

Titanium dioxide photocatalysis for the pulp and paper industry wastewater treatment

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Abstract

This paper provides an in depth discussion on the titanium dioxide photocatalysis for the treatment of pulp and paper industry wastewater. The mechanism behind TiO_2 photocatalysis, various reaction variables and application of TiO_2 photocatalysis for the remediation of pulp and paper mill wastewater are discussed. TiO_2 photocatalysis can cause rapid and complete degradation of nearly all electron rich organic compounds. It involves in situ generation of very reactive non-selective oxidizing species i.e. OH^\cdot radicals. Some laboratory experiments were performed to study the effect of catalyst dose and reaction time on the photodegradation efficiency. Paper mill wastewater was treated with UV/ TiO_2 process at pH 7 in a slurry type of reactor under artificial UV light. The catalyst dose (0.25 to 1.50 g/L) and reaction time (0.50 to 8.0 h) were varied for studying their effect on the degradation efficiency. The degradation efficiency was measured in terms of percent reduction in COD and colour of the wastewater. Up to 0.75 g/L of TiO_2 the degradation efficiency increased but beyond this it decreased. The degradation rate during the first hour of treatment was very fast. After 4 h of treatment the degradation efficiency became more or less constant and there was no significant increase. The optimum results were obtained at a TiO_2 dose of 0.75 g/L and reaction time of 4 h.

Keywords: Pulp & paper industry, titanium dioxide (TiO_2), heterogeneous photocatalysis, wastewater treatment, AOP's.

Introduction

Water pollution is a serious problem for the pulp and paper industry due to the huge quantity and quality of wastewater generated. The pulp produced by chemical pulping requires bleaching to produce bright pulps. The elemental chlorine and chlorine compounds used for bleaching are known to generate various kinds of chlorinated phenols, phenolic carboxylic acids, dicarboxylic acids, resin acids and hydrocarbons originating from lignin and/or extractions of wood in the bleach wastewater. Some of these chloroorganics are bioaccumulative, toxic, mutagenic and resistant to biodegradation. Hence these compounds pose a serious threat to the environment (Bajpai & Bajpai, 1996; Perez *et al.*, 2002; Roy *et al.*, 2004). Current biological remediation processes suffer from low efficiency and incomplete degradation of these toxicants. Hence there is a need for some new treatment technologies i.e. advanced oxidation processes (AOP's). These processes rely on the in situ generation of very reactive oxidizing species i.e. hydroxyl radicals for the degradation of organic compounds (Garcia *et al.*, 2009; Thiruvengkatachari *et al.*, 2008). OH^\cdot radicals are reactive electrophiles (2.33 V oxidation potential) hence cause rapid degradation of nearly all electron rich organic compounds (Gogate & Pandit, 2004). The heterogeneous photocatalysis (UV/catalyst & UV/catalyst/ H_2O_2), one of the AOP's utilizing TiO_2 or ZnO as a catalyst is a very efficient technique for environmental remediation (Catalkaya & Kargi, 2008). This paper provides an in depth discussion on the titanium dioxide photocatalysis for the treatment of paper industry wastewater. The mechanism of TiO_2 photocatalysis, various process variables and application of TiO_2 photocatalysis for the paper mill

wastewater remediation are discussed. The effect of two important reaction parameters i.e. catalyst dose and reaction time on the degradation efficiency of the paper mill wastewater is also studied.

Heterogeneous photocatalysis

The heterogeneous photocatalysis is an emerging technique for the treatment of both aquatic and atmospheric organic contaminants (Fox & Dulay, 1993; Fujishima *et al.*, 1999; Hoffmann *et al.*, 1995; Linsebigler *et al.*, 1995; Mills & Le Hunte, 1997; Ollis, 1985; Blake, 2001; Poyatos *et al.*, 2009). The semiconductor photocatalyst leads to the complete mineralisation of organic compounds, essentially to CO_2 , H_2O , NO_3^- , PO_4^{3-} and halide ions (Gaya & Abdullah, 2008). Various catalysts (TiO_2 , ZnO, MgO, WO_3 , Fe_2O_3 , CdS & ZnS) are being used for heterogeneous photocatalysis. Among them, TiO_2 is the most widely used because it is chemically and biologically inert, photostable, low cost and relatively easy to produce and use (Thiruvengkatachari *et al.*, 2008). Basically, two types of reactors are being used for the heterogeneous photocatalytic wastewater treatment i.e. suspension (catalyst dispersed in solution) and fixed film systems (thin layer of catalyst attached, chemically or physically to an inert support). Suspension one is more preferred than the later because they are normally more efficient due to large surface area available for adsorption of the pollutants. They allow more number of photons to hit the catalyst. Natural sunlight or artificial light sources can be used for photocatalytic degradation (Lee & Mills, 2004; Al-Rasheed, 2005).

Mechanism behind TiO_2 photochemistry

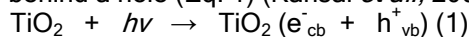
Solid TiO_2 can absorb light radiation near UV region. When a photon of light having energy equal to or greater



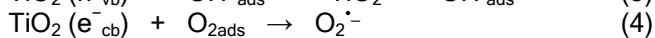
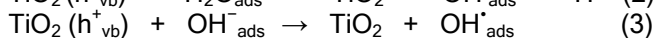
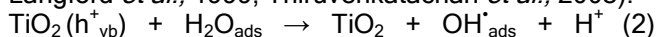
Table 1. TiO₂ photocatalytic treatment of paper mill wastewater.

Lamp	Wastewater source	Treatment method	Major findings	Reference
125W	Bleaching (D)	UV/TiO ₂ /O ₂	80% AOX, 64% COD and 72% colour removed	Perez <i>et al.</i> , 1997
125W	Bleaching (E _{OP})	O ₃ , O ₃ /UV, UV/TiO ₂ /O ₂ , UV/ZnO/O ₂ & V/ZnO/O ₃	Heterogeneous treatment better	Mansilla <i>et al.</i> , 1997
250W	E ₁ , Bleach liquor, Bleaching mixture, Final wastewater and textile	UV/TiO ₂ /O ₂ , UV/ZnO/O ₂ & UV/ZnO/O ₂ (silica gel supported)	50% mineralization and 50% toxicity removed	Zamora <i>et al.</i> , 1998
20W	Coagulated & biologically pretreated CEH, DED, combined (CEH+DED)	UV/TiO ₂ /H ₂ O ₂	43-87% (biotreated) & 20-38% (raw) COD removed	Balcioglu & Arslan, 1998
40W or 16 (75W) tubes	Synthetic & real pulp mill white water	UV/TiO ₂ , UV/H ₂ O ₂ & UV/TiO ₂ /H ₂ O ₂ (Supported & free TiO ₂)	Non-polar organics decreased & polar increased.	Langford <i>et al.</i> , 1999
20W	Sulfate pulp bleaching (mixed raw, CEH, DED, Biotreated)	UV/TiO ₂ /H ₂ O ₂	BOD/COD ratio increased	Balcioglu & Cecen, 1999
40W	Bleaching (C,E,D/C & OE ₁)	UV/TiO ₂ , UV/H ₂ O ₂ & UV/TiO ₂ /H ₂ O ₂	60% AOX, COD and colour reduced.	Wang, 1999
125W	Bleaching (DE _{OP} & CE _{OP})	UV/TiO ₂ /O ₂ & UV/ZnO/O ₂ (suspended/ supported)	Biodegradability increased, acute toxicity reduced	Yeber <i>et al.</i> , 1999
125W	Bleaching (E _{OP})	UV/TiO ₂ & UV/TiO ₂ /H ₂ O ₂	Chloroorganics, 95% AOX and 50% TOC removed	Perez <i>et al.</i> , 2001
400W/ sunlight	Paper and cellulose mill	Solar/UV+TiO ₂ & UV/TiO ₂ / H ₂ O ₂	H ₂ O ₂ increased efficiency by 173.5%. >80% organic matter mineralised, solar treatment showed excellent results.	Machado <i>et al.</i> , 2003
450W	Paper mill (after primary clarifier)	UV/TiO ₂ /O ₂	90% COD & acute toxicity removed	Boyd & Almquist, 2004
125, 400, 1KW/ sunlight	Paper mill	UV/TiO ₂	Very fast and total mineralization of non-biodegradable contaminants	Sattler <i>et al.</i> , 2004
300W/ sunlight	Cardboard paper	Photo Fenton & UV/TiO ₂	BOD increased by 30-50%.	Amat <i>et al.</i> , 2005
-	Bleaching	UV, UV/TiO ₂ , UV/TiO ₂ /Ru _x Se _y (film) & Biological with UV/TiO ₂ /Ru _x Se _y (film)	92% colour, 97% COD & 99% chlorophenols removed by combined treatment.	Pedroza <i>et al.</i> , 2007
120 W	Bleaching (E _{OP})	UV/TiO ₂ /Cu(II) & UV/TiO ₂ /O ₂	94% colour, 70% COD & 50% TOC removed, biodegradation increased ecotoxicity reduced.	Yeber <i>et al.</i> , 2007
8 (40W)/ sunlight	Bleaching	UV/TiO ₂	86.6% COD removed after 4 hr	Toor <i>et al.</i> , 2007
5 (30W)/ sunlight	Bleaching (C & E)	UV/TiO ₂ & UV/ZnO	COD and BOD reduced.	Kansal <i>et al.</i> , 2008
3 (250W)	O ₃ Bleaching	Electrocoagulation-flotation followed by UV/TiO ₂ /H ₂ O ₂	88% COD reduced, biodegradability increased.	Boroski <i>et al.</i> , 2008
250W	Bleaching	Coagulation-flocculation followed by UV/TiO ₂ /H ₂ O ₂ , UV/TiO ₂ , UV/H ₂ O ₂ & UV	UV/TiO ₂ /H ₂ O ₂ more efficient, biodegradability increased.	Rodrigues <i>et al.</i> , 2008
30W	Mill discharged wastewater	UV/H ₂ O ₂ & UV/TiO ₂ /H ₂ O ₂	UV/TiO ₂ /H ₂ O ₂ capable of degrading total nitrogen and chloro-organics	Ugurlu & Karaoglu, 2009

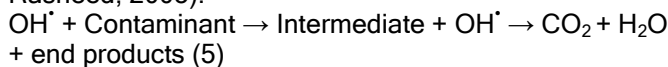
than the band gap energy (3.2 eV for anatase form of TiO_2) of the catalyst, an electron is raised from the valence band (vb) to the conduction band (cb) leaving behind a hole (Eq. 1) (Kansal *et al.*, 2008).



The valence band hole (h_{vb}^+) is a strong oxidant which can either directly oxidize a wide range of adsorbed pollutants by one electron oxidation or by producing OH^\cdot radicals from water/ OH^- ion (Eq. 2 & 3) which can also oxidize organics non-selectively (Eq. 5). While the conduction band electron (e_{cb}^-) is a strong reducing agent. It is readily taken by adsorbed O_2 to produce superoxide ion ($\text{O}_2^{\cdot-}$) (Eq. 4). Thus prevent the electron-hole recombination (John & Yates, 2009; Langford *et al.*, 1999; Thiruvengkatachari *et al.*, 2008).



$\text{O}_2^{\cdot-}$ can also participates in contaminants degradation reactions by the production of H_2O_2 through a series of redox reactions (Linsebigler *et al.*, 1995; Al-Rasheed, 2005).

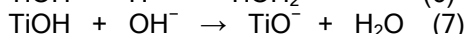


Process variables

a. Catalyst dose: The rate of photocatalytic degradation reaction is directly proportional to concentration of the catalyst and increases with increase in catalyst charge, due to an increase in the number of active sites available on the catalyst surface which in turn increases OH^\cdot and superoxide radicals. But there is a limit for catalyst dose that is required for the photo-oxidation of a particular pollutant, above which the photocatalysis decreases because excess catalyst causes undesirable light scattering and reduced light penetration into the reaction mixture (Gaya & Abdullah, 2008).

b. Nature & concentration of pollutants: The nature and concentration of the organic pollutants strongly affect the photocatalytic degradation reaction. No destruction may be observed for highly concentrated wastewaters. Hence, lower concentrations of the pollutants should be used (Gogate and Pandit, 2004). During photo-oxidation reaction the concentration of organic pollutants is dependent upon photonic efficiency with time. At high concentration, the photonic efficiency gets reduced and the TiO_2 surface becomes saturated causing catalyst deactivation (Gaya & Abdullah, 2008).

c. pH: The pH of the reaction mixture affects the surface charge properties and size of aggregates of the catalyst. The adsorption of the reactants and hence the rate of photodegradation will be maximum near the point of zero charge (pzc) of the catalyst (Chen & Ray, 1998). TiO_2 surface can be protonated or deprotonated under acidic or alkaline condition according to the reactions (6 and 7):



TiO_2 is reported to have higher photo-oxidation at lower pH but excess H^+ ions at very low pH can reduce reaction rate. But in alkaline pH columbic force causes repulsion between OH^- ions and negatively charged surface of the catalyst, thus preventing formation of OH^\cdot radicals and reducing photo-degradation. Hence, optimization of pH is necessary for better degradation results (Gaya & Abdullah, 2008).

d. Light intensity: The rate of the photocatalytic reaction is directly proportional to the amount of radiant energy absorbed by the catalyst. As the intensity of the radiation is increased, the degradation rate of the pollutants also increases. The nature or form of the radiant source does not affect the photo-degradation reaction pathway, i.e. the band-gap sensitization process does not matter (Gaya and Abdullah, 2008). TiO_2 absorbs radiation below the visible region i.e. 400 nm (UV-A) thus limiting its applicability. Hence, research work is going on for the modification of TiO_2 for increasing its photoactivity in the visible region of solar radiation (Choi, 2006; Yang *et al.*, 2010).

Application of TiO_2 photocatalysis for pulp & paper industry

The TiO_2 heterogeneous photocatalysis has been used effectively for the remediation of pulp and paper mill wastewater either singly or in combination with other chemical, physicochemical/ or biological treatment methods and promising results have been obtained. A review of the work done during the recent years in the field of TiO_2 heterogeneous photo-catalytic treatment of pulp and paper mill wastewater is presented in the Table 1. Perez *et al.* (1997) reported that photocatalysis can efficiently reduce the organic load from the ECF (Elemental chlorine free) bleaching wastewater. Mansilla *et al.* (1997) observed that treatment with heterogeneous photocatalysis is more effective than homogeneous systems for the degradation of phenolic and polyphenolic compounds. Zamora *et al.* (1998) studied that TiO_2 was more efficient than ZnO and both were better than immobilized ZnO for the photodegradation of cellulose industry wastewater. Balcioglu and Arslan (1998) investigated that $\text{UV}/\text{TiO}_2/\text{H}_2\text{O}_2$ was more efficient in removal of pollutants from pulp wastewater. Treatment efficiency depended upon extent/type of pretreatment and initial COD. Langford *et al.* (1999) reported complete photodegradation of both dissolved and colloidal organic matter in paper mill white waters. Balcioglu and Cecen (1999) observed increase in biodegradability during photocatalysis of sulphate pulp bleaching wastewater. Wang (1999) observed that $\text{UV}/\text{H}_2\text{O}_2$ is better than UV/TiO_2 for the photo-degradation of paper mill wastewater. Synergistic effect was obtained when both were used together. Yeber *et al.* (1999) investigated that supported and suspended systems were equally efficient but with different reaction times. Similarly, Perez *et al.* (2001) investigated that

photocatalysis is efficient for the reduction of AOX, TOC, total phenols and toxicity from the cellulose ECF bleaching wastewater. Machado *et al.* (2003) investigated that P25 is a better photocatalyst than anatase form of TiO₂ for photodegradation of paper mill wastewater. The addition of H₂O₂ increased the efficiency. Boyd and Almquist (2004) found out that photocatalysis with TiO₂ is an effective method for the degradation of COD and toxicity from pulp and paper mill wastewaters with initial COD concentrations of 500 mg/L or less. Promising results has also been obtained in the solar photocatalytic treatment of paper mill wastewaters (Sattler *et al.*, 2004; Amat *et al.* 2005). Pedroza *et al.* (2007) investigated that sequential, biological and photocatalytic treatment resulted in about complete degradation of bleaching wastewater in terms of COD, colour and chlorophenols. Yeber *et al.* (2007) used Cu (II) as an electron acceptor for the photocatalytic oxidation. Toor *et al.* (2007) reported that the rate of degradation of bleach plant wastewater increases with increase in UV intensity, increase in aperture to volume ratio and decrease in initial COD concentration. Kansal *et al.* (2008) observed that TiO₂ is a better photocatalyst for acidic while ZnO for basic bleach plant wastewater. Promising results has also been obtained with electrocoagulation-flotation (EC) followed by photocatalysis (Boroski *et al.* 2008; Rodrigues *et al.* 2008). Ugurlu and Karaoglu (2009) investigated that the degradation rate for the UV/TiO₂/H₂O₂ system was higher than for UV/H₂O₂ system during photodegradation of paper mill wastewater.

Paper mill wastewater treatment

Some experiments were performed in the laboratory for studying the effect of two important reaction variables (i.e. catalyst dose and reaction time) on the photo-degradation efficiency.

Experimental

Titanium dioxide was obtained from Fisher Scientific (SQ grade) and was used as received. Other reagents and chemicals used were of analytical grade and were used without any further purification. pH of the aqueous solutions were adjusted with 1 M H₂SO₄ or 1M NaOH solutions. Wastewater (after primary clarifier) (912.7 mg/L COD & 1678.5 mg/L Pt-Co colour) was procured from a nearby paper mill in India and stored in freeze at 4^oC before use. The factory uses mixed hardwood (Eucalyptus/Poplar, 60:40) kraft pulp as raw material.

Photocatalytic experiments were carried out in a wooden made UV chamber (77 cm × 36 cm × 71 cm) equipped with 4 UV tubes (λ=365 nm) each of 18W (Philips) on the top side 15 cm away from the sample (Fig. 1). 500 mL diluted (2 times) paper mill wastewater was adjusted to pH 7 and subjected to photo-degradation in a borosilicate glass bowl (1L). Desired amount of TiO₂ was added and the aqueous suspension

was magnetically stirred for 30 min before switching on the UV lamps. After completion of the reaction water loss was made up by distilled water and kept for settling. After settling, supernatant was collected and used after centrifuging (to remove TiO₂ agglomerates) for analysis. Chemical oxygen demand (COD) was determined by closed reflux titrimetric method. The colour was measured at 465 nm using UV-VIS double beam spectrophotometer (SPEKOL 2000, Analytic Jena) (Clesceri *et al.*, 1998). The rate of degradation was followed in terms of the reduction in COD and colour of the wastewater. The percentage degradation was calculated as follows:

$$\text{Degradation (\%)} = [(C_0 - C) / C_0] \times 100$$

Where, C₀ = initial concentration, C = concentration after photo-degradation. All the experiments were performed in duplicate and average values were reported.

Results and discussion

As can be seen from the fig. 2 the percent COD and colour removal increased as the catalyst loading increased from 0.25 to 0.75 g/L. But as the catalyst load increased beyond 0.75 g/L, the degradation efficiency decreased. We obtained optimum degradation efficiency (54.5% COD & 83.7% colour removal) at a catalyst dose of 0.75 g/L after 4 h of treatment. According to literature excess of the catalyst may inhibit photo-catalytic degradation by causing turbidity and light scattering as discussed earlier (Chen & Ray, 1998). The effect of reaction time (0.5 to 8 h) on the degradation efficiency was also studied at a constant catalyst dose of 0.75 g/L. A fast decrease in wastewater COD and colour was observed during the first hour of treatment (Fig. 3). Literature reports fast degradation rate for TiO₂ photocatalysis within a short period of time leading to complete oxidation of organics (Tanaka *et al.*, 2000). After 1 h the rate of degradation slows down and after a particular time period (4 h) it became more or less constant and there was no significant increase with time. It can be explained by the fact that adsorption of organic matter on the TiO₂ surface forms a layer that hinders the photo-degradation by diminishing the supply of oxygen to the catalyst surface (Catalkaya & Kargi, 2008). After 4 h of reaction we obtained 52.2% and 82% reduction in COD and colour respectively.

Conclusion

The TiO₂ heterogeneous photocatalysis has proved to be a promising technology for the degradation of paper industry wastewater. In the laboratory experiments we obtained maximum degradation efficiency at a catalyst dose of 0.75 g/L (54.5% COD and 83.7% colour removal). Further increase in catalyst concentration caused decrease in degradation efficiency. A fast decrease in wastewater COD and colour was observed during the first hour of treatment. 4 hour of treatment was found as the optimum time for the

photodegradation at which 52.2% COD and 82% colour reduction was obtained. Hence proper reactor design and optimization of process parameters is essential for obtaining the best degradation efficiency. The Sun is a natural and renewable source of UV radiation that is abundantly available on the Planet's surface and free from environmental pollution. Hence, the utilization of solar irradiation as a light source should be promoted instead of electricity for large scale industrial application in order to reduce the environmental impact and making the process economically viable.

Acknowledgement

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Fig. 1. Schematic diagram of photocatalytic reactor.

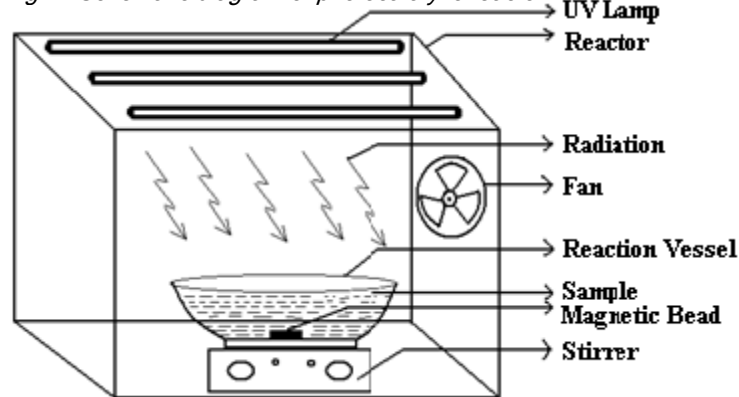


Fig. 2. Effect of catalyst dose on COD and colour removal.

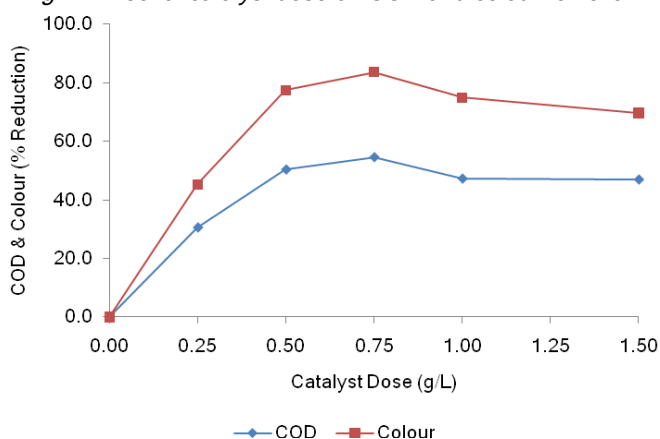
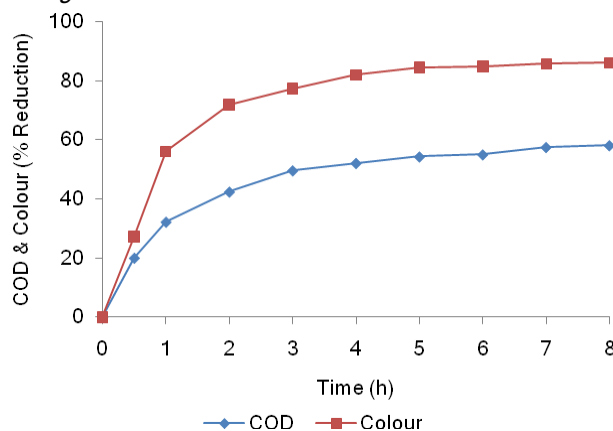


Fig. 3. Effect of reaction time on COD & colour removal.



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