
Comparative Studies on the Photocatalytic Degradation of Acridine Orange Using ZnO and ZnO/TiO₂ Synthesized Catalysts

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ABSTRACT

In this study, we report the successful synthesis of ZnO/TiO₂ catalysts by conventional solid state reaction and their effective use as photocatalytic degradation of Acridine orange (AO) dye under visible irradiation. The synthesized catalyst was characterized in terms of their morphology, structure and bond formation using SEM and FT – IR spectroscopic analysis. The detailed characterisation confirmed the formation of the catalyst which possesses correct morphology with good optical properties. The effect of operating parameters such as initial dye concentration, catalyst loading and solution pH for ZnO and ZnO/TiO₂ was 20 ppm, 2 g/L and 7 respectively at 91% and 98% degradation respectively. The kinetics of AO at optimum conditions followed pseudo first order kinetics with correlation coefficient (R²) value of 0.856 and 0.982, with rate constant of 0.028 and 0.011 respectively.

KEYWORDS: Acridine Orange, Photocatalysis, SEM, Zinc Oxide.

INTRODUCTION

Advanced oxidation processes (AOP) are successful to transform toxic organic compounds (e.g. drugs, pesticides, dyes etc.) into biodegradable substances. AOPs in general are cheap to install but involve high operating cost due to the input of chemicals and energy required [1]. Different AOPs methods are available such as Ozone (O₃), Fenton (Fe₂ + H₂O₂), Electrolysis (electrodes + current), Sonolysis (ultrasound), Photolysis (UV + H₂O₂), Photocatalysis (catalyst + light), Photo-Fenton (solar + fenton). Among the different available AOPs, those driven by light seem to be the most popular technologies for wastewater treatment, and among them semiconductor photocatalysis is particularly attractive due to its relatively low cost and high efficiencies[2].

Metal oxide semiconductors hold great promise for application in conversion of solar to chemical energy by photo-catalysis [1]. Metal oxide semiconductor materials, such as TiO₂, ZnO, Fe₂O₃, CdS, and ZnS have been found to be attractive photocatalyst because they are environmentally sustainable with high catalytic efficiency in the degradation of various detergents, dyes and volatile organic compounds into carbon dioxide and water under UV light irradiation [3]. These cost-efficient, effective, and environment-friendly materials can be used to alleviate environmental problems. Surface area and surface defects of metal oxides are important factors for enhanced photocatalytic activity [4]. Among various semiconductors, zinc oxide (ZnO) exhibits higher efficiency in the photocatalytic degradation of some organic dyes than other semiconductors because it has a comparable band gap (3.2 eV) with relative large quantum efficiency in comparison to TiO₂ which has nearly same band gap with ZnO [5, 6]. Some studies have confirmed that it has a better efficiency than TiO₂ or equal to TiO₂ in photodegradation of dyes even in aqueous solutions [7].

Acridine orange (AO) is a heterocyclic dye containing nitrogen atoms, which is widely used in the fields of printing and dyeing, leather, printing ink and lithography [8]. It has also been used extensively in biological stains. Toxicological investigations indicate that aminoacridine has mutagenic potential [9]. The release of this colored wastewater in the ecosystem is a dramatic source of water pollution, eutrophication and perturbation in aquatic life. Therefore, a method of treating wastewater containing AO is highly desirable now and in the near future [8]. In the present study, the ZnO/TiO₂ catalyst was expected to show the significant enhancement in photocatalytic activity for degradation of AO than the corresponding ZnO catalyst.

MATERIALS AND METHODS

Acridine Orange (98% dye content) was obtained from Sigma Aldrich. ZnO and TiO₂ Powder were from Analar BDH, Ethanol, sodium hydroxide, hydrochloric acid, and methanol were from Global Chemie, Deionized water was used throughout the investigations. The reagents were used as received without further purification. A stock solution of acridine orange dye was prepared by dissolving desired amount of the dye in a 1000 cm³ volumetric flask with small amount of distilled water and filled to the mark.

Synthesis of ZnO/TiO₂

The ZnO/TiO₂ powders was synthesized by conventional solid state reaction using ZnO:TiO₂ at ration 1:1, though the materials are not very sensitive to moisture; the handling of chemicals was carried out in dry atmosphere. The starting materials were mixed in 90ml of ethanol by milling with porcelain mortar and pestle in polyethylene jar for 24 h and dried in oven. Calcination temperature was selected to investigate the reaction, formation of ZnO/TiO₂ at 550 °C for 48 h applied at that temperature and finally the calcinated ZnO/TiO₂ powders were presented to Scanning Electron Microscopy (SEM) (Leica Stereoscan – 440 SEM) and Fourier Transform Infrared Spectroscopy (FTIR) (SHIMADZU FT-IR-8400s FT - IR) for analysis.

Photocatalytic Procedure

The photocatalytic performance of ZnO and ZnO/TiO₂ photocatalysts was carried out in the presence of visible irradiation in an immobilized reactor of dimension 7.5cm × 6cm (height × diameter), surrounded with aluminium reflectors to avoid loss of irradiation. In the experiment, a mixture of dye solution and catalyst was prepared and fed into a beaker. The suspension was continuously agitated with the help of a hot plate stirrer. Prior to the experiment, the heterogeneous mixture was premixed in the dark for about 30 min to establish equilibrium between adsorption and desorption phenomenon on the surface of the catalyst before it was exposed to irradiation of light. After the elapsed of a period an aliquot (3 mL) of the solution was withdrawn from the system, centrifuged and filtered with filter paper before being subjected to analysis. This was to screen any suspended solid present in the samples that will affect the accuracy of the results obtained from UV-Vis spectrophotometer.

Degradation efficiency

The electronic spectrum of AO was recorded over a wavelength ranges 300 - 800 nm using a Perkin Elmer UV winlab UV-Vis spectrophotometer facility. The maximum absorbance wavelength (λ_{max}) of the dye was 470 nm. Therefore, the absorbance of the dye with reaction time was recorded at λ_{max} = 470 nm and concentrations were calculated with aid of calibration curve. Photocatalytic degradation/mineralization efficiency of AO was estimated as follows:

$$\text{Performance \%} = \left(1 - \frac{C_t}{C_o}\right) \times 100 \quad \dots\dots\dots (1)$$

C_o is the initial AO concentration and C_t is the concentration of AO at reaction time t.

RESULTS AND DISCUSSION

Catalyst Characterisation

Scanning electron microscopy (SEM) analysis of ZnO/TiO₂ powders was carried out under optimum conditions to study surface morphology (Figure 1). The particle morphology and size were directly imaged using scanning electron microscopy (SEM). The SEM micrographs of ZnO/TiO₂ powders annealed at 550 °C for 24 h. The porosity like particle seemed to distribute homogeneously. As a result, it was said to be porous structures. Fourier transform infrared spectroscopic (FTIR) spectrum is generally used for the determined the existence of new bond that leads to the formation of synthesized catalyst. The FTIR spectrum of the sample (Fig.2) was recorded at the range of 450-4000 cm⁻¹ for ZnO and ZnO/TiO₂ catalysts respectively. It can be seen that no major impurity peaks corresponding to the organic impurity was observed. The band at 446 cm⁻¹ attributed to Zn – OH stretching vibration of ZnO also shifted to 825 – 898 cm⁻¹ in the synthesized catalyst. The absorption peak shift observed around 1577 and 3406 cm⁻¹ are associated with bending and stretching vibration OH group of chemisorptions/physiosorption water molecule in ZnO surface [10]. While the band at 510 to 650 cm⁻¹ reveal the formation of Ti –O bending vibration [11]. The new peak appeared in treated ZnO-TiO₂ spectra at 679 cm⁻¹ attributed to Zn-O-Ti bonds (Fig2(b)) [12].

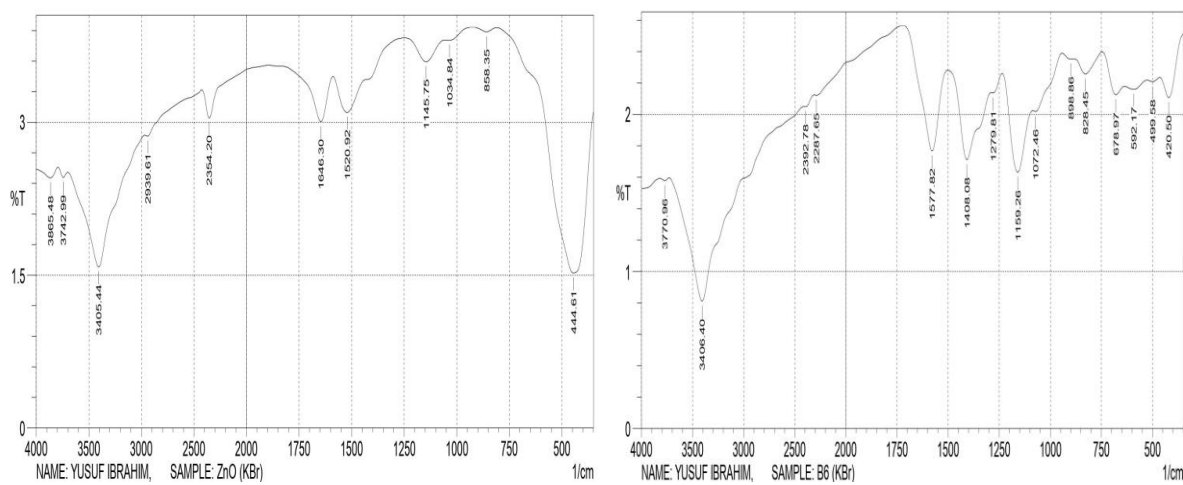


Figure 2: (a) FT –IR of Naked ZnO catalyst

(b) FT –IR of ZnO/TiO₂

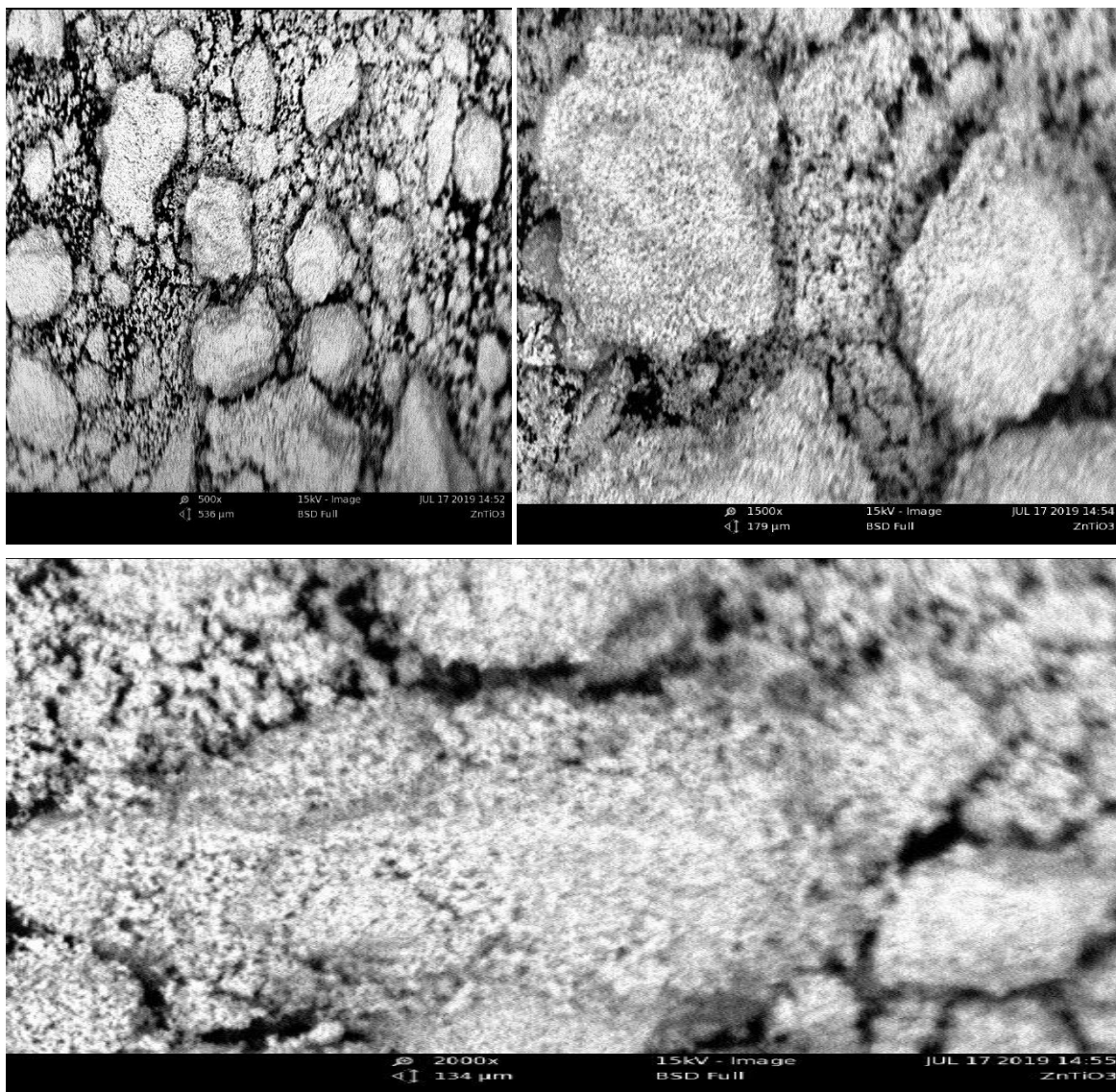


Figure 1: SEM micrographs of ZnO/TiO₂ powders at (a) 350x magnification and 766 micrometer. (b) 500x magnification and 536 micrometer. (c) 2000x magnification and 134 micrometer.

Effect of Reaction Parameters

Effect of Initial Dye Concentration

The effect of initial AO dye concentration was studied over ZnO and ZnO/TiO₂ photocatalysts under visible light irradiation at constant catalyst loading and solution pH was represented in

Figure 3. The tested initial AO concentrations ranges from 20 – 60 ppm in the presence of 2.0 g/l and 1.5 g/l ZnO : ZnO/TiO₂ and solution pH of 7.

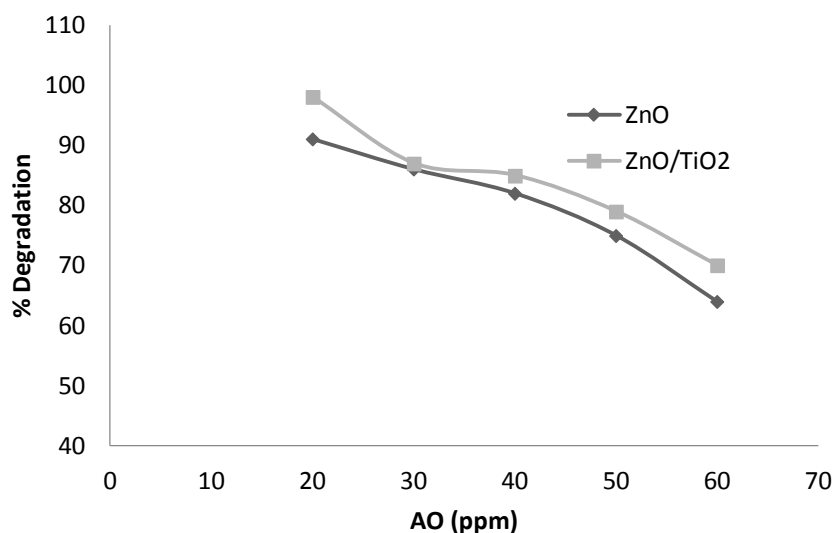


Figure 3: Effect of initial dye concentration on the photocatalytic degradation of AO dye.

From the result, the degradation efficiency of AO dye decreased as the initial concentration increased. The decrease in the degradation efficiency at high concentration could be due to the dye solution becoming denser which can hinder the light from reaching the catalyst surface. Thus, lesser photon can reach the catalyst surface which can result in lesser generation of active radicals to degrade the dye. At high concentration of AO dye, the increased amount of AO can also increase the adsorption of AO molecules onto the catalyst surface. Since the number of active radicals generated on the surface of the catalyst did not increase under the constant light intensity and irradiation time, there will be lesser active radicals to attack the dye molecules and led to lower degradation efficiency. Furthermore, the concentration of intermediates also increased with increasing dye concentration. When the radicals attacked the dye molecules at high concentration, a lot of intermediates can be generated. These intermediates can compete with the parent molecules for limited active sites on the catalyst surface[13].

Effect of pH

The effect of the initial pH of the dye was studied as pH is considered to be one of the most important parameters that can affect the photocatalytic activity of the AO dye. The initial pH of the dye was varied from pH 5 to 9. The studies were carried out with 20 ppm AO dye solution and 2.0 g/l ZnO, 1.5g/l ZnO/TiO₂ catalyst dose respectively. From the figure, as the pH of dye solution increases (5 - 7) the degradation increases and further decrease with increase in pH (8 - 9) for ZnO while for ZnO/TiO₂ the increase with increase from in pH from 5 – 8 then decreases at the pH of 9.

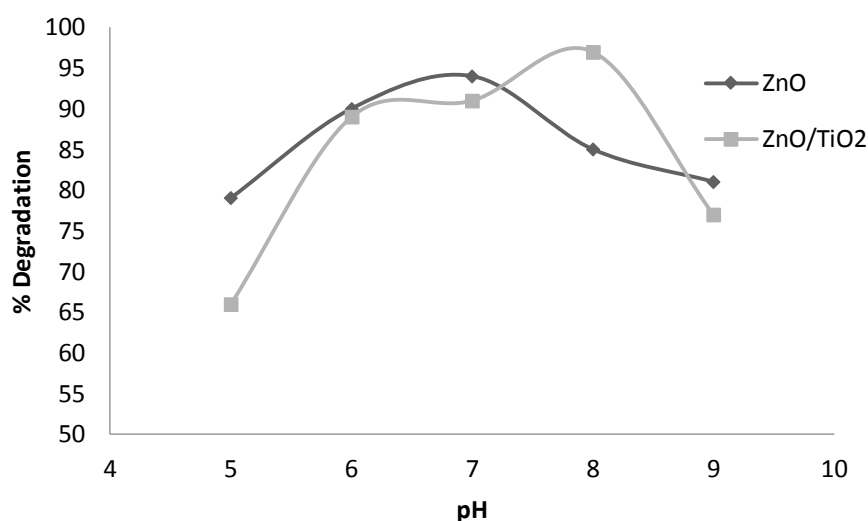


Figure 4: Effect of pH on the photocatalytic degradation of AO.

The effect of solution pH on the degradation rate can be explained mainly by adsorption of dye on ZnO surface. In acidic suspensions, the adsorption of dye molecules on the ZnO particles was significantly increased compared to the extent of adsorption in alkaline suspension. This is attributed to the fact that ZnO shows an amphoteric character so that either a positive or a negative charge can be developed on its surface. The ZnO surface is positively charged in acidic solution and negatively charged in basic solution. Because the dye is negatively charged, the acidic solution favours the adsorption of dye onto photocatalyst surface [14].

Effect of Catalyst Loading

After optimizing pH, the catalyst loading is another important parameter which has strong influence on the degradation kinetics of dye solution. In order to determine the optimal amount of catalyst concentration, a series of experiments were carried out using different amount of catalyst varying from 0.5 g to 2.5 g, at optimized pH of 7.0 and 20 ppm initial dye concentration at 160 min reaction time. The result is presented in figure 5. The graph depicts that as the amount of catalyst increases the efficiency of degradation also increases, than a slight decrease is observed when more catalyst was added.

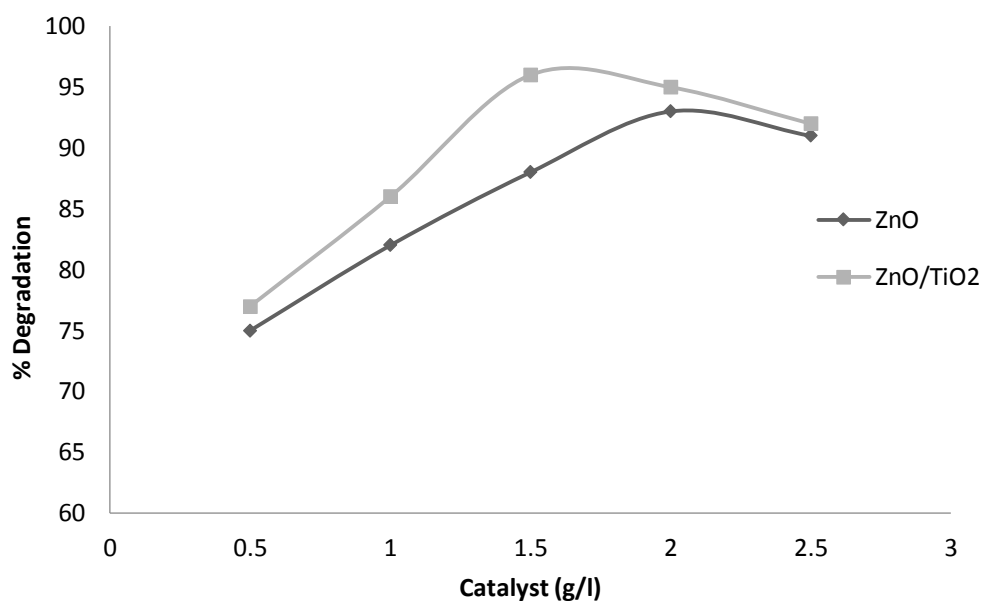


Figure 5: Effect of catalyst loading on the photocatalytic degradation of AO.

Maximum degradation rate has been achieved with catalyst dose of 2.0 g/l and 1.5 g/l for ZnO and ZnO/TiO₂ catalyst respectively and it was considered as the optimum dose for the degradation of AO dye solution for subsequent analysis. The increased degradation rate that follows the increase in the catalyst loading can be attributed to the fact that a larger amount of photons are absorbed, thus accelerating the process. When all the dye molecules are adsorbed on ZnO no improvement will be observed by adding catalyst [15].

Kinetic Studies

The kinetic studies of the photocatalytic degradation of AO at the optimum condition have been investigated in terms of pseudo first order and pseudo second order kinetics equation. The rate constant (k) for this heterogeneous photocatalysis was evaluated as a function of the initial concentration of original species. It is quite evident from the table 1, that the process profile followed an apparent pseudo-first order kinetic with correlation coefficient (R^2) value ZnO and ZnO/TiO₂ of 0.856 and 0.982 with rate constant of 0.028 and 0.011 respectively.

Table.1: Summary of Kinetic Studies ZnO and ZnO/TiO₂ Photocatalysis.

Catalyst	Pseudo First Order		Pseudo Second Order	
	K (min ⁻¹)	R ²	K (min ⁻¹)	R ²
ZnO	0.028	0.856	0.003	0.593
ZnO/TiO ₂	0.011	0.982	0.035	0.953

CONCLUSION

AOP's is efficient for treating organic contaminant in waste water, due to the production of highly oxidant ($\cdot\text{OH}$) that is capable of degrading organic contaminant. In this paper AO dye in water has been successfully degraded in the presence of ZnO and ZnO/TiO₂ photocatalysts. The effect of operational parameters, pH (5–9), catalyst dosage (0.5 – 2.5g/l), initial concentration of AO (20 – 60 mg/L), at contact time (160 min) was investigated to study the interactive effects of the process parameters and the optimum conditions. The presence of TiO₂ modification by reaction with ZnO lead to the synthesis of new materials ZnO/TiO₂ that is active in photocatalytic degradation of AO present in waste water. The mixing of two metal oxides by conventional solid state reaction accelerated the creation of electron hole. Illumination of ZnO/TiO₂ gave 98% degradation at the optimum conditions; 1.5 g/l catalyst dosage, pH 8 and AO concentration of 20 ppm. While for ZnO, 91% of the AO dye was degraded at optimum conditions; 2g/l catalyst dosage, pH 7, and AO concentration 20 ppm. The photocatalytic process realized by the ZnO/TiO₂ offers utilization of catalysts oxidant leading to complete mineralisation of AO catalyst.

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