

# Performance study of Photocatalysis on the degradation of Lignin from Pulp and Paper industry wastewater

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**Abstract:** Lignin, being major contaminant in pulp and paper mill effluents, cannot be efficiently and economically removed by conventional treatment processes. Photocatalysis is a natural process of pollutant degradation in water. It has proven wide application potential in the field of water and wastewater treatment. This paper describes the performance study of Photocatalysis on the degradation of Lignin from Pulp and Paper industry wastewater. Experimentations were conducted on pure Lignin- water media to evaluate the performance of photocatalytic slurry phase reactor for Lignin oxidation. Experimentations were conducted for pH and Catalyst dose optimization. It has been found that most rapid oxidation is achieved at pH 5.5. A catalyst concentration of 2000mg/l has optimised oxidation potential for 2% Lignin-water solution for 2 Hours of UV exposure. Utilizing the obtained optimistic values, other operational parameters can be evaluated for modeling the Photocatalytic Reactor.

**Keywords – Photocatalysis, Pulp and Paper mill wastewater, Slurry phase reactor, UV/TiO<sub>2</sub>**

## I. INTRODUCTION

Traditionally, the water contained impurities which were removed easily by conventional technology. The wastewaters also contained organic bio-degradable impurities that were removed by biological treatment. However with the development of science and technology, industrialization and changed life style, the wastewater characteristics also have changed. Today, industrial and domestic wastewaters contain huge amount of non-biodegradable organics. They cannot be removed by biological methods. They are finding way into drinking water sources and are also joining the food chain.

Photo-catalysis is the only viable and economically feasible option for the removal of non-biodegradable organics. The technology is being used for wastewaters as well as for waters also. The technology was developed in 1970s with the pioneer works of Fujishima (1972). Today it is one of the most preferred areas of research in wastewater treatment.

The present work has proposed to remove Lignin from the wastewater using this technology. Lignin is a long chain organic polymer found in the wastewaters of pulp and paper industries. It is non-biodegradable. The conventional techniques used for the removal of lignin are adsorption, RO etc. they simply change the phase of the problem but does not solve it. Researchers have also used fungi for the treatment of lignin. Yet its separation from the wastewater is very difficult. Moreover the process is slow and too sensitive.

Photo-catalysis is a robust, effective and economically viable technology for such type of wastewaters. Little research work is available till now in this regard. The present work is for the removal of lignin using photo-catalysis technology. The technology will be used in the slurry phase reactor. The design parameters of the reactor and operational parameters of the process will be investigated.

## II. RELATED WORK

The basic process of photo-catalysis has been explored deeply by researchers. Phenol has remained as the first choice of earlier researchers as a probe chemical for degradation. Alberici *et. al.* (1997) have used this technology for removal of VOCs. Brillas *et. al.* (1998) presented a scientific look into the process and described the electron transfer phenomenon. Augugliaro *et. al.* (1999) and Cao *et. al.* (2000) applied the process for treatment of Toluene

in gaseous phase. Alex *et. al.* (2003) used this technology for removal of benzoic acids using specially designed cascade reactor configuration. Later researchers showed interest in the investigations of formation of intermediate products of the process too as stated by Pal *et. al.*(2000). Al Hakimi *et. al.* (2003) applied photo-catalysis technology for treatment of industrial wastewaters. Alpert *et. al.* (1991) treated hazardous waste using photo-catalysis. Researchers are working on developing composites of Titanium having even better performances. Ananta *et. al.* (2003) have reported development of Zirconium Titanate thin film for photo-catalysis. The use of photo-catalysis for removal of Halogenated Compounds had started as early as in 1970s. Carey *et. al.* (1976) reported the degradation of Polychlorinated Biphenyls and Barbeni *et. al.* (1985) reported the degradation of Penta-Chloro-Phenol Chlorinated using slurry phase reactors. Leprot *et. al.* (1993) have used degraded propanol by the Photo-catalysis method. The use of this process for disinfection of waters has been used since 1990s. Domenech *et. al.* (1993) have reported the application of photo-catalysis for disinfection of waters. Researchers also explored a variety of innovative configurations to apply the technology. Bedford *et. al.* (1994) proposed a new concept of shallow pond like reactor facilitated with solar concentrators. Husain *et. al.* (2000) proposed a combined system for photo-catalytic and photo-thermal applications. Zhang *et. al.* (2001) has proposed a rotating drum based reactor for the film phase process.

The technology has been applied for a variety of wastewaters. Muradov *et. al.* (1994) applied the technology for treatment of extremely explosive substance Nitro-Glycerin. Beckbolet (1996) used this technology for treatment of landfill leachates. Minero *et. al.* (1996) degraded Atrazine using Photo-catalysis process. Black Daneil (1996) and Goswami *et. al.* (1998) have presented a Bibliography of the work done by researchers to us this technology for Air and Water purification. The kinetic studies of the process have been done by many workers. Boudart *et. al.* (1984), Hussain *et. al.* (1988), Sabate *et. al.* (1991) and Jose *et. al.* (1993) have proposed few initial models to describe the kinetics of the photo-degradation process. Black *et. al.* (1991) have given bibliography of kinetic models describing the composite behavior of the process. Klausner *et. al.* (1994) have determined the reaction rate constants for the process using curve fitting techniques. Louis *et. al.* (1996) described the effect of operating parameters like temperature etc. on the photo-degradation process using Ethylene as a probe chemical. Photo-catalysis has been widely used in the degradation of Azo-dyes. Reeves *et. al.* (1992), Pelegrini *et. al.* (1999), Chun *et. al.* (2003) and Hinda *et. al.* (2002) and Daneshwar *et. al.* (2003) have used this technology for industrial wastewaters containing Azo-dyes. Rao *et. al.* (2003) has investigated the influence of common metallic ions on the slurry phase reactor performance.

Deposition of thin films initially had remained in the realm of patents. Natrajan *et. al.* (1998) applied spray pyrolysis technology for film deposition. Loddo *et. al.* (1999) have developed a combination of Rutile and Anatase TiO<sub>2</sub> based film to degrade 4-Nitro-Phenol. Mills *et. al.* (2003) worked on deposition of thin films. Gullierd *et. al.* (2002) have described Sol-gel technology for preparation of Titanium film. The doping of Titania to enhance its reactivity in the visible light has also been studied by researchers. Komova *et. al.* (2000) have used Copper to dope the Titania and increased the photo-catalytic activity. The film based reactors are also widely being used by researchers to degrade complex organics. Noorjahan *et. al.* (2003) have used thin film based reactor to degrade H-acid. Researchers have attempted to estimate the photonic efficiency of this photon-driven process. Serpone *et. al.* (1999a) and Serpone *et. al.* (1999b) have described the method of estimation of photonic efficiency and quantum yield also.

The developments in the photo-catalysis technology had been quite rapid and diversified in recent years. Chang *et. al.* (2010) has presented a review of recent developments in photo-catalysis technology. They have highlighted the emerging fields of research in this arena.

### III. PROPOSED METHODOLOGY

pH has a very profound effect on reaction rate. Hence it needs to be optimized at the initial stage. The pH of wastewaters containing Lignin is near to 9. The pH has been varied in the present case by HCL for lower side and by NaOH for higher side. pH has been varied from 5.0 to 10.5 for the experimental studies. This is so because too high too low pH may be impracticable for field applications too. While varying the pH, the catalyst concentration and Lignin concentration is kept as constant. Experimentations have been conducted to degrade the Lignin using different pH ranges in the Photocatalytic slurry phase reactor. The effect of pH on COD removal rate is depicted in the Graphs. Thus the pH has been optimized. This pH has been maintained throughout the experimentations. Catalyst suspensions are prepared with different concentrations and their transmissivity has been measured. Catalyst concentration in the slurry phase photo-catalytic reactor is very important parameters that affect the reaction rate. However, the catalyst concentration also causes scattering of light and their by reduces the light available which is the driving force of the photo-catalytic reaction. Hence there is an optimum concentration of catalyst which gives

the highest reaction rate. It will be dependent upon the intensity of light source. Hence, the light source intensity during experimentation is kept constant. It is practicable to work out the optimum catalyst concentration with reference to this intensity of light. Thus the optimum concentration of catalyst considering the radiation source available is established. This concentration is used as the optimum concentration.

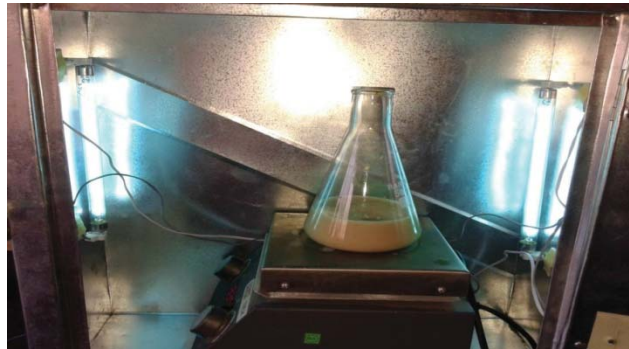
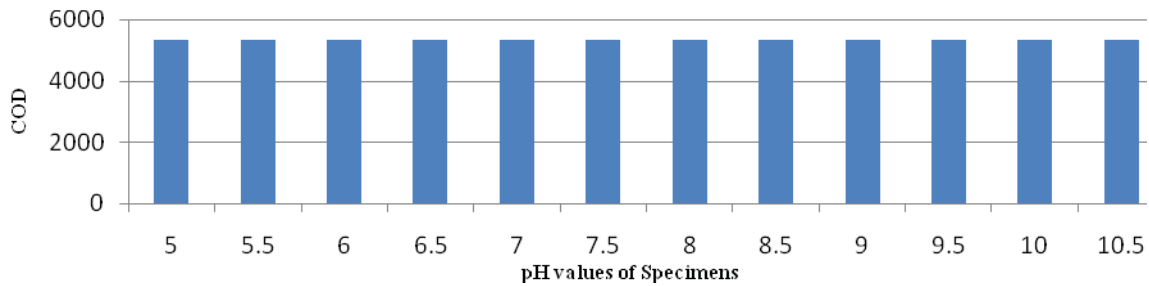


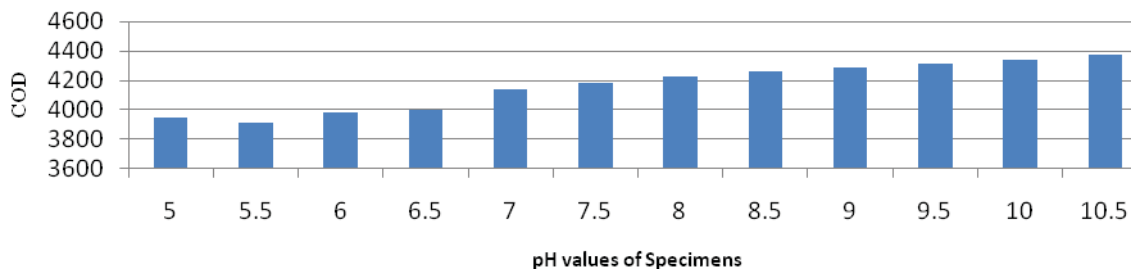
Figure1: Experimental setup showing the slurry phase Photocatalytic UV Reactor

#### IV. RESULT

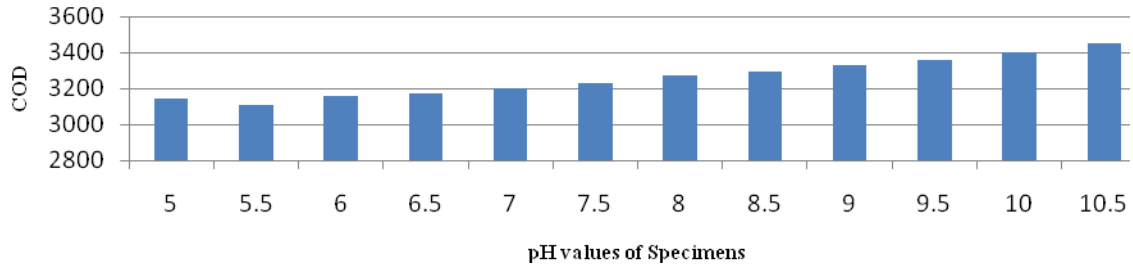
##### 4.1 Graphs showing effect on COD reduction of the Photo catalytic reactor at varying pH



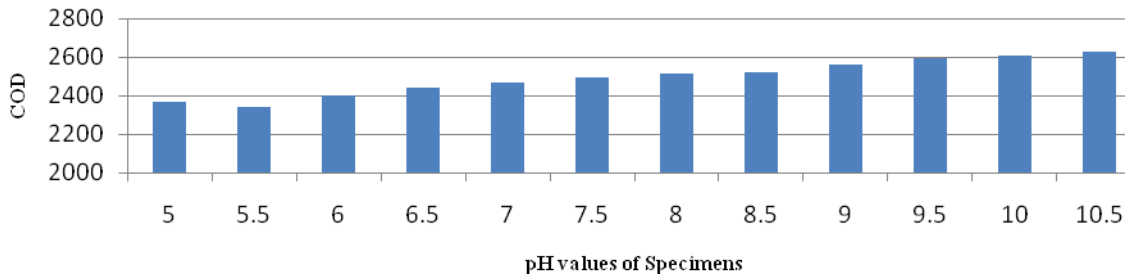
Graph 1: Variation in COD at different pH values for Lignin-water media at initial time.



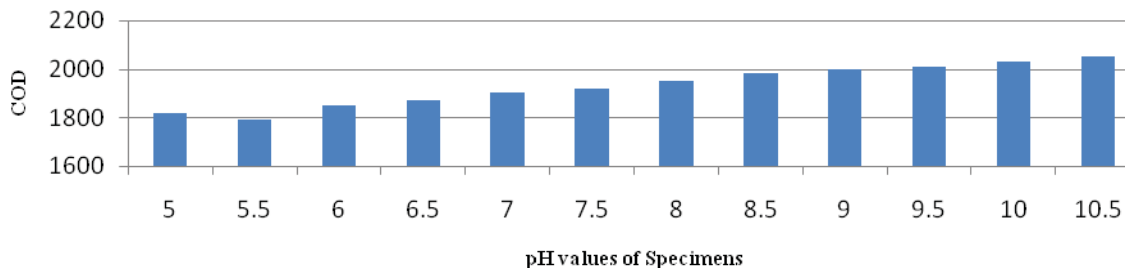
Graph 2: Variation in COD at different pH values for Lignin-water media after 30 minutes.



Graph 3: Variation in COD at different pH values for Lignin-water media after 60 minutes

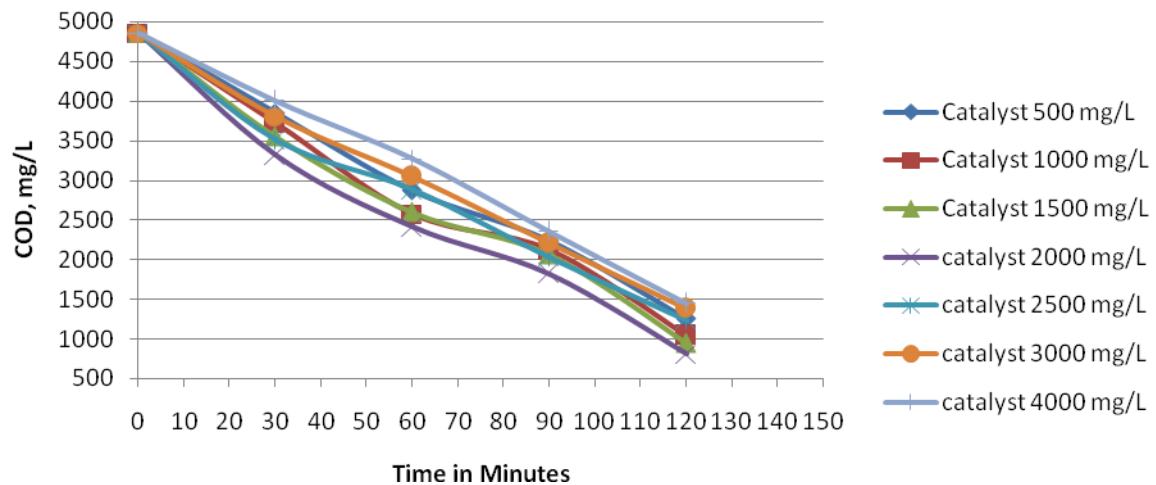


Graph 4: Variation in COD at different pH values for Lignin-water media after 90 minutes



Graph 5: Variation in COD at different pH values for Lignin-water media after 120 minutes

4.2 Graph showing effect on COD reduction of the Photo catalytic reactor at varying Catalyst concentrations



Graph 6: Variation in COD at different Catalyst Concentrations for Lignin-water media w.r.t. Time

## V. CONCLUSION

It can be concluded from the present study that the Photo-catalysis can be an emerging area of wastewater treatment technology. The process is effective though, complex and needs rigorous investigations. Experimentations have shown significant effect of pH variation upon oxidation of Lignin in wastewater via COD tests. From the above experimentations it can be observed that the optimum pH is 5.5 giving highest oxidation efficiency for Lignin in photo catalytic batch reactor. Catalyst concentration has also shown an influencing factor in the oxidation process as it tends to scatter the light in the slurry and thereby affecting reaction. From above studies it can be concluded that the catalyst concentration of 2000 mg/l has optimized COD removal for 2% Lignin-water media when treated for 2 Hours in the Photocatalytic slurry phase reactor. The optimum pH and optimum concentration of catalyst has been established in the studies carried out. Furthermore, effects of other operational parameters need to be studied.

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