

## Studies on TiO<sub>2</sub>/ZnO photocatalysed degradation of lignin

S.K. Kansal<sup>a,\*</sup>, M. Singh<sup>b</sup>, D. Sud<sup>c</sup>

<sup>a</sup> Department of Chemical Engineering & Technology, Panjab University, Chandigarh 160014, India

<sup>b</sup> Department of Chemical Technology, Sant Longowal Institute of Engineering and Technology, Longowal 148106, Sangrur, Punjab, India

<sup>c</sup> Department of Chemistry, Sant Longowal Institute of Engineering and Technology, Longowal 148106, Sangrur, Punjab, India

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### Abstract

The photocatalytic degradation of lignin obtained from wheat straw kraft digestion has been investigated by using TiO<sub>2</sub> and ZnO semiconductors. ZnO has been found to be a better photocatalyst than TiO<sub>2</sub>. The different variables studied, include catalyst dose, solution pH, oxidant concentration and initial concentration of the substrate. The degradation of lignin was favorable at pH 11. Optimum values of catalyst dose and oxidant concentration were found to be 1 g/l and  $12.2 \times 10^{-6}$  M, respectively. The degradation of the organic compound was also evaluated as COD removal and increase in the COD removal was observed with increase in degradation rate. An attempt has also been made to explore the applicability of ZnO in immobilized mode for the degradation of lignin under solar light for industrial scale application. Further the comparative evaluation of ZnO in slurry/immobilized mode has been carried out.

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### 1. Introduction

Lignin is second most abundant biopolymer on earth, constituting 30% of the dry weight of softwood and 20% of the hardwood [1]. It contains various phenolic and non-phenolic aromatic structural units formed during its biosynthesis by dehydrogenative polymerization of coneferyl and synapyl alcohols [2]. Lignin is contained in pulp and paper mill effluents, which is a major chemical oxygen demand (COD) component and is responsible for color of the effluents. Therefore, study of lignin degradation is of major environmental interest. In recent years, a promising treatment based on the total oxidation of hazardous organic compounds by using advanced oxidation processes (AOP's) has been reported [3,4]. The common feature of all AOP's is the generation of very reactive free radicals, principally hydroxyl radicals (OH•). The heterogeneous photocatalytic systems (UV/semiconductors) have been extensively studied due to their ability to photosensitize the complete mineralization of a wide range of organic substrates at ambient temperatures and pressures, without the production of harm-

ful by-products, including phenols, amides, aromatics, dyes and pesticides [5–10].

Titanium dioxide (TiO<sub>2</sub>) is generally considered to be the best photocatalyst and has the ability to detoxify water from a number of organic pollutants [6,7,10]. Kobayakawa et al. [11] first reported the use of photocatalytic processes for the complete mineralization of lignin. Tanaka et al. [12] studied the photocatalytic degradation of lignin using TiO<sub>2</sub> and found that it was adsorbed to TiO<sub>2</sub> quickly, and the subsequent illumination resulted in the desorption and degradation, simultaneously. Ksibi et al. [13] studied the degradation products of lignin obtained from alfalfa black liquor digestion. They reported that it could be successfully decolorized and degraded by titania based photocatalysis at room temperature. However widespread use of TiO<sub>2</sub> is uneconomical for large-scale water treatment, thereby interest has been drawn towards the search for suitable alternatives to TiO<sub>2</sub>. Daneshvar et al. [14] reported that the ZnO appears to be suitable alternative to TiO<sub>2</sub> since its photodegradation mechanism has been proven to be similar to that of TiO<sub>2</sub>. Yeber et al. [15] investigated the decolorization and acute toxicity reduction of a cellulose bleaching effluent by photocatalysis using TiO<sub>2</sub> and ZnO supported on glass raschig rings and showed that supported catalysts could efficiently degrade the organic compounds present in pulp and paper bleaching effluent. Peralta-

\* Corresponding author. Tel.: +91 172 2534920; fax: +91 172 2534929.  
E-mail address: [sushilkk1@yahoo.co.in](mailto:sushilkk1@yahoo.co.in) (S.K. Kansal).

Zamora et al. [3] investigated the photoassisted remediation of black liquor obtained from pine wood by using ZnO/TiO<sub>2</sub> and supported ZnO and reported the efficiency of ZnO to be particularly noticeable in the photo oxidation of pulp mill bleaching effluent. Lathasree et al. [9] studied the photocatalytic oxidation of phenol and chlorophenols in the presence of ZnO as photocatalyst.

In northern India, abundance quantity of agricultural residues such as wheat straw, bagasse, etc. is available. The pulp and paper mills are utilizing wheat straw along with long fibres to produce good quality of paper. During kraft/soda pulping, raw material (wood, wheat straw, etc.) is treated with sodium hydroxide and sodium sulphide in alkaline medium at high temperatures and pressures in a high-pressure vessel called digester. Lignin is degraded and solubilized from the wood cell walls, releasing cellulose fibres. To our knowledge there is no report regarding the photocatalytic degradation of lignin obtained from wheat straw. Therefore an attempt has been made to investigate the photocatalytic degradation of lignin obtained from kraft digestion of wheat straw using TiO<sub>2</sub>/ZnO as photocatalysts. In the present study hypochlorite has been used as an oxidant, which is widely employed as an oxidant for pulp bleaching. India being a tropical country, sunlight is abundantly available throughout the year, which can be conveniently exploited for the irradiation of semiconductor. The research on heterogeneous photocatalytic degradation of lignin using solar light may prove to be the effective solution to mitigate the pollution problem of paper mills. Therefore, the degradation of lignin has also been explored under solar irradiation.

## 2. Experimental methods

### 2.1. Materials

ZnO (5 m<sup>2</sup>/g) was purchased from Merck, Germany. Titania P-25 (surface area 50 m<sup>2</sup>/g and average particle size 30 nm) was obtained from Degussa, Germany and was used as received. Lignin was obtained after precipitation from wheat straw black liquor. The black liquor was acidified with dilute hydrochloric acid till the precipitation was complete. The precipitate was then allowed to settle and the supernatant liquid was decanted off. The precipitate was washed repeatedly with distilled water and dried at room temperature. Double distilled water was used for preparation of various solutions. pH of the solutions was adjusted with 1 M HCl or 1 M NaOH. Sodium hypochlorite (4% available Cl<sub>2</sub>, BDH Merck) was used as an oxidant. Reagents used for COD determination were potassium dichromate, sulfuric acid, ferrous ammonium sulfate, silver sulfate, mercuric sulfate, ferroin indicator and were purchased from S.D. Fine Chemicals, India.

### 2.2. Photocatalytic reactor

The photochemical degradation was carried out in specially designed doubled wall reaction vessels in the UV chamber equipped with five UV tubes each of 30 W (Philips), detail is given elsewhere [8]. Measurement of UV light intensity was

done by chemical method, i.e., potassium ferrioxalate actinometry [16]. The obtained intensity was  $2.4 \times 10^{-6}$  einstein/min. Constant stirring of solution was ensured by using magnetic stirrers. The temperature was maintained constant throughout the reaction time by circulating water in the jacketed wall reactor. Under solar irradiation, the experiments were carried out in a borosilicate glass reactor (non-concentrating type slurry reactor) of diameter 0.17 m and capacity 800 ml, covered by a thin plastic film from the top through which 98% of UV rays can pass. The average UV intensity of sunlight in this region was 35 W/m<sup>2</sup> during the experiments. The spectra were taken with UV-vis spectrophotometer (DR 4000, HACH); pH meter (Thermo Orion 920A) was used to measure the pH of the solution; COD (open reflux) was estimated by using standard methods [17].

To study the photocatalytic degradation of lignin in the immobilized mode, the photocatalyst was fixed on to an inert support (pumice stone) by using the procedure given by Noorjahan et al. [18]. The thin bed film slurry pond reactor (TBFSR) of diameter = 0.2 m, and capacity 955 ml was prepared. ZnO was suspended in minimum amount of water (4 g of ZnO in 100 ml of water) and 5 ml of acrylic emulsion was added to it under stirring. The stone was cleaned and ZnO + acrylic emulsion mixture was spread on it with a laboratory spray gun. The coated ZnO film was left for air-drying. Coating was repeated twice to get a uniform film without pin holes. The degradation experiments were performed under solar illumination.

### 2.3. Procedures

For the degradation experiments, fixed amount of photocatalyst either ZnO or TiO<sub>2</sub> was added to 100 ml of lignin solution in each trial. The suspension was subjected to irradiation under UV/solar light. The aqueous suspension was magnetically stirred. Aliquot was taken out at different time intervals with the help of a syringe and then filtered through Millipore syringe filter of 0.45 μm. The rate of degradation was studied in terms of changes in absorption spectra and reduction in COD. The percentage degradation was calculated as follows:

$$\text{degradation (\%)} = 100 \times \left( \frac{C_0 - C}{C_0} \right)$$

where  $C_0$  = initial concentration of lignin,  $C$  = concentration of lignin after photoirradiation. Similar experiments were carried out by varying the catalyst dose (0.5–2.0 g/l), pH of the solution (pH 3–11), oxidant concentration ( $3.06 \times 10^{-6}$  M to  $15.3 \times 10^{-6}$  M) and initial concentration of lignin (10–100 mg/l).

## 3. Results and discussion

### 3.1. UV-vis spectra

Fig. 1 shows the typical time dependent UV-vis spectra. The absorption peak was observed at 277 nm which decreased gradually indicating that the decomposition of the organic compound

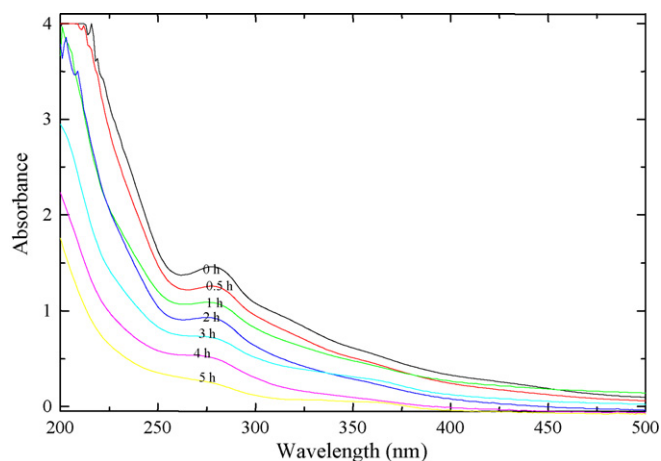


Fig. 1. Time dependent UV-vis absorption spectra of lignin under UV light.

was taking place. In a separate experiment, the absorbance at 277 nm plotted against concentration of lignin gave a linear relationship showing that the absorption measurement offers the convenient method to evaluate the degradation of lignin which is in agreement with earlier findings [12].

### 3.2. Photolysis/photocatalytic degradation of lignin

100 ml of lignin (100 mg/l initial concentration) solutions having natural pH value of 9.7 were treated under UV light alone and in the presence of ZnO (1 g/l) as photocatalyst (Fig. 2). The irradiation in the absence of ZnO showed very little destruction of lignin (5%) in 5 h, whereas in the presence of ZnO, 84% lignin was degraded in 5 h. The weak disappearance of the lignin in the absence of ZnO is assigned to the direct photolysis resulting in weak UV light absorption by the lignin. A comparison of these two experiences showed that the direct photolysis has negligible effect as compared to heterogeneous photocatalytic process on the degradation of lignin. When the adsorption studies of lignin were carried out with TiO<sub>2</sub>/ZnO, it was found that 18% of lignin was adsorbed on to ZnO whereas 10% lignin adsorption was observed with TiO<sub>2</sub> after 15 min.

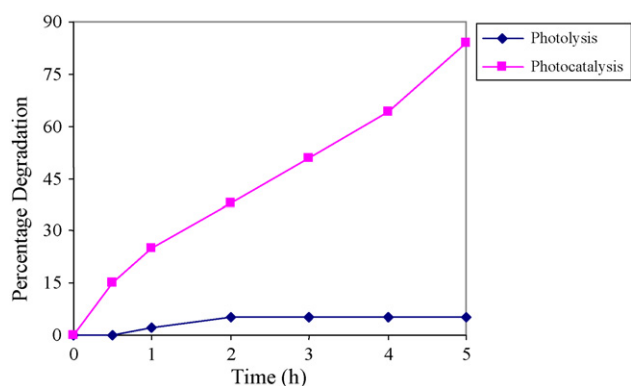


Fig. 2. Degradation of lignin by photolysis and photocatalysis under UV light.

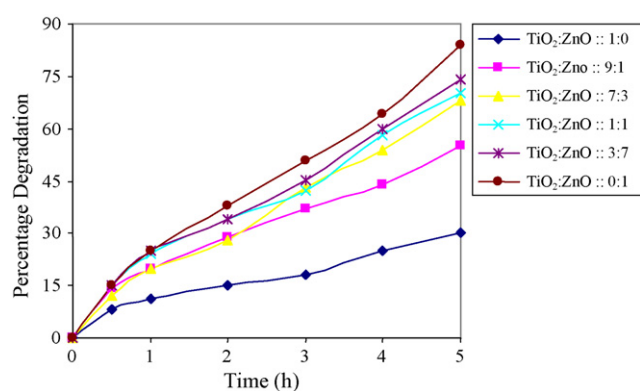


Fig. 3. Effect of different catalysts and their ratios on percentage degradation of lignin under UV light (catalyst dose 1 g/l; pH natural; oxidant concentration  $6.12 \times 10^{-6}$  M).

### 3.3. Degradation of lignin under UV/solar irradiation using various combinations of TiO<sub>2</sub>/ZnO photocatalysts

Fig. 3 illustrates the photodegradation of lignin with illumination of five UV lamps (30 W) in the presence of 1 g/l TiO<sub>2</sub>/ZnO and their different ratios at natural pH with  $6.12 \times 10^{-6}$  M concentration of NaOCl as an oxidant. ZnO showed higher degradation efficiency for lignin than that of TiO<sub>2</sub> or combination of ZnO with TiO<sub>2</sub>. The percentage degradation varied from 30% to 84% for different ratios of TiO<sub>2</sub> and ZnO. The enhancement of photodegradation rate of lignin in the presence of ZnO may be attributed to the fact that it absorbs over a large fraction of UV spectrum and the corresponding threshold of ZnO is 425 nm [19]. Peralta-Zamora et al. [3] obtained similar results while evaluating TiO<sub>2</sub> and ZnO for the remediation of black liquor.

When the efficacy of different catalysts for degradation of lignin was investigated under solar irradiation, similar trend was observed as under UV light but the degradation was achieved in lesser time as compared to under UV irradiation. The results are depicted in Fig. 4. Therefore, further experiments have been performed with ZnO as photocatalyst.

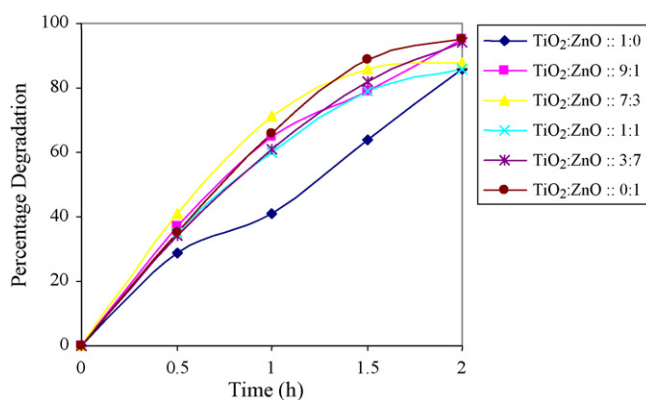


Fig. 4. Effect of different catalysts and their ratios on percentage degradation of lignin under solar light (catalyst dose 1 g/l; pH natural; oxidant concentration  $6.12 \times 10^{-6}$  M).

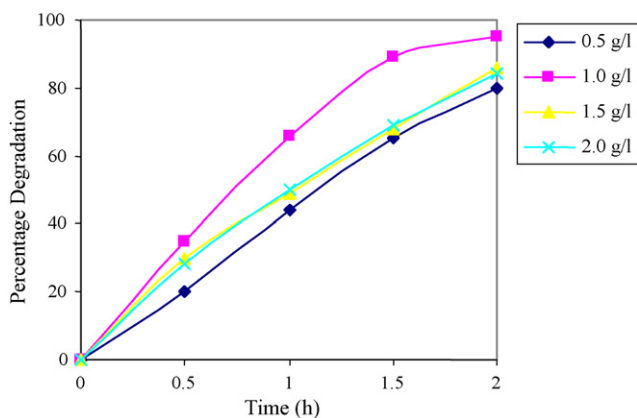


Fig. 5. Effect of catalyst dose on percentage degradation of lignin.

### 3.4. Degradation of lignin using ZnO as photocatalyst

The experiments were carried out to study the degradation of lignin employing ZnO as catalyst under solar light. Various parameters which affect the degradation such as catalyst dose (0.5–2.0 g/l), pH (3–11), oxidant concentration ( $3.06 \times 10^{-6}$  M to  $15.3 \times 10^{-6}$  M), initial concentration of lignin (10–100 mg/l) and time (0–150 min) of degradation were assessed.

#### 3.4.1. Effect of catalyst dose

In order to determine the effect of catalyst loading, the experiments were performed by varying catalyst dose from 0.5 g/l to 2.0 g/l for lignin solutions of 100 mg/l at natural pH (pH 10) and the results are depicted in Fig. 5. Fig. 5 reveals that initial slopes of the curves increase greatly by increasing catalyst loading from 0.5 g/l to 1.0 g/l, thereafter it starts decreasing slowly. The photocatalytic destruction of other organic pollutants also exhibits the same dependency on catalyst dose [20,21]. This can be explained on the basis that optimum catalyst loading is found to be dependent on initial solute concentration because with the increase of catalyst dosage, total active surface area increases, hence availability of more active sites on catalyst surface [22]. At the same time, due to an increase in turbidity of the suspension with high dose of photocatalyst, there will be decrease in penetration of UV light and hence photoactivated volume of suspension decreases [23]. Thus it can be concluded that higher dose of catalyst may not be useful both in view of aggregation as well as reduced irradiation field due to light scattering.

#### 3.4.2. Effect of pH

The role of pH in the rate of photocatalytic degradation was studied in the pH range 3–11 under solar light. The maximum degradation was obtained at pH value 11 as shown in Fig. 6. This is not surprising since variation in pH values entails an alteration in the properties of semiconductor–liquid interface [24], mainly related to the acid–base equilibrium of the adsorbed hydroxyl group [25]. The formation of hydroxyl radical from  $\text{OH}^-$  is favored at high pH. Villasenor and Mansilla, [26] attained almost complete decolorization of kraft black liquor from pine wood at pH value 11.6 using ZnO.

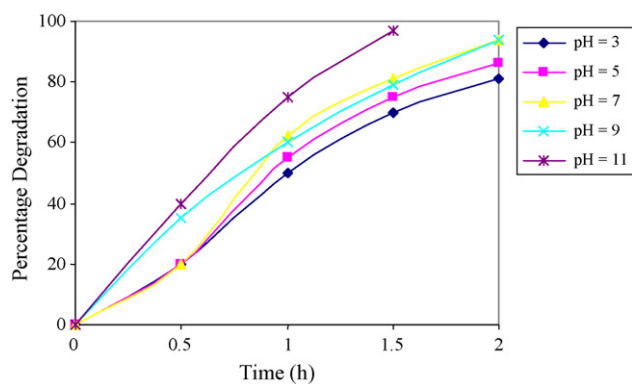


Fig. 6. Effect of pH on percentage degradation of lignin.

#### 3.4.3. Effect of oxidant concentration

The rate of photocatalytic degradation of the organic compounds was significantly improved by the addition of oxidant. Fig. 7 shows that by adding oxidant in the concentration range of  $3.06 \times 10^{-6}$  M to  $15.3 \times 10^{-6}$  M, the rate constant enhances upto  $12.2 \times 10^{-6}$  M concentration of oxidant. Blank experiments were carried out by irradiating the aqueous solution of organic compound in the absence of photocatalyst using optimum concentration of oxidant and no observable loss of the compound was noticed during irradiation. Similar trend was observed for photodegradation of chlorophenols by using UV/TiO<sub>2</sub> in presence of inorganic oxidant perchlorate by Pandiyan et al. [27].

#### 3.4.4. Effect of lignin concentration

Fig. 8 illustrates the percentage degradation as a function of irradiation time for lignin initial concentrations of 10 mg/l, 25 mg/l, 50 mg/l and 100 mg/l under optimized conditions (catalyst dose 1 g/l; pH 11 and oxidant concentration  $12.2 \times 10^{-6}$  M). The complete destruction of the lignin was achieved in 45 min with 10 mg/l initial concentration solution whereas it took 1 h for the complete removal of 25 mg/l initial concentration of lignin solution. It is noteworthy that the percentage degradation of lignin solution depends strongly on the initial concentration of the substrate. The effective degradation could be achieved when lower concentrations of lignin are used. When the initial lignin

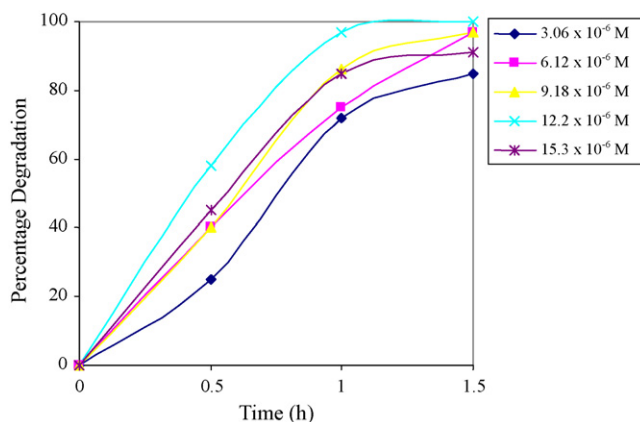


Fig. 7. Effect of oxidant concentration on percentage degradation of lignin.

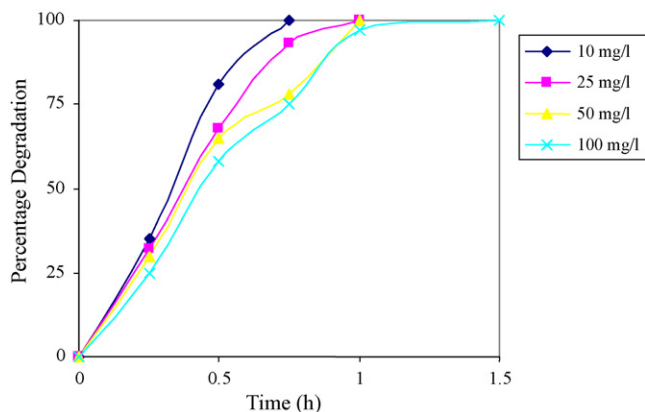


Fig. 8. Effect of initial concentration on percentage degradation of lignin.

concentration becomes higher, it will have inhibitory effect on the photodegradation. This phenomenon can be explained due to the increase of incidental photonic flux irradiating the catalyst in the dilute lignin solution. Thus the rate of hydroxyl radical ( $\text{OH}^\bullet$ ) production increases which would allow the degradation to be faster. Ksibi et al. [13] studied the chemical oxygen demand as a function of irradiation time for different initial concentrations of lignin and noticed that COD removal becomes higher for the weak concentrations of lignin solutions.

#### 3.4.5. COD removal

As the reduction of COD reflects the extent of degradation of an organic species, the percentage change in COD was studied for lignin samples under optimized conditions as a function of irradiation time using solar light. Fig. 9 presents the comparison between percentage degradation and COD removal as a function of irradiation time for initial concentration of lignin 100 mg/l, indicating increase in COD removal, with increase in percentage degradation. Yeber et al. [15] have also reported that the advanced oxidation of pulp mill bleaching effluent removes rapidly the COD especially in photocatalysed systems.

#### 3.5. Degradation of lignin using ZnO as immobilized photocatalyst

The degradation of lignin assisted by ZnO as a photocatalyst under sunlight was also investigated in immobilized systems.

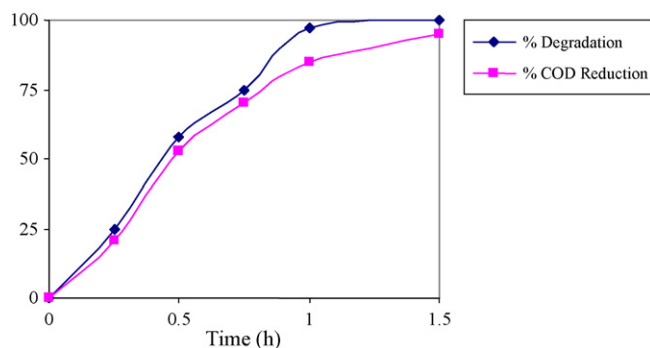


Fig. 9. Comparison between percentage degradation and COD reduction of lignin under solar/slurry mode.

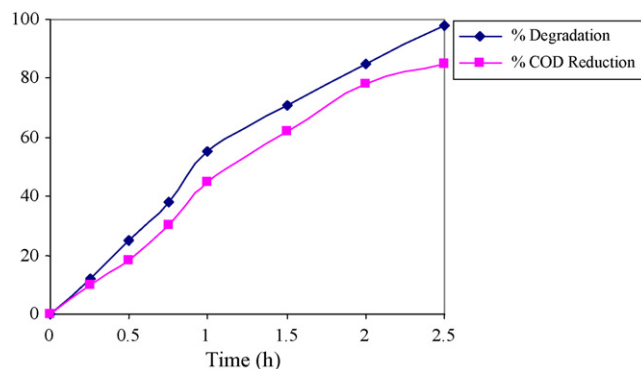


Fig. 10. Comparison between percentage degradation and COD reduction of lignin under solar/immobilized mode.

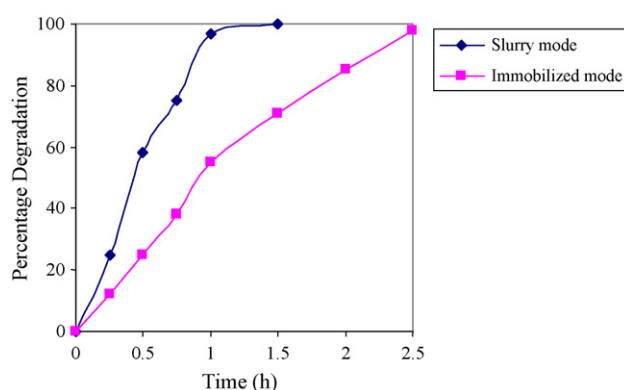


Fig. 11. Comparison of percentage degradation of lignin under solar slurry/immobilized mode.

ZnO was fixed on inert support (pumice stone) according to the procedure explained in Section 2.2. Test sample (100 ml) was irradiated under solar light using TBFSR. The maximum destruction achieved was 98% in 2.5 h of irradiation. The degradation of the organic compound present in the wastewater was also evaluated as COD removal. The COD removal was 85% in 2.5 h of solar irradiation. Fig. 10 depicts the percentage degradation and percentage COD reduction as a function of time.

Fig. 11 shows the comparative evaluation of ZnO in slurry mode and in immobilized form for the photodegradation of lignin. Our results are in agreement with the earlier reports available in literature [28,3], i.e., mainly from laboratory scale investigations, slurry type reactors seem to be more efficient than those based on immobilized catalysts. However for engineering applications, the cost factor may invalidate this mode for industrial wastewater treatment. Other operational advantages of the fixed catalyst include: it doesn't require separation steps before analysis or at the end of photocatalytic treatment, additionally it can be self cleaned after use just by passing water and exposing the immobilized matrix to the sun.

## 4. Conclusions

ZnO has been found to be a better photocatalyst for the degradation of lignin. Photocatalytic degradation of lignin was facilitated by the presence of catalyst or catalyst combined with

an oxidant. Experimental results indicated that the initial rate of photodegradation increased with increase in catalyst dose upto an optimum loading. Further increase in catalyst dose showed no effect. Also the initial rates of photodegradation were high at lower concentrations of lignin. It was seen that supported ZnO could efficiently photocatalyse the degradation of lignin present in pulp and paper mill bleach effluents.

### Acknowledgment

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