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

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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 7.2×10^{-2}M H_2O_2 80% of lignin degraded in 150 min.

KEYWORDS

Advanced oxidation process;
Lignin removal;
Pollutant;
Photo catalysis;
Metal metal oxide mesh.

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[1]. 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 serous aesthetic problem[2], but also interferes with algal and aquatic plant productivity by limiting light transmittance[3]. 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 HOCl 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[4]. 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 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[5]. 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 electrochemical 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 TiO_2, and ultraviolet light later, Jacobsen[7] oxidized linseed oil in a similar manner on TiO_2 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 TiO_2 (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 TiO_2, ZnO, Fe_2O_3, 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 TiO_2. The performance of TiO_2 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] Fujishima[15] deigned 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 TiO_2 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:

$$OH^- + P^+ \rightarrow OH^0 \text{ or } H_2O + p^+ \rightarrow OH^0 + H^+$$

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 TiO_2. In fact, it seems to be experimentally impossible to distinguish between a trapped hole and an adsorbed OH^0 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

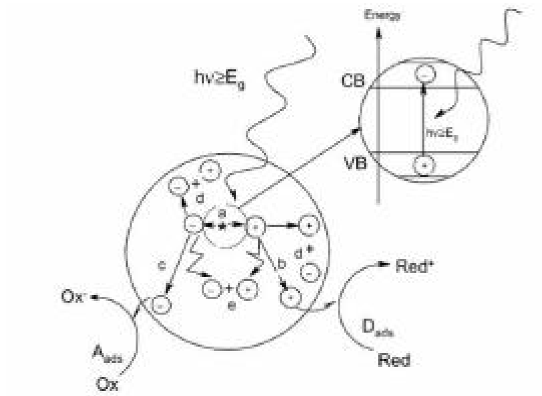

Figure 1: Mechanism of photo catalysis

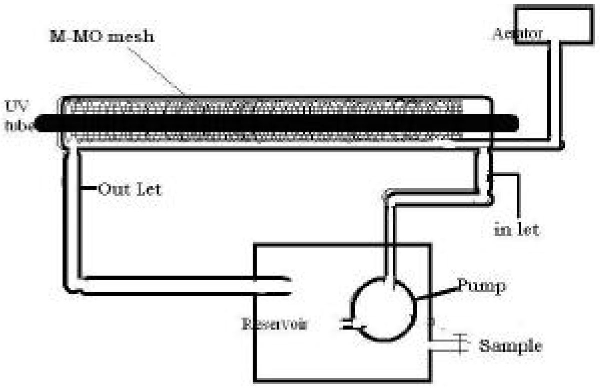

Figure 2: Design of photo-catalytic reactor

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 recalculated through reactor until the phenol was below the detection limit. A constant flow rate of approximately 1l in 45min 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 range 310 nm - 400 nm and 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% H_2SO_4 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 mints and washed with distilled water and kept in oven for 2 hours at 450^0C.

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 34cm × 80cm MMO mesh sheet. During Photo-catalysis, at intervals of 0, 30, 60, 90, 120 and150 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

TABLE 1: Values of COD, BOD and lignin

(a) Degradation studies in presence of UV light, air, Catalyst, Peroxide				(b) Degradation studies in presence of air, Catalyst, Peroxide			
Time	**COD**	**BOD**	**Lignin**	**Time**	**COD**	**BOD**	**Lignin**
0	198	9.7	34	0	178	8.3	31
30	175	9.9	33	30	175	8.4	30
60	158	10.4	27	60	173	8.6	29
90	132	11.3	18	90	170	8.8	30
120	110	12.6	12	120	166	9.2	28
150	82	13.8	6.8	150	162	9.5	30
(c) Degradation studies in presence of UV light, catalyst, peroxide				**(d) Degradation studies in presence of UV light, air, peroxide**			
Time	**COD**	**BOD**	**Lignin**	**Time**	**COD**	**BOD**	**Lignin**
0	213	10.9	38	0	192	9.8	36
30	207	11.3	36	30	187	10.2	34
60	194	11.7	32	60	182	10.5	30
90	183	12.3	28	90	173	10.8	26
120	171	12.8	25	120	164	11.3	21
150	160	13.2	21	150	151	11.8	19
(e) Degradation studies in presence of UV light, air, catalyst							
0	188	10.5	32				
30	176	10.9	28				
60	156	11.3	22				
90	132	11.8	16				
120	113	12.2	12				
150	101	12.8	9.8				

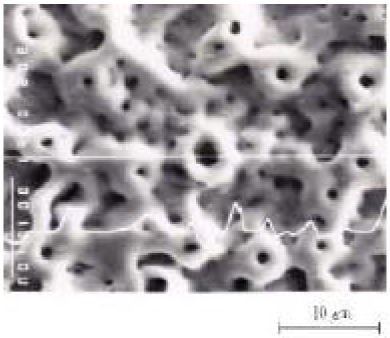

Figure 3: Topography of oxide film formed

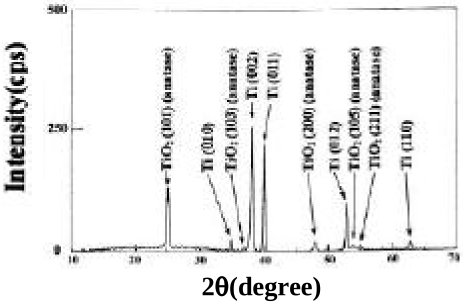

Figure 4: XRD pattern of Ti-O layer

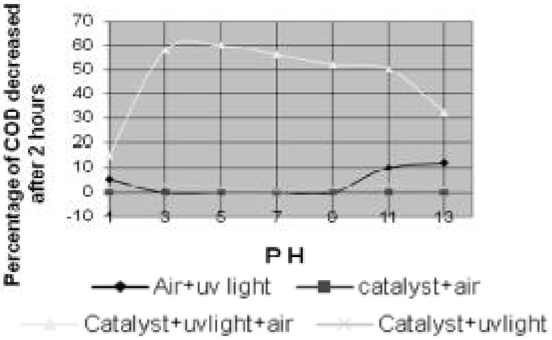

Figure 5: Comparison disappearances at different pH

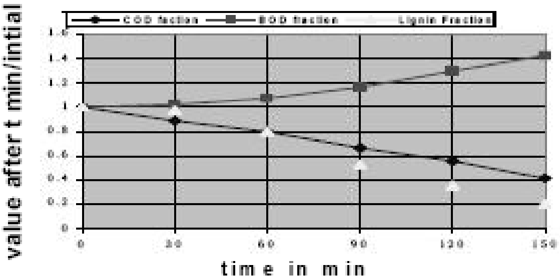

Figure 6: Plot of fraction of V_t/V_0 against time during degradation studies in presence of UV light, air, Catalyst, Peroxide

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 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

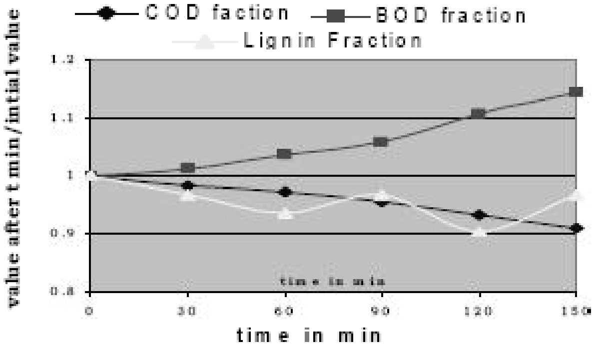

Figure 7: Plot of fraction of V_t/V_0 against time during degradation studies in presence of air, Catalyst, Peroxide

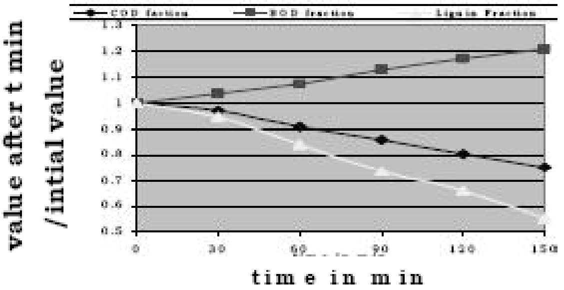

Figure 8 : Plot of fraction of V_t/V_0 against time during degradation studies in presence of UV light, Catalyst, Peroxide

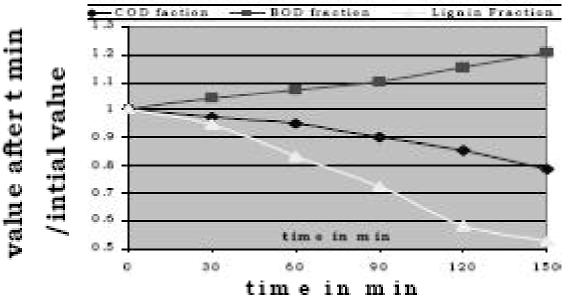

Figure 9: Plot of fraction of V_t/V_0 against time during degradation studies in presence of UV light, air, peroxide

performed at pH 6-7 as it is the natural prevailing condition of effluent. Through at lab conditions it is possible to maintain pH 3 in view of future experiments likely to be conducted we have chosen natural pH condition. It is evident that to degrade effluent water of paper mill effectively uv light, catalyst, oxygen all are required. 80% of lignin is removed from effluent, there is a gain of 42% in BOD value indicating the biodegradability of effluent has increasing and 59% of COD reduced in 150 min in the absence of UV light only 4% of lignin removed, 9% reduction in COD and 10% rise in BOD in 150 min indicating the activity of hydrogen 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 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 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 photo catalysis process. The bio degradability of lignin polymer can be increased through photo catalysis process

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