

# Photocatalytic Degradation of Tannery Waste Sludge using Titanium Dioxide

Sujatha Gurudev<sup>1\*</sup>, Rachitha R<sup>2\*</sup> and Lalsangzela Sailo<sup>3</sup>

<sup>1,2\*</sup>Post Graduate Student, Department of Energy and Environmental Engineering,  
Vellore Institute of Technology (VIT), Vellore-632014, Tamil Nadu, India

<sup>3</sup>Department of Energy and Environmental Engineering,

Vellore Institute of Technology (VIT), Vellore-632014, Tamil Nadu, India

E-mail: <sup>1</sup>sujathagurudev@gmail.com, <sup>2</sup>rachitha09@hotmail.com, <sup>3</sup>lalsangzela.sailo@vit.ac.in

**Abstract**—In this paper, Titanium Dioxide (TiO<sub>2</sub>) assisted photocatalysis was applied to tannery wastewater from a tanning industry wastewater treatment plant in order to investigate the technical feasibility of the technology as secondary and also as a tertiary treatment. The effect of the various process variables on the reduction of Chemical Oxygen Demand (COD) performance of the process is investigated. The effective COD reduction as a function of time, effect of temperature and the effect of pH is studied. The rate of photo degradation increased linearly with time of irradiation when titanium dioxide was used. The maximum removal efficiency was obtained at pH 3 with an irradiation time of 5 hours with a catalyst dosage of 150mg/L and the efficiency of COD reduction was observed to be 85%. Results presented in this study indicated that visible light/TiO<sub>2</sub> systems could be efficiently used for photo degradation of tannery wastewater sludge. The possibility of using solar light to excite the photo catalyst is promising results regarding the feasibility of this technology.

**Keywords:** Photocatalysis, TiO<sub>2</sub>, tannery wastewater sludge

## 1. INTRODUCTION

The pollution of hazardous metals is increasing with extensive of industrial developments [1]. The tannery sludge purification is still today a theme of a large interest. Nowadays, treatments involving depuration technologies allow to obtain effluents with chemical-physical characteristics in respect to the environmental existing standards. From the traditional wastewaters treatments, huge amounts of sewage sludge are produced. Specifically, after the biological treatment wastewaters still contain organic pollutants which are not degradable called as recalcitrant compounds [12]. These pollutants agents are removed using chemical-physical processes that produce large quantity of sludge. To reduce the production of sludge by these wastewaters tertiary treatments new systems must thus be explored [2].

During the past few years, photocatalysis has been extensively used, mainly because it has the capacity of degrading a huge number of recalcitrant substances in liquid and gaseous systems using procedures with relatively low cost [8]. The so

called photocatalytic detoxification has been discussed as a promising technology for the wastewater treatment in the scientific literature since 1976. Photocatalysis is considered an effective system for the mineralization of many organics through the generation of radicals such as •OH and O<sub>2</sub><sup>•-</sup>, reducing considerably the organic load of effluents [18].

Advanced Oxidation Process (AOPs) have demonstrated their usefulness in the purification of industrial wastewater, achieving a total or partial mineralization of organic pollutants [11, 6]. Recent developments of Advanced Oxidation Processes (AOPs), have led to new improvements of the oxidative degradation of the organic compounds. The main mechanism of AOPs function is the generation of highly reactive free radicals. Hydroxyl radicals (HO•) are effective in destroying organic chemicals because they are reactive electrophiles (electron preferring) that react rapidly and non-selectively with nearly all electron-rich organic compounds. They have an oxidation potential of 2.33 V and exhibit faster rates of oxidation reactions comparing to conventional oxidants such as H<sub>2</sub>O<sub>2</sub> or KMnO<sub>4</sub> [7]. Once generated, the hydroxyl radicals can attack organic chemicals by radical addition, hydrogen abstraction and electron transfer [15]. In the following reactions, R is used to describe the reacting organic compound.



The oxidative degradation process goes on through two initial steps that generate free radicals •OH which attack the organic molecules degrading in CO<sub>2</sub> and H<sub>2</sub>O. Fig.1 shows schematically the mechanism of photocatalysis. The essential reactive species are oxygen as anions OH<sup>-</sup> which behave respectively as electron attractor and electron donator, acquiring and giving only one electron, which then goes to regenerate TiO<sub>2</sub>.

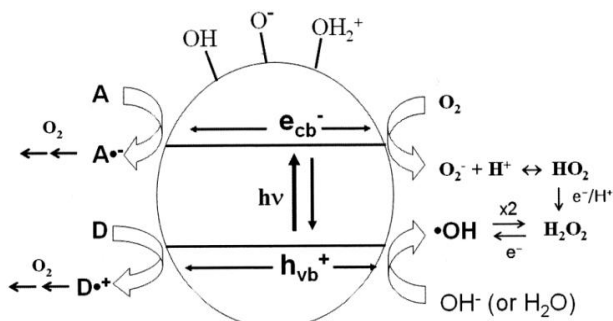


Fig. 1: Principle mechanism of photocatalysis

A great number of methods are classified under the broad definition of AOPs (Table 1). Most of them use a combination of strong oxidizing agents (e.g.  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ ) with catalysts (e.g. transition metal ions) and irradiation (e.g. ultraviolet, visible). Among different available AOPs producing hydroxyl radicals, titanium dioxide/UV light process, hydrogen peroxide/UV light process and Fenton's reactions seem to be some of the most popular technologies for wastewater [17].

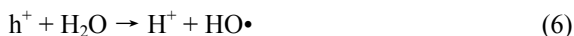
Table 1: Different Advanced oxidation processes available

Hydrogen peroxide/UV light	Ozone/Titanium dioxide
Hydrogen peroxide/ozone	Fenton's reactions ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ , $\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ )
Titanium dioxide/UV	Sonolysis
Ozone/UV/Hydrogen peroxide	Catalytic oxidation
Ozone/Titanium dioxide/Hydrogen peroxide	Supercritical water oxidation
Ozone/UV	Ozone sonolysis

(Source: Choi et al.,2009)

### 1.1 Use of Titanium Dioxide /UV light process

Titanium dioxide,  $\text{TiO}_2$ , in its anatase form, is the semiconductor studied the most, as it presents some desired characteristics: high photocatalytic activity, relatively low cost, stability aqueous systems, and low ecotoxicity [16]. In  $\text{TiO}_2$ /UV light process, a titanium peroxide semiconductor absorbs UV light and generates hydroxyl radicals. Specifically, during UV illumination of  $\text{TiO}_2$ , conduction band electrons and valence band holes are initially yielded (Eq. 4). Band electrons interact with surface adsorbed molecular oxygen to yield superoxide radical anions (Eq. 5), while band holes interact with water to produce hydroxyl radical (Eq. 6) [5]. Ultraviolet light with  $\lambda < 380$  nm and, therefore, with energy greater than the  $\text{TiO}_2$  band gap, induces the transfer of electrons from the valence band to the conduction one. The charged species can recombine with each other (releasing the absorbed energy as heat) or migrate to the photocatalyst particle surface.



Organic compounds can undergo oxidative degradation through their reactions with valence bond holes, hydroxyl and peroxide radicals as well as reductive cleavage through their reactions with electrons. The mechanisms of the photocatalytic oxidation ( $\text{TiO}_2$ /UV) of organic contaminants have been extensively studied [8]. Hydroxyl radical has been pointed out as the main responsible species for the oxidative degradation of organic pollutants. The advantages of this process are the operation at ambient conditions, the lack of mass transfer limitations when nanoparticles are used as photocatalysts and the possible use of solar irradiation. Moreover,  $\text{TiO}_2$  is a cheap, readily available material and the photo generated holes are highly oxidizing. In addition,  $\text{TiO}_2$  is capable for oxidation of a wide range of organic compounds into harmless compounds such as  $\text{CO}_2$  and  $\text{H}_2\text{O}$  [3].

The major factors affecting  $\text{TiO}_2$ /UV light process are initial organic load, amount of catalyst, reactor's design, UV irradiation time, temperature, solution's pH, light intensity and presence of ionic species. The use of excessive amounts of catalyst may reduce the amount of energy being transferred into the medium due to the opacity offered by the catalyst particles [7]. Reactor's design should assure that uniform irradiation of the catalyst surface is achieved [13]. For temperature values between 20 and  $80^\circ\text{C}$ , a minor effect of temperature has been noticed. However, at temperature higher than  $80^\circ\text{C}$ , a reduction of the reaction rate has been reported [10]. Solution's pH has a complex effect on photocatalytic oxidation rates. For weakly acidic pollutants, reaction rates increase at lower pH [4]. On the other hand, pollutants which are hydrolyzed under alkaline conditions may show an increase of reaction rate with increase of pH [6]. Finally, the presence of ionic species could affect the degradation process via adsorption of the pollutants, absorption of UV light and reaction with hydroxyl radicals [7].

The aim of the present study was to investigate the technical feasibility of photocatalysis of tannery sludge which was collected from a centralised tannery wastewater treatment. The study was conducted irradiating the sample to sunlight in presence of the catalyst  $\text{TiO}_2$ . The influencing parameters were analysed and the chemical oxygen demand (COD) reduction was also determined.

## 2. MATERIALS AND METHODOLOGY

### 2.1. Materials

The tannery sludge used in this study was obtained from an Industry located in Ranipet, an industrial hub of Vellore city in the state of Tamil Nadu. It is a mixture composed of primary sludge and excess sludge from biological process.  $\text{TiO}_2$  is the catalyst employed in this study that will accelerate the reactions of oxidation. Flexible tube of diameter 1 cm has been used in order to circulate the wastewater for photocatalytic degradation.

## 2.2 Preparation of samples

The solution of sludge was obtained by diluting 10 g of the collected tannery sludge in 1000 mL of distilled water and stirred until all the lumps dissolved, to get a neutral solution whose pH was found to be 8.37. Similarly alkaline and acidic solutions were prepared using 0.1 N NaOH and 0.1 N H<sub>2</sub>SO<sub>4</sub> solutions whose pH were found to be 12.07 and 3.4 respectively. Initial COD of these samples were analysed.

## 2.3 Experimental setup

The experimental arrangement for the treatment process adopted in the study includes the flexible tube of length 3m through which the solution flows and absorbs the solar radiations, a 2 L capacity plastic container to hold the solution and valves to maintain uniform flow. The tube is attached parallel to each other onto the card board as shown in the Fig. 2. Aluminium foil was wrapped on the hard cardboard to reflect the light and facilitate the treatment process. Valves were connected at inlet and outlet. The experiments were conducted in an open atmosphere during noontime when the sunlight was at its peak, in the month of March and April, 2015 on the roof of GDN building, VIT University.



Fig. 2: Experimental Set up

## 2.4 Experimental procedure

The batch studies were carried out by adding a known amount of TiO<sub>2</sub> (i.e, 0.15g) which was known by prior optimization was added to 1000 mL of sludge solution of known pH and stirred thoroughly. It was made to pass through the inlet of the photo reactor tube to reach the outlet through gravity flow. The inlet and outlet were closed. The sample was exposed to sunlight. The irradiation time was being varied from about 1 to 7 hours in the present study when the temperature is high and almost constant viz., 26°C to 35°C. The solar radiation corresponding to the particular hour of the day of the conduction of the experiment was obtained from RET screen software.

At predetermined times 5ml samples of the reaction mixture were withdrawn and filtered in order to remove the fine particles of TiO<sub>2</sub> before analysis. The supernatant was

analysed for COD to determine the COD reduction using Standard Method- American Public Health Association (APHA, 2012). Further, experiments were conducted for neutral, alkaline and acidic solutions to optimize the conditions for pH. The percentage of COD reduction was calculated using the following equation

$$\text{COD reduction (\%)} = ((C_0 - C) / C_0) * 100$$

Where, Co is initial COD concentration (mg/L) and C is final concentration of COD (mg/l) at a given time.

## 3. RESULTS AND DISCUSSIONS

The results of various experiment performed are shown and appropriate discussion are made in this section. Table 2 shows the different parameters before and after photocatalytic treatment of the tannery sludge. The efficiency of the catalyst (TiO<sub>2</sub>) was found to vary with time and the solar irradiation. The major change in the efficiency was seen in acidic, neutral and alkaline medium. The COD removal was about 50% in the alkaline range, 77.5% in the natural existing range and about 85% in the acidic range.

Table 2: Results of analysis

Parameters	Strength of the solution	Before treatment (mg/L)	After the treatment subjected to photocatalysis (mg/L)
COD	Alkaline range	1280	640
	Natural range	960	258
	Acidic range	1280	192



Fig. 3: Reduction in color after treatment.

### 3.1 Comparison of Chemical Oxygen Demand (COD) removal efficiency as a function of time

The rate of COD removal and also color removal was found to increase significantly with time of irradiation. Under optimal conditions, the extent of COD removal was found to be 85% for different time periods ranging from 10.00 a.m to 5.00 p.m under sunlight. The first hour sample showed an efficiency of just 25%. It was also found that the color of the sludge also reduces with the increasing irradiation to the sunlight.

Some findings from the study conducted by Esplugas, (2002) [6], on photodegradation of real textile industrial wastewater have shown that the photodegradation is directly proportional with the time of irradiation of TiO<sub>2</sub>.

The studies conducted by Joshi and Shrivatsa, (2011) [9], showed that though the percentage of removal increases with photocatalysts concentration and it is constant after equilibrium time.

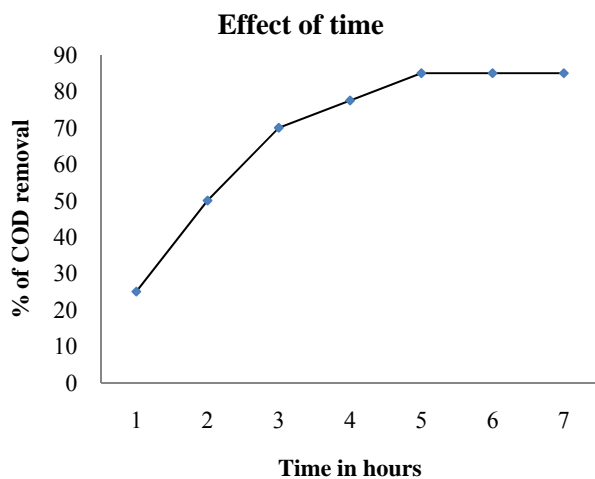


Fig. 3.1: Kinetics of COD removal with time of sunlight exposure

### 3.2 Effect of temperature on the COD removal

The effect of COD removal is dependent on the availability of sufficient sunlight. Temperature plays a very important role in the COD removal and also on the decolorization process and the maximum temperature plays a better role. Irradiation at a high temperature is the important factor to be considered for the maximum reduction of COD than exposing it for more time with less solar intensity.

Removal efficiency was observed to be less during cloudy days due to less solar intensity which leads to less efficiency in the reduction in color therefore conducting the experiment during bright sunny days that has a temperature of about 28<sup>o</sup> C - 32<sup>o</sup>C is advisable to obtain maximum removal efficiency of color and COD. Fallah Hussain (2008), has concluded from his studies that the activation energy for the photocatalytic degradation of tannery wastewater is dependent on the temperature which is indirectly related to the transport of photoelectron through the catalyst to the adsorbed oxygen on the surface.

The presence of about 6-8 hours of sunlight is very much necessary for the treatment process. The present study was made with a maximum exposure time of about 8 hours with a maximum temperature of about 34<sup>o</sup>C. This is well achieved in the places that have sufficient solar energy. As the temperature increases the rate of decolorization also increases, with the reduction in the COD.

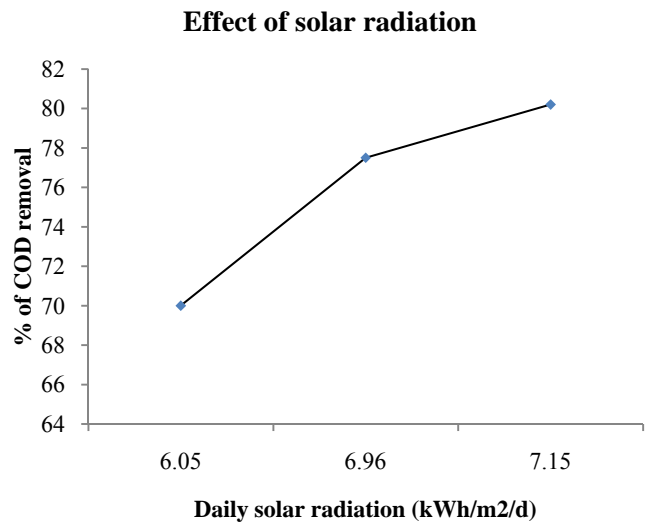


Fig. 3.2: Variation in COD removal due to the effect of temperature

### 3.3 Effect of the pH

The effect of pH was one of the most significant factor which influences the COD reduction. It was found that the maximum COD reduction was achieved in the acidic pH of 3. Degradation of typical inorganic pollutants from wastewater is increased with decreasing pH. The effect of pH on the removal of chromium by different photo catalysts like TiO<sub>2</sub>, ZnO, and CdS on of different influent chromium concentrations was studied by Senthilkumar et al. (2006) [14], Ku and Jung, (2001) [10], studied that the removal of chromium from wastewater using photocatalysts is highly dependent on the pH of the solution.

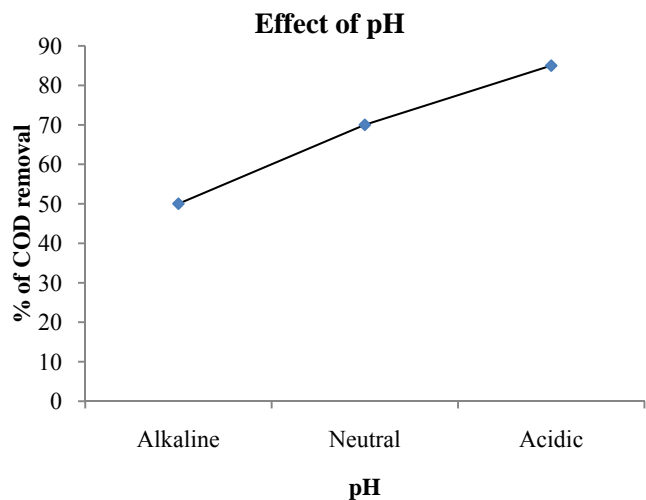


Fig. 3.3: Variation in COD removal efficiency due to the effect of pH

pH was an important variable in the evaluation of aqueous phase mediated photocatalytic degradation reactions. It influenced the surface electric charge of TiO<sub>2</sub> catalyst. Usually the catalyst surface is positively charged at acidic medium and negatively charged at basic medium. In acidic media, electrons tend to move into the surface of catalyst for the electrostatic attraction between the positive charged TiO<sub>2</sub> and negative charged electrons. They react with the oxygen molecules absorbed around the TiO<sub>2</sub> surface to form oxidizing species such as •O<sub>2</sub><sup>-</sup> and •OOH.

#### 4. CONCLUSIONS

Solar photocatalytic treatment has proved as an efficient technique for tannery wastewater and sludge through a photocatalytic process and the transformation is practically complete in a reasonable irradiation time. Results presented in this project indicated that visible light/TiO<sub>2</sub> systems could be efficiently used for photo degradation of tannery wastewater sludge. The results indicate that the degree of photo degradation was affected by different parameters with pH being the main influencing parameter. The results of this research clearly demonstrate the importance of choosing the optimum degradation parameters to obtain a high photocatalytic decolorization rate, which is essential for any practical application of photocatalytic oxidation processes using different photocatalysts. The results suggest that the use of solar light irradiation could be a feasible technique for reduction of the high COD prevalent in the tannery waste sludge and also for its decolorization and it could also become a cost effective technique at industrial scale application. This work can also be extended to study the effect of photo degradation of tannery wastewater also. The photo catalytic activity on COD or color degradation can be further enhanced by doping with cationic or anionic dopant.

#### REFERENCES

- [1] Bhatkhande DS, Pangarkar V.G, Beenackers AACM, 'Photocatalytic degradation for environmental application- a review', *Journal of Chem Technology, Biotechnology*, 2001, 77:102-116, 2001.
- [2] Castiello D, Puccini M, Maurizio S, Seggian M, 'Treatment of Tannery wastewater using photocatalytic process with nanomolecular materials', *Journal of Chemistry*, 2005.
- [3] Chatterjee D. and Dasgupta S, 'Visible light induced photocatalytic degradation of organic Pollutants', *J. Photochem. Photobiology*, 2005, 6, 186-205.
- [4] Choi W. and Hoffmann M.R, 'Novel photocatalytic mechanism for CHCl<sub>3</sub>, CHBr<sub>3</sub> and CClCO<sub>2</sub> degradation and the fate of photo generated trihalomethyl radicals on TiO<sub>2</sub>', *Environ.Sci. Technol.*, 2009, 37, 89-95.
- [5] Crittenden J.C., Trussell R.R., Hand D.W., Howe K.J. and Tchobanoglous G. *Water treatment: Principles and Design*, second ed., Wiley, New Jersey, 2005.
- [6] Esplugas S., Gimenez J., Contreras S., Pascual E., Rodriguez M., Comparison of Different Advanced Oxidation Processes for Phenol Degradation, *Water Research*, 2002, 36, p. 1034.
- [7] Gogate P.R. and Pandit A.B., A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions, *Adv. Environ. Res.*, 2004, 8, 501-551
- [8] Hoffmann, M. R., Martin, S. T., Choi, W. Y., & Bahnemann, D.W, 'Environmental applications of semiconductor photocatalysis'. *Chemical Reviews*, 2009, 95(1), 69-96.
- [9] Joshi M, Shrivatsava S V, Photocatalytic degradation of Chromium (VI) from wastewater using nanomaterials like TiO<sub>2</sub>, ZnO, and CdS, *Appl Nanosci*, 2011, 1, 147:155
- [10] Ku Y, Jung I L, Photocatalytic reduction of Cr(VI) in aqueous solution by UV irradiation with the presence of titanium dioxide, *Water Res*, 2001, 35(1):135-142.
- [11] Lai W C, Juan C J, Ko B W, 'An overview: Recent developments of Titanium Oxide Nanotubes as Photocatalyst for dye degradation', *International Journal of Photoenergy*, 2014, 10:524135.
- [12] Linsebigler, A. L., Lu, G. Q., & Yates, J. T, 'Photocatalysis on TiO<sub>2</sub> surfaces—principles, mechanisms, and selected result', *Chemical Reviews*, 2011, 95(3), 735-758.
- [13] Ray A.K., 'Design, modeling and experimentation of a new large-scale photocatalytic reactor for water treatment', *Chem. Eng. Sci.*, 1999, 54, 3113-3125.
- [14] Senthilkumar S, Kalaamani P, Porkodi K, Varadrajana PR, Adsorption of dissolved from aqueous phase on to activated carbon prepared from agricultural waste, *Bioresour Technol*, 2006, 97:1618-1625.
- [15] SES, *The UV/Oxidation Handbook*, Solarchem Environmental Systems, Markham, Ontario, Canada, 1994.
- [16] Stafford, U., Gray, K. A., & Kamat, P. V, 'Photocatalytic degradation of organic contaminants: Halophenols and related model compounds', *Heterogeneous Chemistry Reviews*, 1996, 3(2), 77-104.
- [17] Stasinakis A, 'Use of selected advanced oxidation processes (AOP's) for wastewater treatment –A mini review', *Global NEST Journal*, 2008, 10(3), p:376-385.
- [18] Vigo F. and Cagliari M, 'Photocatalytic oxidation applied to olive mill wastewaters treatment', *Riv. Ital. Sostanze Grasse*, 2010, 76, 345-353.