ISSN:1007-1172

PAPER ID: JSJ.U-3036

UGC-CARE Approved (Group - II) Active Journal - 2020

JOURNAL OF SHANGHAI JIAOTONG UNIVERSITY

website: shjtdxxb-e.cn e-mail: editorjsju@gmail.com

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SUNLIGHT MEDIATED PHOTOCATALYTIC DEGRADATION OF RhB BY BiOCl/Fe PHOTOCATALYST

Authored by

S. S. Shende

Department of Chemistry, Late N. P. W. College, Lakhni, India.

Has been published in

VOLUME 17, ISSUE 4, APRIL - 2021

Dr. Xuhui Feng
Editor-in-Chief

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Scopus

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Journal of Shanghai Jiaotong University

ISSN: 1007-1172

SUNLIGHT MEDIATED PHOTOCATALYTIC DEGRADATION OF RhB BY BiOCl/Fe PHOTOCATALYST

N. D. Vilayatkar[1], P. K. Rahangdale[2], R. S. Ukare[3], S. S. Shende[4] & R. R. Kurzekar[5*]

[1] Department of Chemistry, S. S. J. College, Arjuni/Mor, India
[2] Department of Chemistry, B.M.V. College, Amgaon, India
[3] Department of Physics, C. J. Patel College, Tirora, India
[4] Department of Chemistry, Late N. P. W. College, Lakhni, India.
[5*]Department of Chemistry, C. J. Patel College, Tirora, India.

Abstract

Sunlight mediated photocatalytic degradation of rhodamine B (RhB) dye was studied using chemical coprecipitation (CC) method using BiOCl/Fe ($T = 50^0$C) photocatalyst. $BiCl_3$ was used as the starting material along with hydrochloric acid in the chemical coprecipitation of BiOCl/Fe. The photocatalytic behavior of the prepared BiOCl/Fe was tested through the degradation of RhB dye. The degradation of organic molecules follows first order kinetics. The effect of various parameters such as initial dye concentration, catalyst loading, pH of the medium, reusability of photocatalyst on the photodegradation of RhB dye were investigated. An actual textile effluent containing RhB as a major constituent along with other dyes and dyeing auxiliaries was treated using chemical co precipitation synthesized BiOCl/Fe. The reduction in the chemical oxygen demand (COD) of the treated effluent revealed a complete mineralization of the organic molecules. It was found that photocatalytic degradation of rhodamine B from aqueous solutions by BiOCl/Fe is an effective, economical and environment friendly.

Keywords: BiOCl/Fe nanocomposite, Chemical coprecipitation, Textile effluent, Rhodamine (RhB)dye, Photocatalysis

1. Introduction

In a view of planetary energy utilization, the development of semiconductor photocatalysts for organic pollutant degradation and water splitting is a challenging and indispensable topic of modern research [1]. Rhodamine B (RhB) dye is an organic chloride salt having N-[9-(2-carboxyphenyl)-6-(diethylamino)-3H-xanthen-3-ylidene]-N-ethylethanaminium, i.e. $C_{28}H_{31}ClN_2O_3$ as the counter ion and widely used in industrial purposes, such as printing and dyeing in textile, paper, paints, leathers etc not only this it is also used to determine the rate and direction of flow. However, this dye causes serious environmental and biological problems, even capable to induce irritation to the skin, eyes. Thus, the removal of dye from water is a great challenge and a pressing task [2]. Now a days, TiO_2 photocatalyst is widely used for photodegradation of dyes which is only active under UV light irradiation due to its wide band gap (3.20 eV). In the past few decades, many researchers have focused their efforts on exploiting visible light driven semiconductor photocatalysts for photodegradation of dyes. Z. Zou et al. [3] reported In(1-x)Ni(x)TaO(4) (x = 0-0.2) photocatalyst could split water and generate H_2 and O_2 under visible light.

Many new visible light induced photocatalysts have also been reported, for photodegradation of dyes, such as Bi_2O_3[4] and photocatalytic activity of Bi_2O_3 under visible light irradiation with Cu(II) [5], Bi_2WO_6 nanocrystals[6,7], $CaBi_2O_4$[8] and Bi_5O_7I [9], which are also found to be active for degrading organic contaminants or splitting water under visible-light irradiation. In all of the novel visible light driven photocatalysts, $BiVO_4$ with a narrow band gap

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(Eg=2.40 eV) has attracted considerable interest for its good visible light induced photocatalytic property [10]. Various synthesis methods have been employed for the preparation of $BiVO_4$ photocatalyst, such as sonochemical method [11], hydrothermal treatment [12], chemical bath deposition [13], coprecipitation method [14], aqueous process [15] etc.

The focus of the present work is to synthesize BiOCl/Fe nanoparticles under chemical coprecipitation (CC) and use it in the photocatalytic degradation of RhB (C.I. No: 45170, formulaweight = 479.02g/mole) using sunlight illumination. The rate determining parameters like initial dye concentration, catalyst loading, pH of the medium, reusability of the photocatalyst on the photodegradation of RhB were studied in detail. However, since the decolorization is not indicative of the mineralization of the dye, therefore we investigated the photocatalytic performance of the BiOCl/Fe by the estimation of chemical oxygen demand (COD) in the degradation of a widely used dye RhB were calculated. The study of RhB degradation and understanding its reaction kinetics helped to consider actual method for the photocatalytic study, in view of its complexity in containing diverse types of dyes and other chemicals, the effluent was collected from a textile industry.

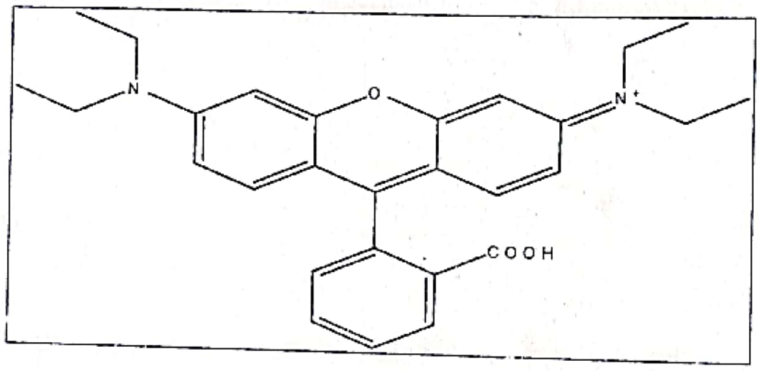

Fig.(1): Structure of Rhodamine B dye.

2. Experimental

2.1 Synthesis of BiOCl/Fe nanocomposite Photocatalysts

The Fe coupled BiOCl nanocomposite photocatalysts were prepared by a chemical coprecipitation method at 50°C. For that, $BiCl_3$ was dissolved in 1 M HCl, and then the Ferrous nitrate were introduced into the clear solution of $BiCl_3$ in different weights (0, 5, 10, and 20 wt%). The pH of the suspension was then adjusted to nine with the dropwise addition of aqueous ammonia under vigorous stirring. The brown colored precipitate was obtained after aging for 20 min. Finally, the precipitates were collected by centrifugation, washed with deionized water several times, and dried at 60°C for 8 Hrs. For comparison purpose, pure BiOCl was also prepared under the identical experimental conditions [16].

2.2: Photocatalytic degradation

In photocatalytic experiments, RhB dye (50 ml) and the catalyst (BiOCl/Fe), were taken in a beaker and exposed to sunlight for 180 minutes. Dye samples of about 2–3 ml were taken out at a regular interval from the test solution, centrifuged for 4–5 min at 950–1000 rpm and their absorbance were recorded at 550 nm using a spectrophotometer (Model: 2371, Elico, India). COD was estimated before and after the treatment using $K_2Cr_2O_7$oxidation method. The same photocatalytic experimental set up was employed for the textile effluent treatment. The photodegradation efficiency was calculated from the equation given below.

$$\text{Photodegradation efficiency} = \text{Initial COD} - \frac{\text{Final COD}}{\text{Initial COD}} * 100$$

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3. Results and Discussion

3.1 XRD

The X-ray powder diffraction pattern photograph of BiOCl/Fe obtained with a Chemical coprecipitation method are shown in Fig.(1). The phase purity of the prepared material is examined by powder X- ray diffractometer (XRD) using Cu K_α radiation (λ= 1.541 A°) with a nickel filter to estimate crystallinity of the phases. All of the diffractions peaks are precisely indexed to the Bragg diffraction of tetragonal structure of BiOCL-Fe (JCPDS files 06-0249).

The crystalline size was calculated from the broad XRD peaks using the Scherrer equation(1).

$$d = \frac{k\lambda}{\beta \cos\theta} \quad \text{.....(1)}$$

Where, λ is incident wavelength h, k, l are Millar indices and θ is Bragg's angle , β is the diffracted full width at half maximum and d is average grain size.

Where the average grain size which is found to be in the range 174 to 190 nm.

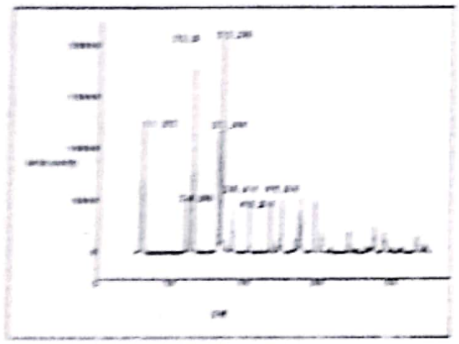

Fig.(2): XRD of Synthesized BiOCl-Fe

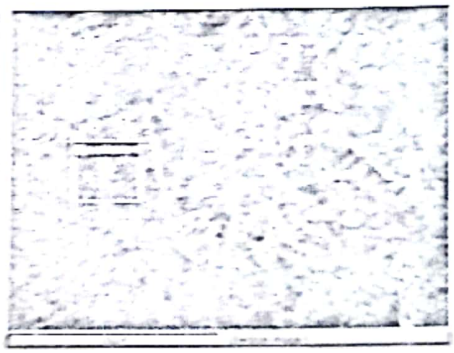

Fig. (3): SEM of pure BiOCl-Fe particles

3.2 SEM and EDS analysis

Fig.(3) shows the SEM image of pure BiOCl-Fe particles that shows particles are uniform in shape and well dispersed with high porosity. The pores and voids presents on the surface of samples are due to the gases released during synthesis process.Fro the SEM image, the particle size of prepared BiOCl-Fe is found in few micrometer range. Element analysis of pure BiOCl-Fe done by EDX spectra Fig. (4), which confirm the presence of Bi, O, Cl and Fe elements in a compound. Which shows the Bi and Fe are dominants elements in sample, although chloride and oxygen are also found in the sample.

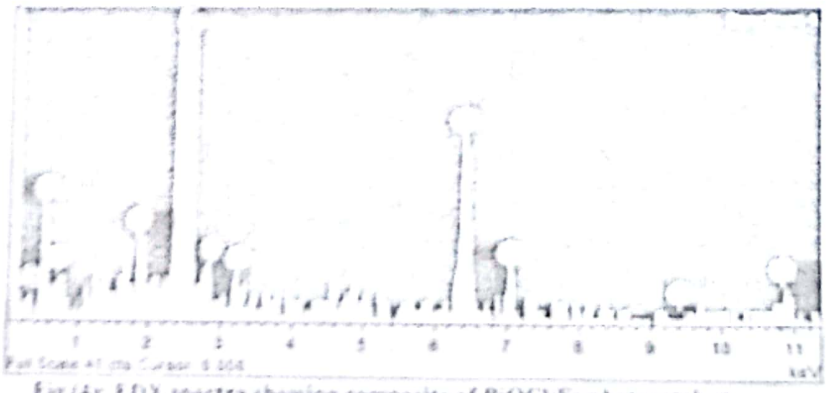

Fig.(4): EDX spectra showing composite of BiOCl Fe photocatalyst

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3.3 Photodegradation study of RhB

Photodegradation process assisted by a semiconductor depends on various parameters like nature and concentration of the organic substrate, concentration and of the semiconductor, light source and intensity, pH, etc[17]. The present investigation also reveals that BiOCl-Fe induced photocatalysis of RhB follows the first order kinetics with respect to RhB concentration.

3.3.1 Effect of initial dye concentration

The effect of initial RhB concentration on the degradation efficiency was studied by varying the concentration from 5.8 to 33.81 ppm and keeping BiOCl-Fe(200 mg/100 ml) as constant. The degradation efficiency of RB was found to decrease with an increase in the initial dye concentration, Fig.(5). With increased dye molecules the solution became more intense colored and the path length of photons entering the solution decreased thereby only fewer photons reached the catalyst surface. Therefore, the production of hydroxyl and superoxide radicals was limited. At still higher concentration of the dye, the path length was further reduced and the photodegradation was found to be negligible.

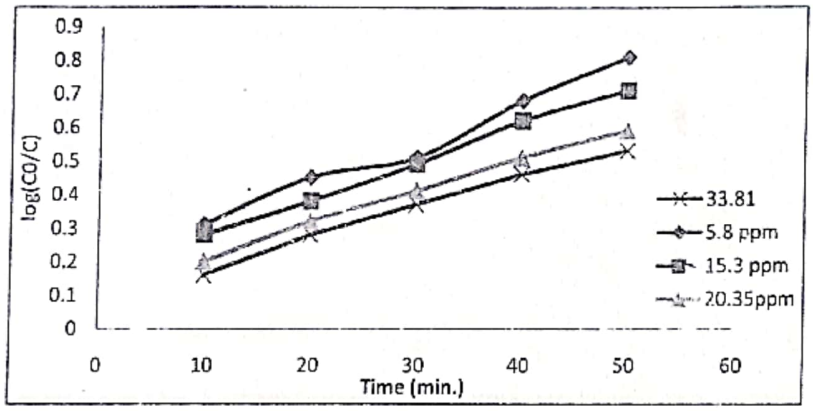

Fig.(5): Effect of initial dye concentration(RhB) on photodegradation efficiency of theBiOCl-FeNps.

3.3.2 Effect of BiOCl-Fe loading

Experiments were carried out by taking different amounts of BiOCl-Fe and keeping dye concentration constant at 20.35 ppm (Fig. 6). It was found that the rate constant increases up to 300 mg/50 ml of the dye solution, beyond which it shows a drastic reduction. The increase in the degradation efficiency of RhB with an increase in the catalyst amount may be due to an increase inthe active sites available on the catalyst surface for the reaction, which in turn increases the rate of radical formation. The reduction in the rate constant when the catalyst amount is increased beyond 300 mg/50 ml, is due to light scattering and reduction in light penetration through the solution.With a higher catalyst loading the deactivation of activated molecules by collision with ground state moleculesdominates the reaction, thus reducing the rate of reaction [18, 19].

3.3.3 Effect of pH

The pH of the dye solution in the present study was adjusted using varying concentrations of HNO_3 or NaOH. The minimum rate constant was recorded at pH 7 and increased with acidic as well as alkaline pH values (Fig. 7). The pH affects not only the surface properties of BiOCl/Fe nanocomposite but also the dissociation of dye molecules and the formation of hydroxyl radicals [20]. Enforcement of the reaction rate under alkaline condition could be attributed to the increase of hydroxyl ions, which induces more hydroxyl radical formation. In the acidic condition, the

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perhydroxyl radical can form hydrogen peroxide, which the hydroxyl radical. Thus an increase or decrease in pH from neutral value increases the rate of reaction, because the formed -OH radicals alsoinitiates the degradation reaction.

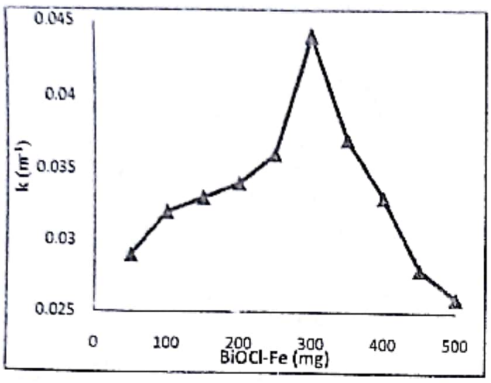

Fig.(6):Effect of BiOCl/Fe loading on rate of photodegradation of RhB

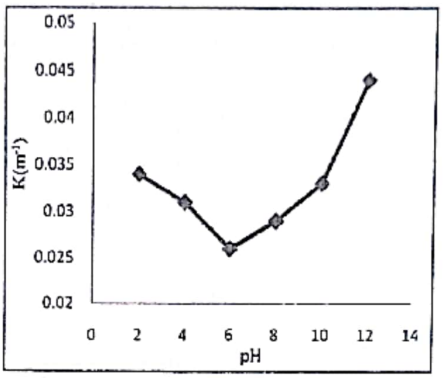

Fig. (7): Effect of pH on rate constant of photodegradation of RhB

3.3.4 Efficiency of reused catalyst

The BiOCl-Fe nanocomposite used in the photocatalytic treatment was centrifuged, dried at 30-40^{0}C in a hot air oven before it was reused as such in the succeeding photocatalytic experiment. The photodegradation efficiency of BiOCl/Fenanocomposite shows only a marginal change after repetitive use (Fig.8). These results indicate the cost effectiveness of this method.

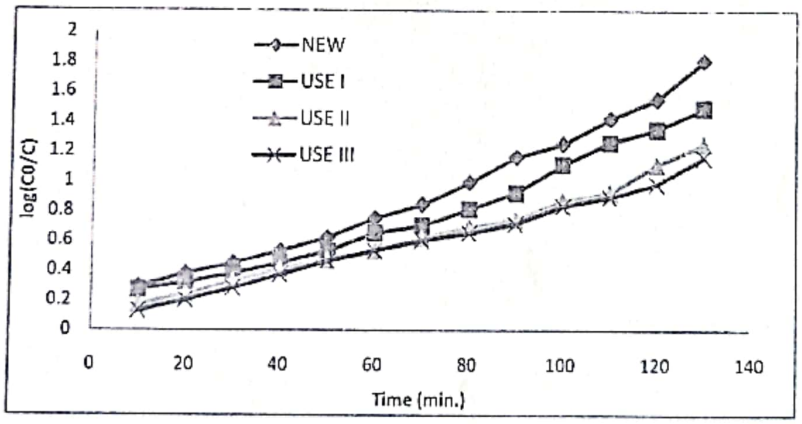

Fig.*(8): Photodegradation efficiency of the catalyst when reused.*

3.3.5 Estimation of chemical oxygen demand (COD)

The chemical oxygen demand test is widely used, as an effective technique to measure the organic strength of wastewater. The test allows the measurement of waste in term of total quantity of oxygen required for the oxidation of organic matter to $CO_2$and water. The COD of the dye solution before and after the treatment was estimated.The reduction in COD values of the treated dye solutionindicates the mineralization of dye molecules along with the color removal. Table 1 gives COD values of blankand treated dye solutions.

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Table 1.COD values of initial and treated RB dye solutions.

Dye concentration (ppm)	Initial COD (mg/l)	Final COD(mg/l)	Photodegradation efficiency
38.32	19.12	6.32	66.94
47.90	23.9	1.05	98.95
95.80	47.8	15.5	67.57
191.60	95.6	8.85	90.74
383.21	191.2	21.86	88.56

3.4 Photocatalytic treatment of textile effluent

In any textile plant diverse dyes and chemicals are used to impart attractive colors to the textile. In this process enormous amount of wastewater with high concentration of persistent dyes and chemicals are generated. An effluent with such diverse composition has been considered for the photocatalytic degradation in the present study. The visible spectrum of the textile effluent employed in the present study was recorded and λ_{max} was found to be 520 nm. The effluent was used in the photodegradation studies with a required dilution. The initial COD of the effluent was 1348.44 mg/l and the %T (measured at 520 nm) was found to be 41% after dilution. Sun light was used as the source of illumination. Results of the photocatalytic treatment of industrial effluent using BiOCl-FeNanocomposite are given in Table 2. It can be seen from table that, the reduction in COD confirms the destruction of the organic molecules in the effluents along with colour removal.

Table 2.Photocatalytic treatment of the effluent.

Exposure duration	% T	Final COD	Efficiency(%)
1	67	1018.72	20.31
2	75	962.64	24.7
4	86	705.81	44.79
6	93	458.7	64.12
8	96	320.52	74.92
10	98	179.5	85.95

4. Conclusions

Preparation of photocatalytic BiOCl/Fe was carried out under Chemical coprecipitation method. The rapid photocatalytic degradation of RhB dye was concluded by using kinetic parameters as concentration of the dye, concentration of the BiOCl/Fe and pH. The BiOCl/Fe nanocomposite can be reused for a number of cycles, which will reduce the cost of operation. Textile effluent with diverse composition was effectively treated using BiOCl/Fe nanocomposite. The reduction in COD of the effluent suggests that the dye molecules were completely mineralized along with color removal. Thus, prepared catalyst BiOCl/Fe can be used for rapid degradation of RhB dye.

Acknowledgements

The authors gratefully acknowledge the support of the UGC project, for providing financial assistance, CSIR NEERI Nagpur for providing E-library facilities for literature survey. Authors are thankful to the Director IICT, Hyderabad for EDX, XRD, and SEM studies.Special thanks are extended to Dr. Brijesh Pare, Department of chemistry, Madhav Science P.G. College, Ujjain, for his valuable guidance during the investigation.

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References

[1] Parul, Kamalpreet Kaur, Rahul Badru, Prit Pal Singh, Sandeep Kaushal, Jou. of Environment Chem. Engineering,(8), 103666, (2020),pp.1-20,.

[2] H. Kaur and R. Kaur. J. Mater. Environ. Sci., 5 (6), (2014), pp.1830-1838.

[3] Z. Zou, J. Ye, K. Sayama, H. Arakawa, Nature 414, (2001), pp 625–627.

[4] Hai-Ying Jiang, Jingjing Liu,Kun Cheng,Wenbin Sun, and Jun Lin*. *Phys. Chem. C* 117, (39), (2013), 20029–20036.

[5] Jinli Hu , Hongmeli Li, Caijin Huang, Xiaoqing Qui, appl. Cat. B: Environment 142-143, (2013), pp 598-603.

[6] Dipankar Saha, Espen D. Bojesen, Aref Hasen Mamakhel, and Bo B. Iversen, American Chemical Society, (Inorganic Chemistry), 13, https://dx.doi.org/10.1021/acs.inorgchem.0c01249, (2020) pp 9364–9373.

[7] Z.J. Zhang, W.Z. Wang, M. Shang, W.Z. Yin, J. Hazard. Mater. 177, (2010), pp1013–1018.

[8] J. Tang, Z. Zou, J. Ye, Angew. Chem. Int. Ed. 43, (2004), pp.4463–4466.

[9] S.M. Sun, W.Z. Wang, L. Zhang, L. Zhou, W.Z. Yin, M. Shang, Environ. Sci. Technol.43, (2009), 2005–2010.

[10] K. Sayama, A. Nomura, T. Arai, T. Sugita, R. Abe, M. Yanagida, T. Oi, Y. Iwasaki, Y.Abe, H. Sugihara, J. Phys. Chem. B 110, (2006), pp 11352–11360.

[11] W. Liu, L.X. Cao, G. Su, H.S. Liu, X.F. Wang, L. Zhang, Ultrason. Sonochem. 17, (2010), pp669–674.

[12] Y.N. Guo, X. Yang, F.Y. Ma, K.X. Li, L. Xu, X. Yuan, Y.H. Guo, Appl. Surf. Sci. 256, (2010), pp-2215–2222,.

[13] M.C. Neves, T. Trindade, Thin Solid Films 406, (2002), pp.93–97.

[14] A.M. Cruz, U.M.G. Perez, Mater. Res. Bull. 45, (2010), pp-135–141.

[15] W.Z. Yin, W.Z. Wang, L. Zhou, S.M. Sun, L. Zhang, J. Hazard. Mater. 173, (2010), pp.-194–199.

[16] J. Liang, G.Q. Zhu, P. J. Liu,NanosciNanotechnol. 14, (2014),pp- 4185-4190.

[17] S. Song, Z. Sheng, Y. Liu, H. Wang, and Z. Wu, J. Environmental Sciences, vol. 24, no. 8, (2012), pp-1519–1524

[18] S. Sohrabnezhad, A. Pourahmad, and E. Radaee, J. Hazardous Materials, vol. 170, no. 1, (2009),pp 184–190.

[19] X. Zhang, F. Wu, X. Wu, P. Chen, and N. Deng, vol. 157, no. 2-3, (2008), pp- 300–307.

[20] J.M. Herrmann, C.Guillaed, P. Pichat, J. Elsvare Catalysis Today, (1993),pp177-20.

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