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Solar Photodegradation of Methyl Orange and Phenol Using Silica Supported ZnO Catalyst

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Abstract—**A photocatalyst prepared by binding ZnO particles using colloidal SiO_2 and heating at 300^oC for 9 hours was applied to degrade phenol and Methyl orange dye under solar irradiation. The influence of operating parameters such as catalyst loading and pH was studied. Furthermore the kinetics involved in the degradation of methyl orange and phenol were examined, and the degradation was found to follow first order kinetics.**

Index Terms—**Photodegradation, ZnO, methyl orange, phenol.**

I. INTRODUCTION

A substantial amount of organic pollutants are released from various industrial processes. Among these organic pollutants are phenol, its derivatives and synthetic dyes. Phenol and its derivatives are the most commonly encountered organic pollutants in industrial effluents that are linked to severe environmental problems [1]. Of major concern is that phenolic compounds are carcinogenic, mutagenic and teratogenic [2].

Extensive studies on photocatalytic degradation of phenolic compounds such as phenol, chlorophenols, and nitrophenols have been conducted. However, in these studies photodegradation is achieved using TiO_2 upon illumination with near-UV light [3]-[7]. Synthetic dyes are mainly found in waste water from textile and paper industries [8]. This is in addition to other chemicals such as surfactants, chelating agents, and pH regulators employed in the manufacturing processes. The resulting wastewater is highly complex and presents challenges when it comes to treatment due to the presence of non-biodegradable compounds. Various methods have been developed for removal of synthetic dyes from such wastewaters with the aim of ameliorating their impact on the aquatic environment. Conventional water treatment methods such as sedimentation, filtration, chemical and membrane technologies are not viable due to high operating costs Moreover these methods result in production of toxic secondary pollutants that also have to be treated [9].

Advanced oxidation processes (AOPs) have emerged as a promising approach for treatment of wastewaters containing problematic organic compounds. The most widely used oxidants for AOPs include semiconductors/photocatalysts such as TiO_2 [10], hydrogen peroxide [11], ozone [12] and electrochemical oxidation [13]. Of these AOPs photocatalysis is a promising technique to deal with contaminated waters. It has been extensively investigated in the recent years because it is able to completely oxide organic molecules at a low energy cost. The effects of various operating parameters such as temperature, pH, initial concentration of organic compounds, light intensity, and catalyst dosage have been investigated. In addition the photodegradation of organic pollutants using suspended and immobilized catalysts has also been compared [14].

The successful demonstration of the photocatalytic ability of titania (TiO_2) to remove organic pollutants, particularly dyes, from wastewater attracted wide attention. The source of light has been mostly ultraviolet (UV). However, Zinc oxide (ZnO), with comparable bandgap energy as that of TiO_2 (rutile), has hardly drawn as much attention as a photocatalyst. The unpopularity of ZnO as a photocatalyst can be attributed to the effect of UV irradiation of its aqueous slurry [15] which results in the formation of Zn^{2+}(aq) and H_2O_2 in the presence of air. On the other hand, TiO_2 is photochemically stable. Despite its photoinstability early studies of ZnO as a photocatalyst demonstrate that it has high reaction and mineralization rates [16] as a result of its ability to generate the hydroxyl ion efficiently [17]. In addition compared to TiO_2, ZnO absorbs a large fraction of the solar spectrum and more light quanta [18]-[22]. Furthermore ZnO has been found to satisfactorily degrade an azo dye, brilliant orange [19], non-azo dye, Bractive T Blue [20], and methyl orange [23] from aqueous suspensions at the normal pH, approximately 6, of the dyes by visible light with an intensity of approximately 0.18 mW cm^{-2}.

In the present study the supported photocatalyst was prepared by immobilising solid ZnO on colloidal silica particles. The product was tested for its efficacy to degrade phenol and methyl orange.

II. EXPERIMENTAL

A. Materials

ZnO (Merck, Germany), silica (Merck, Germany), phenol (Industrial Analytical, RSA), methyl orange (Industrial Analytical, RSA), UV-VIS Spectrophotometer (Shimadzu UV-Visible 1800 Spectrophotometer, Japan)

B. Preparation of Catalysts

The photocatalyst was prepared using ZnO and colloidal silica. Colloidal SiO_2 and ZnO were mixed in 100 mL of

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MilliQ water and the mixture vigorously stirred for 1 hour to ensure homogeneity. Then resultant product was filtered and dried in an oven at a temperature of 180 ℃ for 4 hours. Thereafter the product was calcined at a temperature of 350 ^{o}C for 9 hours.

C. Photodegradation Experiments

The photocatalytic activity of the prepared powders were tested for degradation of phenol and methyl orange with an initial concentration of 10 mg/L and 20 mg/L, respectively. The reaction was carried out in a mechanically agitated batch reactor of volume 500 mL. As a result mass transfer limitations were not anticipated since the catalyst was finely divided and suspended. The following variables were studied: initial concentrations of phenol and methyl orange, initial pH, catalyst loading, irradiation time. Sampling was done by withdrawing 15 mL of the 500 mL irradiated solution, every 20 minutes for 4 hours. Before analysis the samples were filtered through a 0.45 µm membrane filter. All experiments were run in triplicate and the relative standard deviation (RSD) was employed to assess the error associated with the analysis. Phenol was quantified using a UV-Vis spectrophotometer at a wavelength of 270 nm. The concentration of methyl orange was determined at a wavelength of 464 nm. The photocatalytic degradation efficiency was calculated using the formula:

$$\frac{A_0 - A_t}{A_0} \times 100 \qquad (1)$$

where A_o = absorbance before irradiation and A_t = absorbance at time *t*.

III. RESULTS AND DISCUSSION

A. Effect of Catalyst Loading

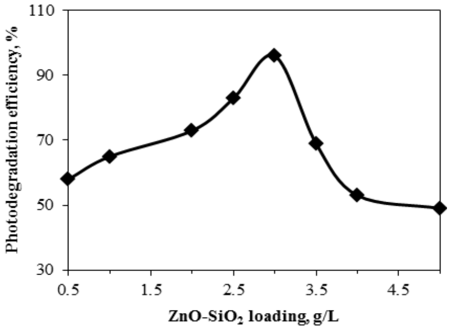

Fig. 1. The effect of catalyst concentration on photodegradation efficiency of methyl orange.

The dependency of the degradation efficiency of methyl orange and phenol on the catalyst loading is shown in Fig. 1 and Fig. 2, respectively. The results showed that photodegradation efficiency increased with an increase in catalyst loading to an optimum loading after which it decreased. Maximum degradation of methyl orange and phenol was found to be at 3.0 g/L and 1.5 g/L, respectively. This observation can be explained in terms of the availability of active sites on the surface of the catalyst and the penetration of solar radiation into the suspension [24]. An increase in catalyst dosage results in an increase in total active surface area of catalyst which in turn results in an increase in the photodegradation efficiency. However, this effect is counteracted at high catalyst dosages due to increased turbidity of the suspension. The increased turbidity reduces pernetration of the much needed solar radiation due to scattering, hence a decrease in photodegradation efficiency at high catalyst dosage.

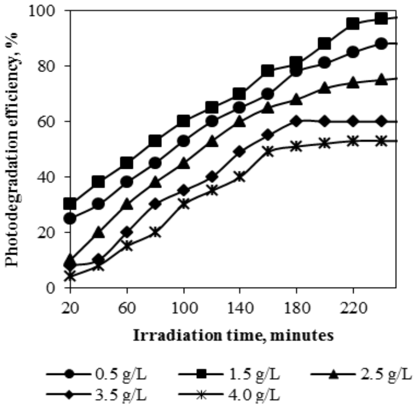

Fig. 2. The effect of catalyst concentration on the photodegradation efficiency of phenol.

B. Effect of pH

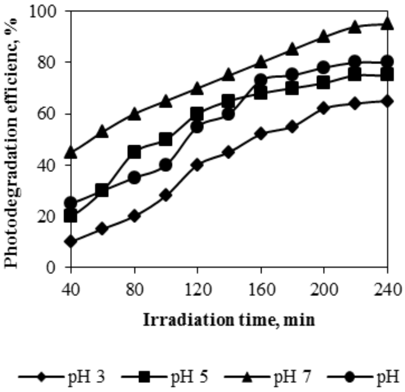

Fig. 3. The effect of pH on the photodegradation efficiency of methyl orange.

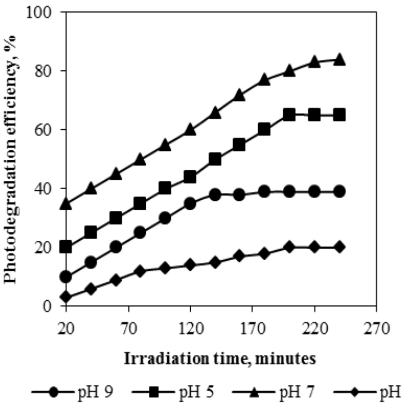

Fig. 4. The effect of pH on the photodegradation efficiency of phenol.

The influence of pH on the photodegradation efficiency of methyl orange and phenol is illustrated in Fig. 3 and Fig. 4, respectively. The highest degradation efficiency of methyl orange and phenol was obtained at pH close to 7. This observation can be explained in terms of the charges of methyl orange, phenol and the surface of the catalyst [25].

The point of zero charge (PZC) for ZnO is about a pH of 9.3 [26]. Above the PZC the surface of ZnO-SiO_2 catalyst particle is negatively charged. Below this pH value the surfaces are positively charged. On the other hand methyl orange molecules exist as anions in a wide pH range. Hence when the pH of the solution is below the PZC methyl orange anions are readily adsorbed onto catalyst surface via coulombic interactions..

At high acidic condition phenol exists in its protonated form and acquires a positive charge which gets less adsorbed and in turn less degraded by the positively charged catalyst surface due to coulombic repulsion. At less acidic to neutral pH (pH 5.2 and 7.2), phenol remains primarily in its non-ionic form; with minimum water solubility and the adsorption onto the photocatalyst is enhanced resulting in increased removal rates. Phenol exists as negatively charged phenolate ion at higher pH medium. The surface of the composite exhibits a negatively charged surface at the solution pH > pH_{zpc}. Hence, coulombic repulsion between the phenolate anions and the negatively charged catalyst surface decreases the adsorption onto the surface of the catalyst.

C. Kinetics of the Photocatalytic Degradation

The photocatalytic degradation of methyl orange and phenol on the surface of ZnO-SiO_2 catalyst follows pseudo first order kinetics law, expressed as follows:

$$- In\, {}^{C}\!/_{C_0} = kt \tag{2}$$

where C and C_o are the reactant concentrations at time $t = t$ and $t_o = 0$, respectively, k and t are rate constant and time, respectively. The relationship between $-InC/C_o$ and reaction time, t, is depicted in Fig. 5 and Fig. 6 for phenol and methyl orange , respectively. It can be seen that there exists a linear relationship between $-InC/C_o$ and reaction time, t.

The pseudo first order reaction constant k and linear regression coefficient for methyl orange and phenol with different initial concentrations are listed in Table I. From the Table it can be seen that the reaction rate constant decreases with increase in initial concentration. This observation can be explained by considering the Langmuir-Hinshelwood model. According to the model the reactants are first adsorbed onto the surface of the catalyst. Thereafter the degradation occurs under irradiation. As the initial concentration of reactants increases the molecules aggregate on the surface of the catalyst. This results in quenching of the excited molecules [27]. The probability for quenching increases with increase in initial concentration. Consequently, the photocatalytic degradation efficiency of methyl orange and phenol decreases with increase in initial concentration.

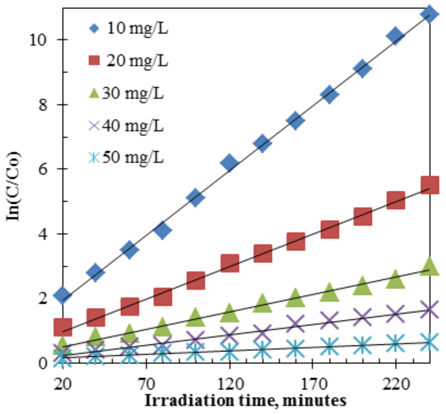

Fig. 5. Kinetics of the photocatalytic degradation of phenol.

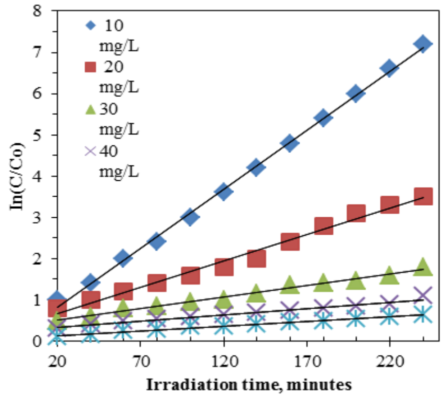

Fig. 6. Kinetics of the photodegradation of methyl orange.

TABLE I: REACTION RATE CONSTANTS FOR METHYL ORANGE AND PHENOL DEGRADATION WITH DIFFERENT INITIAL CONCENTRATIONS

Initial concentration (mg/L)	**ZnO-SiO_2 conc (g/L)**		**Methyl orange**		**Phenol**	
	Methyl orange	**Phenol**	**rate constant (*k*)**	**r^2**	**rate constant (*k*)**	**r^2**
10	3.0	1.5	0.0287	0.9982	0.0401	0.9980
20	3.0	1.5	0.1280	0.9864	0.0201	0.9972
30	3.0	1.5	0.0056	0.9875	0.0107	0.9941
40	3.0	1.5	0.0030	0.9686	0.0063	0.9865
50	3.0	1.5	0.0024	0.9874	0.0022	0.9937

IV. CONCLUSIONS

A photocatalyst consisting of ZnO immobilised on SiO_2 was prepared via calcination the of the precursor material at a temperature of 350°C for 9 hours. studies were carried out to find out the effects of catalyst loading and pH on the photodegradation efficiency of methyl orange and phenol. It was observed that the photodegradation efficiency increased with catalyst loading up to a maximum. Thereafter the photodegradation efficiency decreased. The maximum photodegradation efficiency were observed at 3.0 g/L and 1.5 g/L catalyst loading for methyl orange and phenol, respectively. The photocatalytic activity of ZnO-SiO_2 was also found to be strongly dependant on the pH of the methyl orange and phenol solutions. Good photodegradation efficiency was observed at pH 7 for methyl orange and pH 5 to 7 for phenol.

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REFERENCES

[1] N. B. Jin, W. K. Christopher, and C. C. Saint, "Recent development in photocatalytic water treatment technology: a review," *Water Research*, vol. 44, pp. 2997-3027, 2010.

[2] A. Ahmaruzzaman, "Adsorption of phenolic compounds on low-cost adsorbents: A review," *Advances in Colloid and Interface Science*, vol. 143, pp. 48-67, 2008.

[3] C. Hu, Y. Z. Wang, and H. X. Tang, "Destruction of phenol aqueous solution by photocatalysis or direct photolysis," *Chemosphere*, pp. 1205–1209, 2000.

[4] S. Lathasree, A. N. Rao, B. SivaSankar, V. Sadasivam, and K. Rengaraj, "Heterogeneous photocatalytic mineralization of phenols in aqueous solutions," *J. Mol. Catal. A: Chem.*, vol. 223. pp. 233–241, 2004.

[5] A. M. Peiro, J. A. Ayllon, J. Peral, and X. Domenech, "TiO2-photocatalyzed degradation of phenol and *ortho*-substituted phenolic compounds," *Appl. Catal. B: Environ*, vol. 30, pp. 359–373, 2001.

[6] D. Fabbri, A. B. Prevot, and E. Pramauro, "Effect of surface microstructures on photocatalytic degradation of phenol and chlorophenols," *Appl. Catal. B: Environ.*, vol. 62, pp 21–27, 2006.

[7] A. Di Paola, V. AuGugliaro, L. Palmisano, and E. Savinov, "Heterogeneous photocatalytic degradation of nitrophenols, J. Photochem. Photobiol," *A: Chem.*, vol 155, pp. 207–214, 2003.

[8] D. Wrobel, A. Boguta, and R. M. Ion, "Mixtures of Synthetic Organic Dyes in a Photoelectrochemical cell," *Journal of Photochemistry and Photobiology A*, vol. 138, pp. 7–22, 2001.

[9] U. I. Gaya and A. H. Abdullah, "Heterogeneous Photocatalytic Degradation of Organic Contaminants over Titanium Dioxide: A review of Fundamentals, Progress and Problems," *Journal of Photochemistry and Photobiology C*, vol. 9, pp. 1–12, 2008.

[10] P. Bansal, D. Singh, and D. Sud, "Photocatalytic Degradation of Azo Dye in Aqueous TiO_2 Suspension: Reaction Pathway and Identification of Intermediates Products by LC/MS," *Separation and Purification Technology*, vol. 72, pp. 357–364, 2010.

[11] M. Pera-Titus, V. Garcıa-Molina, M. A. Banos, J. Gimenez, and S. Esplugas, "Degradation of Chlorophenols by Means of Advanced Oxidation Processes: A General Review," *Applied Catalalyis B: Environmental*, vol. 47, pp. 219–256, 2004.

[12] P. Colindres, H. Yee-Madeira, and E. Reguera, "Removal of Reactive Black 5 from Aqueous Solution by Ozone for Water Reuse in Textile Dyeing Processes," *Desalination*, vol. 258, pp. 154–158, 2010.

[13] C. A. Martınez-Huitle and E. Brillas, "Decontamination of Wastewaters Containing Synthetic Organic Dyes by Electrochemical Methods: A General Review," *Applied Catalalyis B: Environmental*, vol. 87, pp. 105–145, 2009.

[14] J. Grzechulska and A. W. Morawski, "Photocatalytic labyrinth flow reactor with immobilized P-25 TiO_2 bed for removal of phenol from water," *Applied Catalysis. B: Environmental*, vol. 46, pp. 415–419, 2003.

[15] J. Domenech and A. Prieto, "Stability of ZnO particles in aqueous suspensions under UV illumination," *J. Phys. Chem*., vol. 90, pp. 1123-1128, 1986.

[16] I. Poulios, D. Makri, and X. Prohaska, "Photocatalytic treatment of olive milling waste water: oxidation of protocatechuic acid," *Global Nest: the Int. J.*, vol. 1, pp. 55-61, 1999.

[17] E. R. Carraway, A. J. Hoffman, and M. R. Hoffmann, "Photocatalytic oxidation of organic acids on quantum-sized semiconductor colloids," *Environ. Sci. Technol.*, vol. 28, pp. 786-791, 1994.

[18] R. I. Bickley, T. Gonzalez-Carreno, J. S. Lee, L. Palmisano, and R. J. D. Tilley, "A structural investigation of titanium dioxide photocatalyst," *J. Solid State Chem*., vol. 92, pp. 178–190, 1991.

[19] T. Ohno, K. Sarukawa, K. Tokieda, and M. Matsumura, "Morphology of a TiO2 photocatalyst (Degussa P 25) consisting of anatase and rutile crystalline phases," *J. Catal*., vol. 203, pp. 82–86, 2001.

[20] V. Maurion, C. Minero, E. Pelizzetti, P. Piccinini, N. Serpone, and H. Hidaka, "The fate organic nitrogen under photocatalytic conditions: degradation of nitrophenols and aminophenols on irradiated TiO_2," *J. Photochem. Photobiol. A: Chem.*, vol. 109, pp. 171–176, 1997.

[21] B. Bayarri, J. Gimenez, D. Curco, and S. Esplugas, "Photocatalytic degradation of 2,4-dichlorophenol by TiO_2/UV: kinetics, actinometries and models," *Catal. Today*, vol. 101, pp. 227–236, 2005.

[22] R. A. Doong, C. H. Chen, R. A. Maithreepala, and S. M. Chang, "The influence of pH and cadmium sulfide on photocatalytic degradation of 2-chlorphenol in titanium dioxide suspension," *Water Res*., vol. 35, pp 2873–2880, 2001.

[23] M. Muslim, M. A. Habib, A. J. Mahmood, T. S. A. Islam, and I. M. I. Ismail, "Zinc oxide-mediated photocatalytic decolorization of Ponceau S in aqueous suspension by visible light," *International Nano Letters*, vol. 2, pp. 30-38, 2012.

[24] M. S. T. Goncalves, A. M. F. Oliveira-Campos, E. M. M. S. Pinto, P. M. S. Plasencia and M. J. R. P. Queiroz, "Photochemical Treatment of Solutions of Azo Dyes Containing TiO2," *Chemosphere*, vol. 39, pp. 781-786, 1999.

[25] W. Nam, J. Kim, and G. Y. Han, "Photocatalytic Oxidation of Methyl Orange in a Three-Phase Fluidized Bed Reactor," *Chemosphere*, vol. 47, pp. 1019-1024, 2002

[26] E. Topoglidis, A. E. G. Cass, B. O'Regan, and J. R. Durrant, "Immobilisation and Bioelectrochemistry of Proteins on Nanoporous TiO2 and ZnO Films," *Journal of Electroanalytical Chemistry*, vol. 517, pp. 20-27, 2001.

[27] A. V. Emeline, W. Ryabchuk, and N. Serpone, "Factors affecting the efficiency of a photocatalysed process in aqueous metal-oxide dispersions, prospect of distinguishing between two Kinetic models," *Journal of Photobiology A: Chemistry*, vol. 133, pp. 89-97, 2000.

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