

Photo Induced Catalytic Treatment of Pulp and Paper Industry Wastewater

Shantanu N. Pawar

*Research Student, Civil Engineering Department,
SSBT's College of Engineering and Technology, Jalgaon, Maharashtra, India*

Dr. Mujahid Husain

*Professor and Head, Civil Engineering Department,
SSBT's College of Engineering and Technology, Jalgaon, Maharashtra, India*

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 fields 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 Lignin- water media to evaluate the performance of photocatalytic slurry phase reactor for Lignin oxidation. Experimentations were conducted for different Temperature ranges and contaminant concentrations. From experimentations it has been observed that the optimum temperature is 60°C giving highest oxidation efficiency for Lignin in photo catalytic batch reactor. Contaminant (Lignin) 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. The present experimentation proven that the contaminant concentration of 2000 mg/ l has optimized COD removal for when treated for 1.5 Hours in the Photocatalytic slurry phase reactor. Reactor.

Keywords – Photocatalysis, Pulp and Paper mill wastewater, Slurry phase reactor, UV/TiO₂

I. INTRODUCTION

The wastewater from industries contains impurities which cannot be removed easily by conventional technology always. 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 industrial wastewater characteristics also have changed. Today, industrial wastewaters contain huge amount of non-biodegradable organics. They cannot be removed by biological methods alone. Harmful compounds originating from these are finding way into surface and subsurface drinking water sources and are also joining the food chain.

Photo-catalysis is presently the most 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 water and wastewater treatment.

The present study has been conducted 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. These techniques simply change the phase of the problem but do 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 TiO₂ 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

Reaction temperature has a very profound effect on reaction rate. Hence it needs to be optimized at the initial stage. The average temperature of wastewaters is higher than normal. The temperature has been varied in the present study. Temperature has been varied from 40°C to 80°C for the experimental studies. This is so because too high too low temperature may be impracticable for field applications too. While varying the temperature, the catalyst concentration and Lignin concentration is kept as constant. Experimentations have been conducted to degrade the Lignin using different temperature ranges in the Photocatalytic slurry phase reactor. The effect of temperature on COD removal rate is depicted in the Graphs. Thus the temperature has been optimized. This temperature 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. The presence of Lignin as contaminant has also profound effect on the light transmissivity. It is also 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 and contaminant dose with

reference to this intensity of light. Thus the optimum concentration of catalyst and contaminant considering the radiation source available is established. This concentration is used as the optimum concentration.

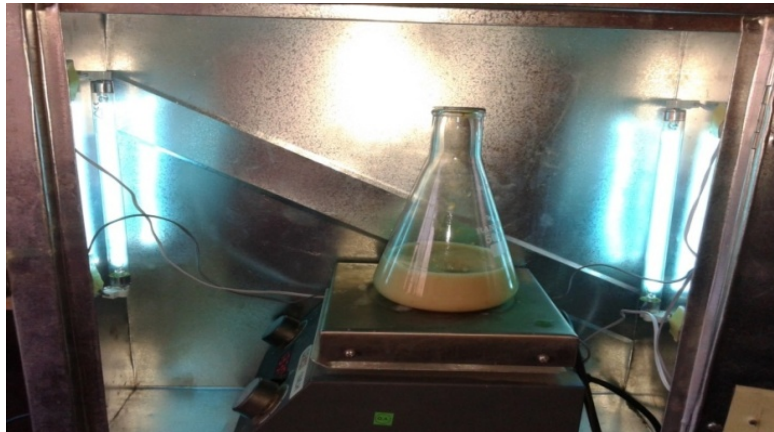
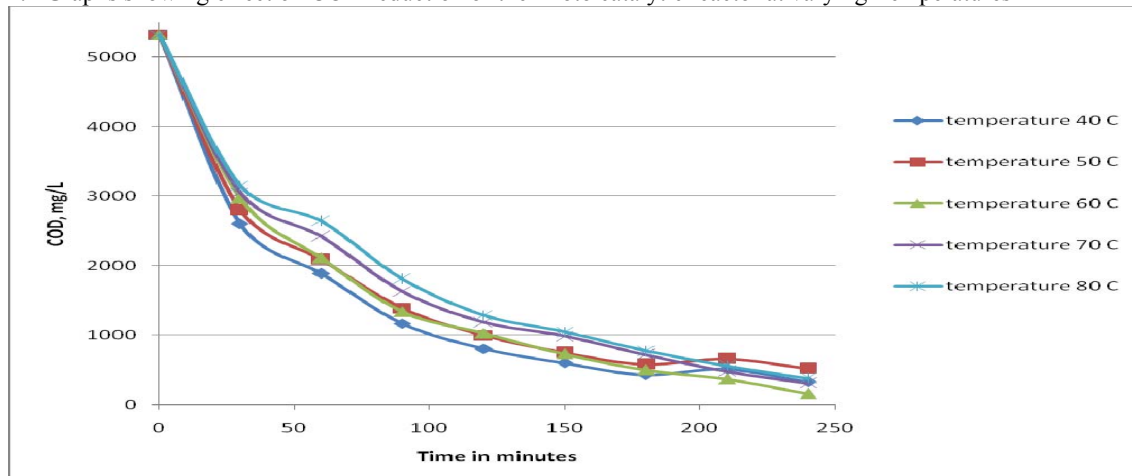


Figure1: Experimental setup showing the slurry phase Photocatalytic UV Reactor

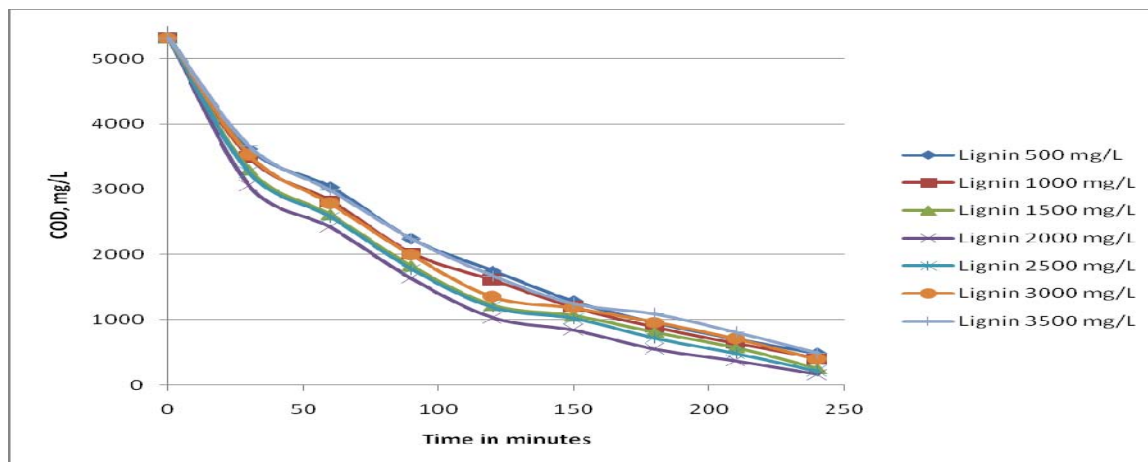
IV. RESULT

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



Graph 1: Variation in COD at different reaction temperatures for Lignin-water media at variable time.

4.2 Graph showing effect on COD reduction of the Photo catalytic reactor at varying Contaminant (Lignin) concentrations



Graph 6: Variation in COD at different contaminant 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 reaction temperature variation upon oxidation of Lignin in wastewater via COD tests. From the above experimentations it can be observed that the optimum temperature is 60°C giving highest oxidation efficiency for Lignin in photo catalytic batch reactor. Contaminant (Lignin) 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 contaminant concentration of 2000 mg/ l has optimized COD removal for when treated for 1.5 Hours in the Photocatalytic slurry phase reactor. The optimum temperature and optimum concentration of contaminant has been established in the studies carried out. Furthermore, effects of other operational parameters need to be studied.

REFERENCES

- [1] Alberici Rosana M. and Wilson F. Jardim [1997] "Photocatalytic destruction of VOCs in the gas-phase using titanium dioxide". *Applied Catalysis B: Environmental* 14, 55-68.
- [2] Brillas Enric, Eva Mur, Roser Sauleda, Laura Sanchez, Jose Peral, Xavier Domenech, Juan Casado [1998] "Aniline mineralization by AOP's: anodic oxidation, photocatalysis, electro-fenton and photoelectro-fenton processes". *Applied Catalysis B: Environmental* 16, 31-42.
- [3] Augugliaro Vincenzo, S. Coluccia, V. Loddo and M. Schiavello [1999] "Photocatalytic oxidation of gaseous toluene on anatase TiO₂ catalyst: mechanistic aspects and FT-IR investigation". *Applied Catalysis B: Environmental* 20, 15-27.
- [4] Cao Lixin, Zi Gao, Steven L. Suib, Timothy N. Obee, Steven O. Hay and James D. Freihaut [2000] "Photocatalytic oxidation of toluene on nano-scale TiO₂ catalysts: studies of deactivation and regeneration". *Journal of catalysis* 196(2), 253-261.
- [5] Alex H. C., Chak K. Chan, John P. Barford and John F. Porter [2003] "Solar photocatalytic thin film cascade reactor for treatment of benzoic acid containing wastewater". *Water Research* 37, 1125-1135.
- [6] Pal Bonmali and Maheshwar Sharon [2000] "Photodegradation of polyaromatic hydrocarbons over thin film of TiO₂ nanoparticles: a study of intermediated photoproducts". *Journal of Molecular Catalysis A: Chemical* 160, 453-460.
- [7] Alhakimi Gamil, Lisa H. Studnicki and Muftah Al-Ghazali [2003] "Photocatalytic destruction of potassium hydrogen phthalate using TiO₂ and sunlight: application for the treatment of industrial wastewater". *Journal of Photochemistry and Photobiology A: Chemistry* 154, 219-228.
- [8] Alpert Daniel J., Jeremy L. Sprung, James E. Pacheco, Michael R. Prairie, Hugh E. Reilly, Thomas A. Milne and Mark R. Nimlos [1991] "Sandia National Laboratories' work in solar detoxification of hazardous wastes". *Solar Energy Materials* 24, 594-607.
- [9] Ananta S., R. Tipakontitikul and T. Tunkasiri [2003] "Synthesis, formation and characterization of zirconium titanate (ZT) powders". *Materials Letters* 57, 2637-2642.
- [10] Carey J. H., Lawrence J. and Tosine H. M. [1976] "Photo-dechlorination of polychlorinated biphenyls in the presence of titanium dioxide in aqueous solutions" *Bulletin in Environment Contamination Toxicology* 16(6) 697-701.
- [11] Lepout P. G., Vlcek A. and Langford C. H. [1993] "The photocatalytic oxidation of propanol by TiO₂". In *Photo-catalytic Purification and Treatment of Water and Air*, Ollis D. F. and Al-Ekabi H. (Eds.), Elsevier, Amsterdam, 373-385.
- [12] Domenech X. [1993] "Photocatalysis for aqueous phase decontamination: is TiO₂ the better choice". In *Photocatalytic Purification and Treatment of Water and Air*, Ollis D. F. and Al-Ekabi H. (Eds.) Elsevier, Amsterdam 337-351.
- [13] Bedford J., Klausner J. F., Goswami D. Y., and Schanze K. [1994] "Performance of non-concentrating solar Photocatalytic oxidation reactors, Part II: Shallow pond configuration". *Journal of Solar Energy Engineering, ASME* 116(1), 8-13.

- [14] Zhang Lianfeng, Tatsuo Kanki, Noriaki Sano and Atsushi Toyoda [2001] "Photocatalytic degradation of organic compounds in aqueous solution by a TiO₂ coated rotating drum reactor using solar light". *Solar Energy* 70(4), 331-337.
- [15] Muradov Nazim Z., Ali T-Raissi and Michel R. Kemme [1994] "Solar detoxification of nitroglycerine-contaminated water using immobilized titania". *Solar Energy* 52(3), 283-288.
- [16] Noorjahan M., M. Pratap Reddy, V. Durgakumari, P. Boule and M. Subrahmanyam, [2003] "Photocatalytic degradation of H-acid over a novel TiO₂ thin film fixed bed reactor and in aqueous suspensions". *Journal of Photochemistry & Photobiology A: Chemistry* 6211, 1-9.
- [17] Serpone Nick and A. Salinaro. [1999a] "Terminology, Relative Photonic efficiency and quantum yields in heterogeneous photocatalysis Part I: suggested protocol (Technical Report)". IUPAC, Commission on photochemistry. *Pure Applied Chemistry* 71, 303-320.
- [18] Serpone Nick and A. Salinaro. [1999b] "Terminology, Relative Photonic efficiency and quantum yields in heterogeneous photocatalysis Part II: experimental determination of quantum yields (Technical Report)". IUPAC, Commission on photochemistry. *Pure Applied Chemistry* 71, 321-335.
- [19] Chang N. M., Jin B., Christopher W. K., Chris Saint (2010) Recent developments in photo-catalytic technology: a review, *Water Research*, 44, 2997-3027