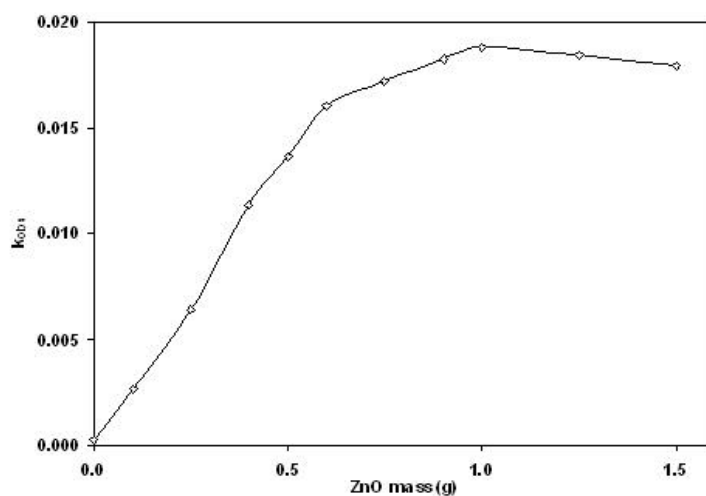
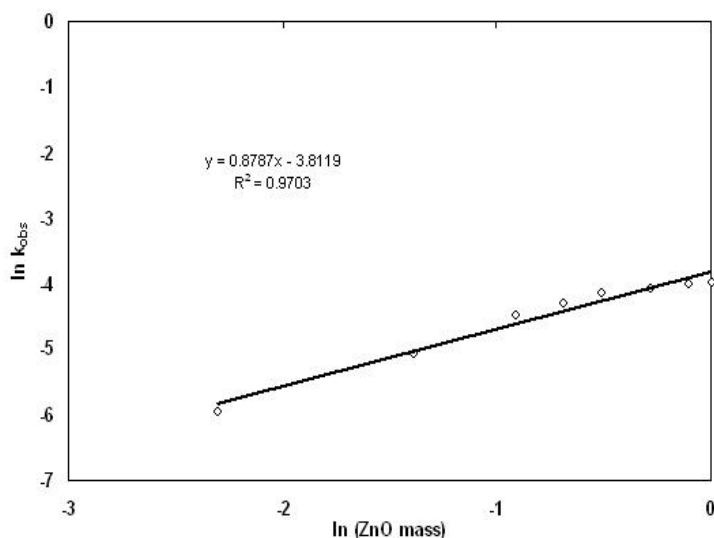


Figure 3: Relationship between $\ln k_{obs}$ and the amount of ZnO (g).



3.2. Photocatalytic degradation kinetics

The initial concentration of the dye has a fundamental effect on the degradation rate, i.e. the kinetic rate constant decreases with the increase of the initial dye concentration [16]. The degradation experiments by UV irradiation of MY aqueous solutions containing ZnO follow the pseudo-first-order kinetics with respect to the concentration of the dye in the bulk solution (C):

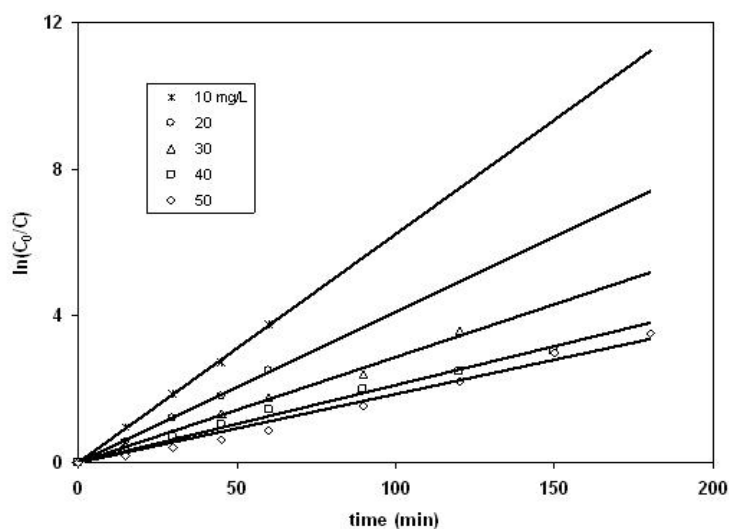
$$r = -\frac{dC}{dt} = k_{obs}C \quad (2)$$

Integration of this equation (with the same restriction of $C = C_0$ at $t = 0$, with C_0 being the initial concentration in the bulk solution and t the reaction time) will lead to the expected relation:

$$\ln\left(\frac{C_0}{C}\right) = k_{obs}t \quad (3)$$

in which k_{obs} is the apparent pseudo-first-order rate constant and is affected by dye concentration. A plot of $\ln(C_0/C)$ versus t for all the experiments with different initial bulk concentration of MY is shown in Figure 4.

Figure 4: Linear variation of $\ln(C_0/C)$ versus time for the photocatalytic degradation of MY at different initial concentrations.



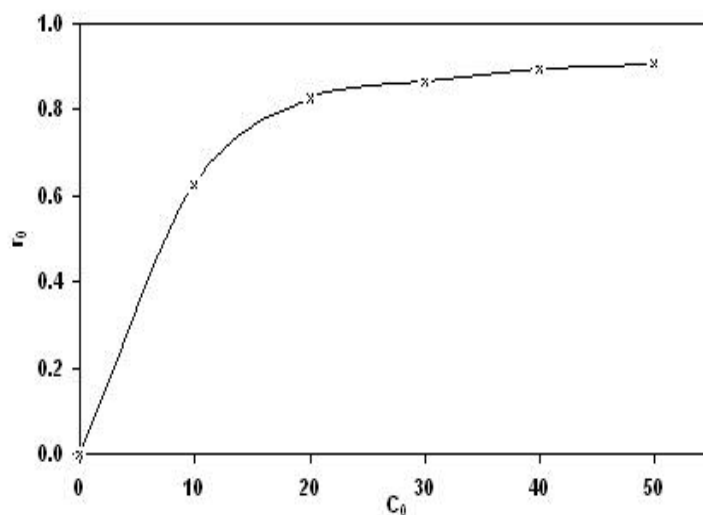
The values of k_{obs} can be obtained directly from the regression analysis of the linear curve in the plot. The values which correspond to different initial concentrations, along with the regression coefficients, are listed in Table 1.

Table 1: Pseudo-first order apparent constant values for the different initial concentrations of MY.

C_0 (mg L ⁻¹)	$k_{obs} \times 100$ (min ⁻¹)	R^2
10	6.23	0.9991
20	4.12	0.9976
30	2.88	0.9937
40	2.11	0.9909
50	1.88	0.9839

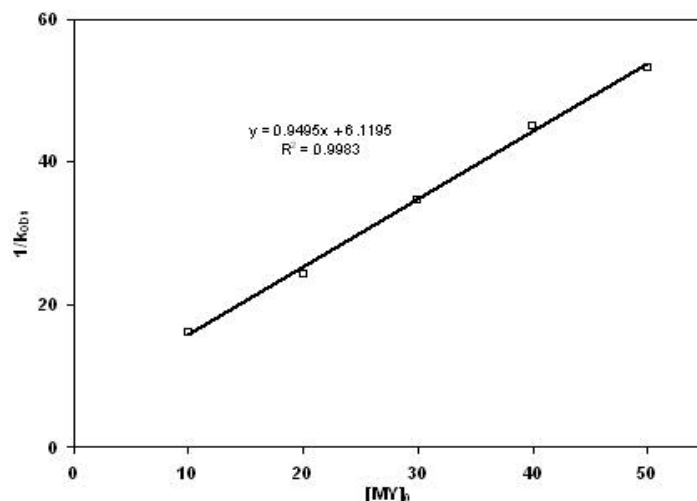
According to the above description, the lower MY concentrations provide the better agreement with the first order reaction. The influence of the initial concentration of MY on the rate constant of photocatalytic degradation is shown in Figure 5. The rate of degradation increases with the initial concentration of MY and then finds a tendency toward independent values with the higher initial concentrations.

Figure 5: Variation of initial rate of MY degradation versus different initial concentrations.



According to Eq. (1), the plot of $1/k_{obs}$ versus $[MY]_0$ represented in Figure 6 shows a linear variation, confirming the Langmuir-Hinshelwood relationship for the initial rates of degradation. The values of k_c and K_{LH} , calculated from the intercept and the slope of the straight line ($R^2=0.9983$) were $1.053 \text{ mg L}^{-1} \text{ min}^{-1}$ and 0.155 L mg^{-1} respectively.

Figure 6: Variation of reciprocal of constant rate versus different initial concentrations of MY.



3.3. Equilibrium dark adsorption

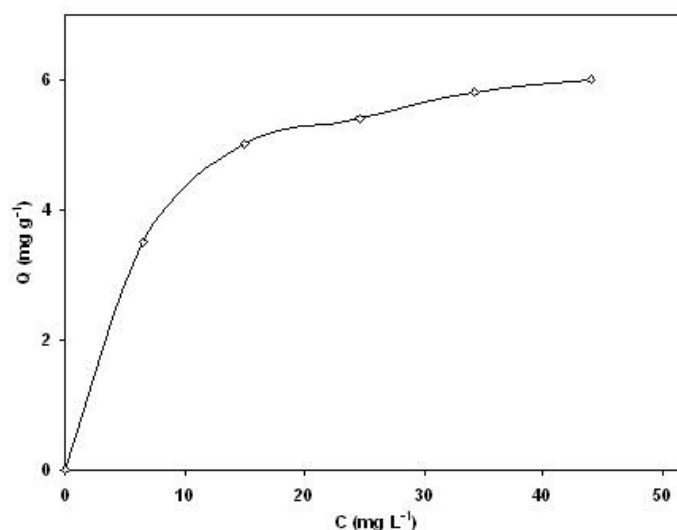
Several authors agreed that when the following assumptions were established, heterogeneous photocatalysis could be analyzed using the Langmuir-Hinshelwood model: (i) there are limited sites of adsorption on the surface of catalyst, (ii) the catalyst surface can be covered to the maximum by one layer; each site can adsorb only one molecule, (iii) there is reversible adsorption reaction, (iv) the surface of catalyst is homogeneous and (v) there is no interaction between molecules adsorbed [11, 17–19]. In this case, the classical Langmuir adsorption model has been applied to numerous compounds in aqueous suspension according to the following expression:

The adsorbed quantity (Q in mg g^{-1}) was calculated as

$$Q = \frac{V\Delta C}{m} \quad (4)$$

where ΔC is the difference between the initial concentration (C_0) and the equilibrium concentration (C), V is the volume (1 L), and m is the mass of ZnO (1 g). Figure 7 shows the results for the dark adsorption of MY on the catalyst surface in the initial concentration range up to 50 mg L^{-1} .

Figure 7: Adsorption isotherm of MY on ZnO, quantity adsorbed as a function of equilibrium concentration.



The adsorption behavior displayed by the dye adsorbed molecules onto ZnO with monolayer coverage of the catalyst surface following the Langmuir adsorption model at the low concentration range:

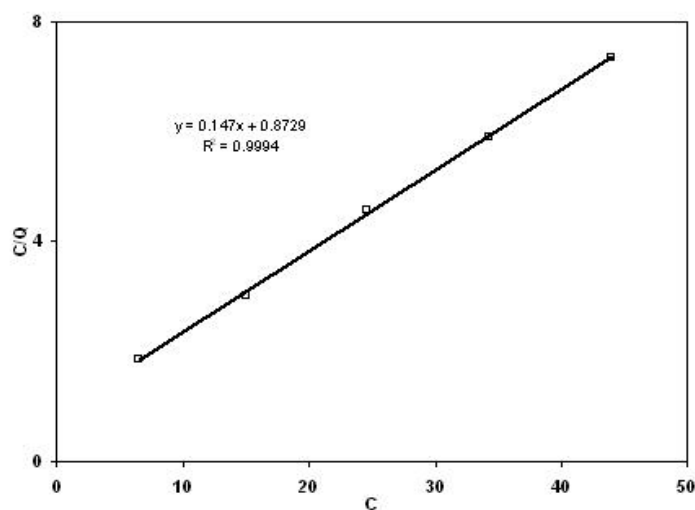
$$Q = \frac{Q_{\max} K_{ads} C}{1 + K_{ads} C} \quad (5)$$

where Q_{\max} is the maximum absorbable dye quantity and K_{ads} is the equilibrium constant for adsorption. This relationship can be written in linear form as:

$$\frac{C}{Q} = \frac{1}{Q_{\max} K_{ads}} + \frac{C}{Q_{\max}} \quad (6)$$

C/Q versus C plot is shown in Figure 8; Langmuir adsorption constant (K_{ads}) and the maximum absorbable dye quantity (Q_{\max}) were calculated from this figure as $0.168 \text{ (L mg}^{-1}\text{)}$ and $6.802 \text{ (mg g}^{-1}\text{)}$, respectively.

Figure 8: Establishment of Langmuir monolayer adsorption constants for adsorption of MY on ZnO.



Since, adsorption constant in kinetic model determined in our case is found to be close to that obtained in the dark ($K_{ads} = 1.07K_{LH}$), the photocatalytic degradation of 50 mg L^{-1} of MY under its natural pH (6.93) and 1 g L^{-1} of ZnO follows satisfactorily the Langmuir-Hinshelwood model. However, in other studies, it was reported that K_{LH} measured under irradiation could be substantially different from K_{ads} measured in the dark [15, 20].

4. Conclusion

The Metanil Yellow is easily degraded by ZnO assisted photocatalysis in aqueous dispersion under irradiation by UV light. We learned that catalyst concentration can affect the degradation rate. The dependence of the ZnO concentration on the initial decolorization rate can be explained as $(r_0 \alpha [ZnO]^{0.87})$, when the ZnO concentration is less than 1 g L^{-1} . The Langmuir-Hinshelwood kinetic model showed a good agreement for the initial rates of degradation with the appropriate reaction rate constant and the substrate adsorption constant values of $k_c = 1.053 \text{ mg L}^{-1} \text{ min}^{-1}$ and $K_{LH} = 0.155 \text{ mg}^{-1} \text{ L}$, respectively. Langmuir adsorption constant (K_{ads}) and the maximum absorbable dye quantity (Q_{\max}) were calculated as $0.168 \text{ (L mg}^{-1}\text{)}$ and $6.802 \text{ (mg g}^{-1}\text{)}$. Adsorption constant in kinetic model is found to be close to that obtained in the dark thus, the photocatalytic degradation of MY follows satisfactorily the Langmuir-Hinshelwood model.

Competing Interests

None declared.

Authors' Contributions

Both authors contributed equally to this work.

References

- Hoffmann MR, Martin ST, Choi W, Bahnemann DW, 1995. Environmental applications of semiconductor photocatalysis. *Chemical Reviews*, 95: 69-96.
- Ohko Y, Iuchi KI, Niwa C, Tatsuma T, Nakashima T, Iguchi T, *et al.*, 2002. 17 beta-estradiol degradation by TiO₂ photocatalysis as a means of reducing estrogenic activity. *Environmental Science & Technology*, 36: 4175-4181.

3. Galindo C, Jacques P, Kalt A, 2001. Photooxidation of the phenylazonaphthol AO20 on TiO₂: kinetic and mechanistic investigation. *Chemosphere*, 45: 997-1005.
4. Matthews RW, 1992. Photocatalytic oxidation of organic contaminants in water: An aid to environmental preservation. *Pure and Applied Chemistry*, 64: 1285-1290.
5. Dijkstra MFJ, Michorius A, Buwalda H, Panneman HJ, Winkelman JGM, Beenackers AACM, 2001. Comparison of the efficiency of immobilized and suspended systems in photocatalytic degradation. *Catalysis Today*, 66: 487-494.
6. Fu X, Zeltner WA, Anderson MA, 1996. *Semiconductor Nanoclusters Studies in Surface Science and Catalysis*. Edited by Kamat PV, Meisel D. Elsevier Science, Amsterdam, 445-461.
7. Li Y, Niu J, Yin L, 2011. Photocatalytic degradation kinetics and mechanism of pentachlorophenol based on superoxide radicals. *Journal of Environmental Sciences*, 23: 1911-1918.
8. Saïen J, Khezrianjoo S, 2008. Degradation of the fungicide carbendazim in aqueous solutions with UV/TiO₂ process; optimization, kinetics and toxicity studies. *Journal of Hazardous Materials*, 157: 269-276.
9. Vasanth Kumar K, Porkodi K, Selvaganapathi A, 2007. Constrain in solving Langmuir-Hinshelwood kinetic expression for the photocatalytic degradation of Auramine O aqueous solutions by ZnO catalyst. *Dyes and Pigments*, 75: 246-249.
10. Krishnakumar B, Swaminathan M, 2011. Influence of operational parameters on photocatalytic degradation of a genotoxic azo dye Acid Violet 7 in aqueous ZnO suspensions. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 81: 739-744.
11. Ohtani B, 2008. Preparing articles on photocatalysis — Beyond the illusions, misconceptions and speculation. *Chemistry Letters*, 37: 217-229.
12. Sleiman M, Vildoza D, Ferronato C, Moreira RFP, 2007. Photocatalytic degradation of azo dye Metanil Yellow: Optimization and kinetic modeling using a chemometric approach. *Applied Catalysis B: Environmental*, 77: 1-11.
13. Daneshvar N, Aleboye A, Khataee AR, 2005. The evaluation of electrical energy per order (E_{EO}) for photooxidative decolorization of four textile dye solutions by the kinetic model. *Chemosphere*, 59: 761-767.
14. Parra S, Olivero J, Pulgarin C, 2002. Relationships between physicochemical properties and photoreactivity of four biorecalcitrant phenylurea herbicides in aqueous TiO₂ suspension. *Applied Catalysis B: Environmental*, 36: 75-85.
15. Sauer T, Cesconeto Neto G, José HJ, Moreira RFP, 2002. Kinetics of photocatalytic degradation of reactive dyes in a TiO₂ slurry reactor. *Journal of Photochemistry and Photobiology A: Chemistry*, 149: 147-154.
16. Silva CG, Faria JL, 2003. Photochemical and photocatalytic degradation of an azo dye in aqueous solution by UV irradiation. *Journal of Photochemistry and Photobiology A: Chemistry*, 155: 133-143.
17. Konstantinou IK, Albanis TA, 2004. TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations a review. *Applied Catalysis B: Environmental*, 49: 1-14.
18. Vautier M, Guillard C, Hermann JM, 2001. Photocatalytic degradation of dyes in water: case study of Indigo and Indigo Carmine. *Journal of Catalysis*, 201: 46-59.
19. Cunningham J, Al-Sayyed G, Srijaranai S, 1994. Adsorption of model pollutants onto TiO₂ particles in relation to photoremediation of contaminated water. In: *Aquatic and Surface Photochemistry*. Edited by Helz G, Zepp R, Crosby D. Lewis Publications, CRC Press, Boca Raton, Florida, 317-348.
20. Kusvurana E, Samil A, Atanur OM, Erbatur O, 2005. Photocatalytic degradation kinetics of di- and tri-substituted phenolic compounds in aqueous solution by TiO₂/UV. *Applied Catalysis B: Environmental*, 58: 211-216.