Degradation of effluent of paper mill over UV irradiated metal-metal oxide mesh Co axial photo-catalytic reactor

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Received: 23rd April, 2008 ; Accepted: 4th April, 2008

ABSTRACT

In the present paper an attempt made to degrade effluent of paper mill under Photo catalytic condition. Lab scale model instrument fabricated for conducting Advanced oxidation process. Titanium-Titanium oxide prepared and used as catalytic surface. The metal-metal oxide film characterized by SEM and XRD analysis. Effluent of per mill then subjected to photo catalysis. COD, UV absorbance, lignin content measured at regular time intervals. At natural pH 6-7 and temperature conditions, at flow rate of 45 min per liter through coaxial photo catalytic reactor, using 36W UV lamp, with constant aeration under laboratory conditions 70% of lignin removed in 150 min. in presence of $7.2 \times 10^{-2} \text{M } \text{H}_2\text{O}_2$ 80% of lignin degraded in 150 min.

INTRODUCTION

Water detoxification is one of the most challenging global problems. Lignin produced during pulping process for papermaking is an environmental concern for the pulp and paper industry. The lignin contained in fiber is converted to thio- and alkali-lignin during the Kraft pulping process and to lignosulfates in the sulfite pulping process for papermaking. Lignin is responsible for the colour of paper mill waste effluents. Discharge of coloured effluents from the pulp and paper mills is not only a serious aesthetic problem, but also interferes with algal and aquatic plant productivity by limiting light transmittance. Environmental protection regulations are limiting the discharge of coloured waste effluents into receiving waters. Consequently, the pulp and paper industry has a growing interest in alternatives for removal of lignin produced in pulping process for papermaking. Lignin is not decomposed by biodegradation through bacteria. Therefore they accumulate in nature and persist for a long time. As bleaching through HOCI is commonly adapted to remove the colour or to sterilize there is a chance to get chlorination to lignin and lignin derived hydrolysis products. So this result in formation of secondary pollutant like chlorinated organic molecules that are carcinogenic. As conventional biological treatment processes are non destructive for this pollutant. The traditional physical-chemical treatments such as nano-filtration, ozonation, combustion, among others, are efficient but have inherent limitations.
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An Indian Journal

Environmental Science

Current Research Paper

in applicability, effectiveness and cost. Three potential aerobic bacterial strains ITRC S6, ITRC S7 and ITRC S8 were found capable to effectively degrade the kraft lignin (KL) but only 40 to 60 % of lignin can be degraded by them[8]. Advanced Oxidation Processes have been considered as promising for this problem. The photo redox reaction on semiconductor catalysts has been the subject of much attention since the electro-chemical photolysis of water at the semiconductor electrode was first reported by ‘Rionda and Fujishima. The phenomenon of photo-oxidation was observed and recognized in 1921 by Renz[6], who was able to oxidize many organic molecules in the presence of TiO₂ and ultraviolet light later, Jacobsen[7] oxidized linseed oil in a similar manner on TiO₂ and Goodeve and Kitchener[8] reported that organic dyestuffs could be bleached. R.I.Bickley and F.S.Stone[9] photo-oxidized Secondary and tertiary methylbutanols on nonporous TiO₂ (anatase) via an olefin, which is formed by dehydration, to give an aldehyde or a ketone. R.I.Bickley, G.Munuera and F.S.Stone[10] studied The photocatalytic oxidation of isopropanol in a specially designed rotating reaction vessel affording good contact between the incident uv light and the powdered photo-catalyst. Wastewater treatment and purification of polluted air have attracted extensive attentions in the last decades. Photo-catalytic degradation of harmful and toxic organic pollutants, using semiconductors, such as TiO₂, ZnO, Fe₂O₃, CdS, ZnS, is one of the effective ways[11,12]. Among those semiconductors, titanium dioxide is the most promising photo-catalyst owing to its excellent Photo-catalytic activity, physical and chemical stabilities, and non-toxicity. The Photo-catalytic performance is significantly influenced by the crystalline structure of TiO₂. The performance of TiO₂ in anatase phase is more effective than that in rutile phase[13]. Several publications have appeared concerning the Photo-catalytic processes used to dispose of environmentally harmful or carcinogenic organics at semiconductor/water interfaces. Various immobilization methods like immobilizing on glass beards, sand etc tried by various researchers. Koichi Kobayakawa, Chotaro Sato, Yuichi Sato and Akira[14] designed and evaluated continuous-flow photo-reactor packed with titanium dioxide immobilized on large silica gel beads to decompose oxalic acid in excess water. Dionysios D.Dionysiou, Amid P. Khodadoust, Ann M.Kern, Makram T.Suidan, Isabelle Baudin and Jean-Michel Laine[16] designed a bench-scale TiO₂ rotating disk reactor and performed continuous-mode photo-catalytic degradation of chlorinated phenols and pesticides in water using it. Evaluation of two solar pilot scale fixed-bed photocatalytic reactors was done by A.J.Feitz, B.H.Boyden and T.D.Waite[17]. They compared by taking phenol as reference compound to be degraded. In one reactor immobilization done on glass fiber mesh and puckered coated raching rings were used in second reactor. A seven fold improvement in processing rate was achieved using a packed-bed reactor. Carla Sofia Aureliano Antuns studied photocatalyzed degradation of lignin model compounds and indicated the role of electron scavengers[18]. In the present work we made an attempt to use anodized titanium mesh as photocatalyst.

Principle of photo catalysis

When a semiconductor is illuminated with photons of energy equal to or larger than its band gap energy, the promotion of electrons from the valence band into the conduction band occurs. In the presence of adsorbates in equilibrium with a gaseous, liquid or aqueous phase, electrons are attracted by electron acceptors such as oxygen, metal cation, etc., whereas the photo produced holes react with electron donors. In particular, in the presence of liquid water, the fundamental oxidation step would be the formation of highly reactive hydroxyl radical:

\[ \text{OH}^+ + \text{H}^+ \rightarrow \text{OH}_2^+ \text{or} \quad \text{H}_2\text{O} + p^+ \rightarrow \text{OH}^+ + \text{H}^+ \]

However, the direct attack of the organic molecule by photo produced holes to form RH⁺ cation radicals has been proposed and is thermodynamically permissible for most organics and TiO₂. In fact, it seems to be experimentally impossible to distinguish between a trapped hole and an adsorbed OH⁻ radical because of the fast transformation between these species. On the other hand the formation of singlet oxygen has been ruled out in the Photo-catalytic systems. The out line process is given in figure 1.

EXPERIMENTAL

Laboratory system

The laboratory system consists of a recalculating
batch photo reactor fabricated with Pyrex, Teflon components, which are chemically resistant to the chemicals under investigation. Figure 2 is the schematic diagram of the laboratory system. 5 liters sample Water containing phenol was continuously recalcitrant through reactor until the phenol was below the detection limit. A constant flow rate of approximately 1 l in 45 min was always maintained. Oxygen was introduced through a flow meter and distributed via a sintered glass tip to maintain a constant oxygen concentration (20-30 ml min⁻¹). In these experiments the pH of the solution was adjusted by adding an appropriate amount of buffer solution to suspension. Irradiation was carried out with a UV tube light of UV A range, 36 W, having λ max is 365 nm.

M-MO catalyst preparation

Titanium mesh is anodized by the procedure given by T.Sonoda[19]. Titanium mesh of 0.5 mm thickness with mesh 12.5×4.5 mm, width of 130 mm and length of 800 mm is procured from China. The mesh was anodized using 3% H₂SO₄ and 3% phosphoric acid mixture as electrolyte and Titanium foil of same dimension as cathode. DC power source of 200 volt 1 Amp was used. Electrolysis was carried out for 20 min at room temperature. Titanium Oxide layer formed characterized by SEM and XRD techniques. The Mesh allowed to dry for 20 mins and washed with distilled water and kept in oven for 2 hours at 450°C.

Chemicals

All chemicals used are of AR grade procured from Aldrich. All solutions prepared with double demonized water.

Analytical methods

A coaxial photocatalytic reactor fabricated and performance was evaluated through a batch experiments using phenol as a model pollutant. A series of multifactorial batch experiments conducted to optimize the variables pH, size of MMO mesh and load of pollutant in all experiments lignin of grade 3 (commercially available) was used and water flow rate of 22 to 23 ml/sec maintained. From the point of source a sample of 20 to 25 L was collected. Sample was filtered using a normal nylon cloth filter to remove floating and suspending particles and diluted to 1:10 with demonized water. 10 L of prepared sample water was subjected to photocatalysis in MMO photocatalytic reactor using 34 cm × 80 cm MMO mesh sheet. During Photo-catalysis, at intervals of 0, 30, 60, 90, 120 and 150 min the sample is analyzed for COD, BOD and lignin by taking small aliquots from the reservoir. lignin content concentration measured using Lovibond Multidirect. Procedure to determine COD, BOD and lignin is followed as prescribed by Standard Methods for Examination of Water and Waste Water, 21st Ed, APHA, Wahington D.C,[20].

A series of multivariate experiments conducted in presence of UV light, air, Catalyst, Peroxide, in presence of air, Catalyst, Peroxide, in presence of UV light, Catalyst, Peroxide, in presence of UV light, air, Peroxide and in presence of UV light, air, Catalyst. Results are shown in TABLE 1.

RESULTS

The figures 3 and 4 are the SEM of oxide layer
Degradation of effluent of paper mill

TABLE 1: Values of COD, BOD and lignin

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>COD</th>
<th>BOD</th>
<th>Lignin</th>
<th>Time (min)</th>
<th>COD</th>
<th>BOD</th>
<th>Lignin</th>
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<td>9.9</td>
<td>33</td>
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<td>8.4</td>
<td>30</td>
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<tr>
<td>60</td>
<td>158</td>
<td>10.4</td>
<td>27</td>
<td>60</td>
<td>173</td>
<td>8.6</td>
<td>29</td>
</tr>
<tr>
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<td>132</td>
<td>11.3</td>
<td>18</td>
<td>90</td>
<td>170</td>
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<td>6.8</td>
<td>150</td>
<td>162</td>
<td>9.5</td>
<td>30</td>
</tr>
</tbody>
</table>

- (a) Degradation studies in presence of UV light, air, Catalyst, Peroxide
- (b) Degradation studies in presence of air, Catalyst, Peroxide
- (c) Degradation studies in presence of UV light, Catalyst, Peroxide
- (d) Degradation studies in presence of UV light, air, Peroxide
- (e) Degradation studies in presence of UV light, air, catalyst

Figure 3: Topography of oxide film formed

Figure 4: XRD pattern of Ti-O layer

formed on titanium mesh and XRD respectively. SEM shows formation of pores ranging from 0.1 to 0.3 micrometer diameter. The peaks of XRD are attributed to the anatase crystal structure for oxide layer and titanium metal lattices. The results of multivariate experiments are shown in TABLE 1.

**DISCUSSION**

From the results of multivariate experiments it is evident that to degrade lignin effectively uv light, catalyst, air all are required. There is no practical degradation of phenol when catalyst and air alone used. Very slight degradation in absence of catalyst and presence of uv. This may be due to photo reaction. The percentage of COD decreased after 2 hour of photocatalysis at various pH values measured. The values plotted against respective pH values. (Figure 5) At pH 3 the degradation found to be optimum. Graphs are taken to analyze the results obtained in degradation experiments. The ratio of value of variable after t min to value of variable at t = 0 is plotted against time in mints. Figures 5 to 10 are the graphical representations. Though the degradation is found to be at maximum rate at pH 3 under experimental conditions. But the degradation experiments
peroxide. In the absence of air bubbling the dissolved oxygen content limits the reaction. This is supported by the results. Under this condition up to 45% of lignin has removed, only 25% of COD reduction and 21% increase in BOD. In absence of catalyst there is 48% of lignin removal due to UV light the peroxide dissociates and participates in degradation reaction. 22% of reduction in COD and 20% increase in BOD. Results are supporting the role of singlet oxygen in photo catalysis process. The experimental results obtain in absence of hydrogen peroxide are shows the actual removal of lignin with photocatalysis alone. There is 70% removal of lignin, 47% reduction in COD and a gain of 22% of BOD. There is no practical degradation when catalyst and oxygen alone used. Very slight degradation in absence of catalyst/peroxide and presence of uv. This may be due to photo reaction.

CONCLUSIONS

From the results of multivariate experiments it is evident that to degrade lignin (commercially available grade 3) effectively uv light, catalyst, air all are required. There is no practical degradation of phenol when catalyst and air alone used. Very slight degradation in absence of catalyst and presence of uv. This may be due to photo reaction. The percentage of COD decreased after 2 hour of photocatalysis at various pH values measured. The values plotted against respective pH values. At pH 3 the degradation found to be optimum.

The lignin materials and other organic content of effluent of paper mill can be degraded by uv radiation of 36 W in presence of Ti-TiO$_2$ in the natural water pH and temperature conditions. The degradation further can be increased by hydrogen peroxide supported photocatalysis process. The bio degradability of lignin polymer can be increased through photo catalysis process.

ACKNOWLEDGMENT

The authors wish to thank Prof Sri Thagarajan, Prof. M. Nageswara Rao, Centre for Environmental Education and Research, NIT TTR, Taramani, Chennai, Director, Center Tobacco Research Institute, ICAR, Rajahmundry, Andhra Pradesh, Prof E. Rajanarendar Kakatiya University and Director IICT, Hyderabad for their encour-
agreement cooperation. The authors wish to convey thanks to Mr. Kadri superintendent of National institute of Technology for providing SEM and XRD of sample.

REFERENCES