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Treatability studies on bleach effluent of pulp and paper industry by ultraviolet/hydrogen peroxide process with titanium dioxide as catalyst

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***Abstract**: The treatment of bleach effluent from pulp and paper Industry for COD, colour and AOX removal was investigated using Ultra violet/Hydrogen peroxide process photocatalysed by Titanium dioxide. The Ultra violet / Titanium dioxide process was able to remove 48% and 37% of COD and colour. The Ultra violet / Hydrogen peroxide process was able to remove 52% and 59% of COD and colour. The combined process of Ultra violet/Hydrogen peroxide process photocatalysed by Titanium dioxide was found to be more effective in the removal of COD and organics compared with the individual processes at a pH of 7. The combined process of Ultra violet/Hydrogen peroxide process photocatalysed by Titanium dioxide showed the COD, colour and AOX removal efficiency of 76%, 78% and 45% respectively.*

***Keywords:** Photocatalysis, Ultraviolet/Hydrogen peroxide/ Titanium dioxide process, bleach effluent.*

I. Introduction

The pulp and paper industry comes under twelve most polluting industries in India due to the huge quantity and quality of wastewater generated (Singh and Thakur, 2004). The manufacturing processes in the pulp and paper industries produce about 80 m^3 of wastewater per ton of pulp produced (Almeida *et al.*, 2004). More than 250 chemicals have been identified in effluents that are produced at different stages of papermaking (Ali and Sreekrishnan, 2001).

Among the various sections in pulp and paper mills, the bleaching section is considered to be the most polluted. During this stage, chlorine or chlorine dioxide is used to bleach pulp and release chlorinated and nonchlorinated compounds from lignin and wood extractives. Typically, these effluents contain high concentrations of chlorophenolic compounds, chloroacetones and chloroform, which are colored and recalcitrant. It has been reported that production of one ton of paper contributes 100 Kg of color imparting substances and 2-4 Kg of organochlorines to the bleach plant effluents. The high chemical diversity of these pollutants causes a variety of clastogenic, carcinogenic and mutagenic effects on fishes and other aquatic communities in recipient water bodies (Parveen Kumar *et al.*, 2011).

Worldwide, there are many existing biological and chemical treatment processes for paper and board mill effluent such as those based on aerobic, anaerobic, algal, fungal biomass, ozonation, electrochemical, photocatalysis, coagulation-flocculation treatment, etc. These classical treatments have been successful in lowering the chemical and biological oxygen demands (COD, BOD), but their applicability is limited by a great number of problems. Given the limitations of the current biological wastewater treatment, there is an increasing interest to develop a more effective treatment approach to reduce the impacts of pulp mill effluents on the environment (Marcia Regina *et al.,* 2009).

Advanced oxidation processes (AOPs) are among promising technologies that have received increasing interest for the treatment of pulp and paper bleach effluents. Advanced oxidation processes (AOPs) are used to oxidize complex organic constituents found in wastewater that are difficult to degrade biologically into simpler end products. The most common advanced oxidation processes are H_2O_2, UV/O_3, O_3, UV/H_2O_2 and photochemical processes. Photochemical processes are used to degrade toxic organic compounds to CO_2 and H_2O, without use of additional chemical oxidants because the degradation is assisted by high concentration of hydroxyl radicals generated in the process (Metcalf and Eddy, 2004).

The objectives of the study was to treat the bleach effluent sample by Ultra violet/Hydrogen peroxide process photocatalysed by Titanium dioxide for the removal of Organics and Colour and to study the effects of various operational parameters such as control conditions, pH, catalyst dosage, catalyst reuse, Hydrogen peroxide concentration and contact time.

II. Materials and Methods

2.1 Bleach effluent from pulp and paper Industry

Bleach Effluent sample was collected from the Kraft process of pulp and paper industry, where the industry used sugarcane bagasse and hardwood as the raw material.

2.2 Ultraviolet/Hydrogen peroxide/ Titanium dioxide processes

A Heber immersion batch photoreactor (UV) supplied Heber scientific, Chennai with a liquid volume of 1L capacity was used. The reactor was placed in a photo chamber. A 400 W medium pressure mercury lamp with emission wavelength 365 nm was used as a light source in the photoreactor. Because temperature of the lamp influence on UV dose rate, the lamp chamber was cooled by circulated cold water and the temperature of the lamp was maintained at 20°C throughout the experiment. The cold water was supplied by the cooling water supply setup made by LAUDA GMBH & Co, Germany of type WKL 230. 1 mL magnetic stirrer supplied by Remi equipments private Ltd was kept below the sample tube for continuous stirring to get homogenous mixture. A 500 mL of wastewater sample was taken and required dosage of photocatalyst was added. Then the mixture was stirred for 5 minutes using magnetic stirrer to get a homogenous mixture. Then the sample was taken in the photoreactor. The cooling water was allowed to circulate around the UV lamp in the photoreactor. The magnetic stirrer was kept under the sample tube and switched on. The UV lamp was switched on and the photocatalysis sample was taken at required time interval. The sample was centrifuged at 2500 rpm for duration of 20 minutes.

2.3 Analytical control

All samples were submitted to colour and COD analyses. The effluent discolouration was evaluated by measuring the absorbance at 465nm, 525nm and 620nm with a UVVIS spectrometer. AOX measurements were made after pretreatment (Presto Filtration Unit) with activated carbon adsorption using ECS -120 AOX Analyser with ES- Boat water Module.

III. Results and Discussions

In this work, Kraft bleach effluent treatment was done by Ultraviolet/Hydrogen peroxide/ Titanium dioxide processes for 4 hours. The wastewater was characterised for the parameters such as pH, COD, TDS, TSS, chlorides and colour as per standard methods. The wastewater has pH of 6.71, TDS of 1470 mg/L, TSS of 1524 mg/L, COD of 1035 mg/L, chlorides of 370 mg/L and AOX of 1.60 mg/L. The characteristics such as colour, absorbance were measured by means of UV-VIS spectrophotometer. The characteristics of the bleach effluent used in this study are described in Table1.

Table 1 Characteristics of bleach effluent from pulp and paper industry

Sl. No.	Parameter	Value
1	pH	6.71
2	BOD	835 mg/l
3	COD	1035 mg/l
4	Colour	Brown
5	Absorbance at 620 nm	0.295
6	Chloride	370 mg/l
7	AOX	1.84 mg/l

In the Ultra violet / Titanium dioxide process the effect of TiO_2 dosage on the degradation of bleach effluent at its natural pH was studied by varying the TiO_2 dosage from 0 g/L to 1.0 g/L. The degradation of bleach effluent was determined by COD of the treated sample at various time intervals. It was found that maximum COD removal efficiency of 48% was achieved at a catalyst dosage of 1g/L for a contact time of 240 minutes. It was found that minimum of 19% COD removal efficiency takes place at a catalyst dosage of 0.4 g/L for a contact time of 240 minutes. The degradation efficiencies based on the COD removal were calculated and they are illustrated in Figure. 1. TiO_2 is capable for oxidation of a wide range of organic compounds into harmless compounds such as CO_2 and H_2O (Chatterjee and Dasgupta, 2005). TiO_2 system increased the quantum efficiencies either by inhibiting electron-hole pair recombination through scavenging conduction band electrons at the surface of TiO_2 or by offering additional oxygen atom as an electron acceptor to form the superoxide radical ion (Syoufian *et al.*, 2008).

The effect of TiO_2 dosage on the degradation of bleach effluent at its natural pH was studied by varying the TiO_2 dosage from 0 g/L to 1.0 g/L. The absorbance values of the untreated bleach effluent sample at 436nm, 525nm and 620nm was found to be 0.813, 0.494 and 0.295 respectively. The bleach effluent was treated using

UV/Hydrogen peroxide process for 4 hours and the degradation of bleach effluent was determined by the percentage of Colour removal of the treated sample at various time intervals. It was seen that maximum colour removal efficiency of 56% takes place for a catalyst dosage of 0.8 g/L for a contact time of 240 minutes at 525 nm. It was seen that minimum colour removal efficiency of 23% takes place for a catalyst dosage of 0.4 g/L for a contact time of 240 minutes at 620nm.

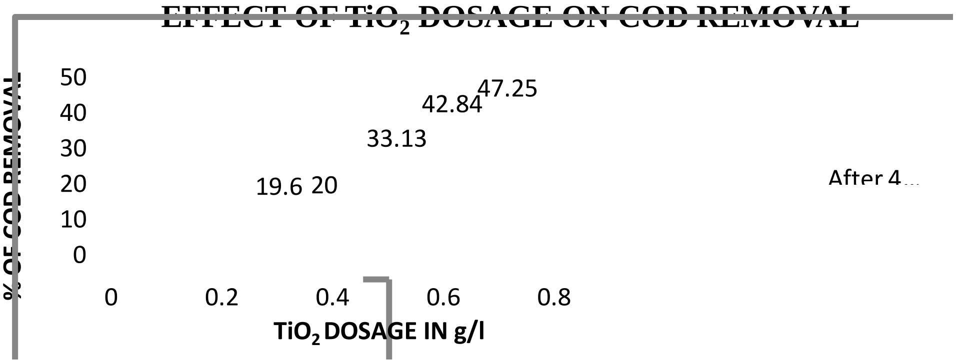
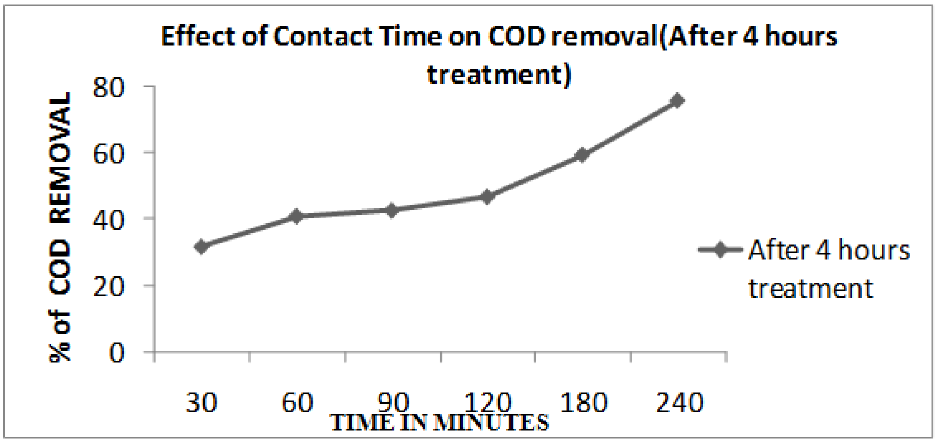


Figure .1 The effect of TiO_2 dosage on the COD removal of bleach effluent

The effect of contact time on COD removal of bleach effluent at its natural pH was studied by conducting the experiment for a contact time of 240 minutes at an optimum dosage of 1g/L and H_2O_2 concentration of 1.2 mL/L. Degradation of bleach effluent was determined by COD of the treated sample at various time intervals. It was found that that degradation efficiency of COD of the bleach effluent was found to be 40% after the first hour of treatment; it was 46% after the second hour of treatment, 59% after the third hour of treatment and 75% after the fourth hour of treatment. The degradation efficiencies based on the COD removal were calculated and they are illustrated in Figure.2. It was seen that the maximum COD removal efficiency of 75 % was observed after a contact time of 240 min.

Kumar Parveen *et al.*, (2011) have studied the decolourization of the kraft bleaching waste water with UV/TiO_2 and $UV/TiO_2/H_2O_2$ advanced oxidation processes. It was seen that the maximum COD removal of 75% was observed after a contact time of 240 min. Abhilasha Dixit *et al.*, (2010) have studied the photochemical oxidation of phenol and chlorophenol aqueous solutions in a batch recycle photochemical reactor using ultraviolet irradiation, hydrogen peroxide and TiO_2 (photocatalyst). The reaction was found to follow the first order kinetics and was influenced by the pH, the input concentration of H_2O_2 and the dosing amount of the TiO_2 photocatalyst. The results indicate maximum of 75% and 79% degradation of phenol and chlorophenol respectively within 90 minutes of radiation time.

The effect of contact time on colour removal of bleach effluent at its natural pH was studied by conducting the experiment for a contact time of 240 minutes at an optimum dosage of 1g/L and H_2O_2 concentration of 1.2 mL/L. The sample was collected and analysed for colour removal and the results and illustrated in Figure 2. Degradation of bleach effluent was determined by colour removal of the treated sample at various time intervals by measuring the absorbance of the treated bleach effluent sample at 436nm, 525nm and 620nm. Enhancement of TiO_2-catalyzed photodegradation of organic compounds by several inorganic oxidants was mainly attributed to the increased electron scavenging from the extra oxidant sources (Hu and Wang , 2003).



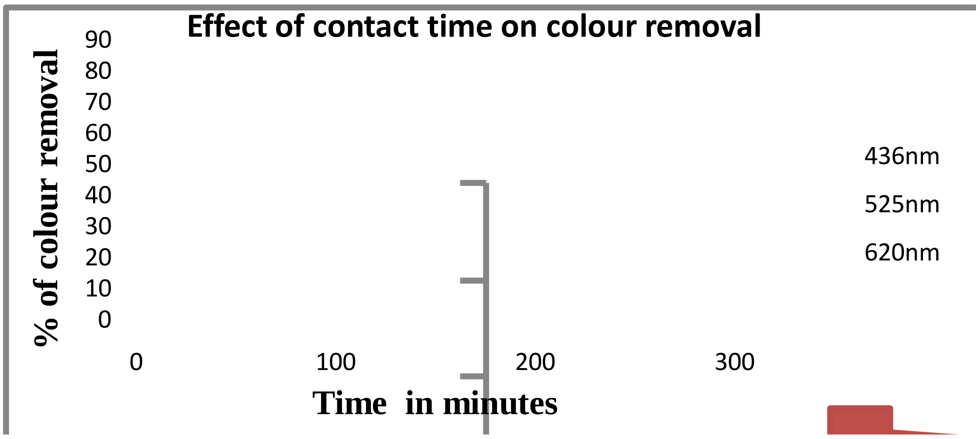


Figure .2. Effect of contact time on the removal of COD and Colour

The effect of pH on the degradation of wastewater was studied the for various pH viz 3, 5, 7 and 9 with optimum dosage of TiO_2 and concentration of H_2O_2. The experimental results are presented in Table 4.8. The COD removal efficiency was found to be 22% at a pH of 3. At a pH of 5 the degradation efficiency was found to be 37%. The COD removal efficiency was found to be 47% at a pH of 9. The degradation efficiencies are illustrated in Fig. 3. In this study, the maximum efficiency of degradation of 75% was observed at a pH of 7 at the end of 4 hours.

In this study, the natural pH of 7 gives significant rate of degradation. Hence the natural pH was selected for further studies. pH plays an important role both in the characteristics of pulp and paper industry effluents and in the reaction mechanisms that can contribute to degradation, namely, hydroxyl radical attack, direct oxidation by the positive hole and direct reduction by the electron in the conducting band. Ramakrishna (2001) found that at a pH of 3 to 5, the rate of degradation is high. pH has a significant effect on the surface charge of TiO_2 at low pH the particles have a positive charge and at high pH a negative charge. Depending upon the charge of organic components present in solution, there may be electrostatic attraction or association between organic components and the TiO_2 surface under pH conditions.

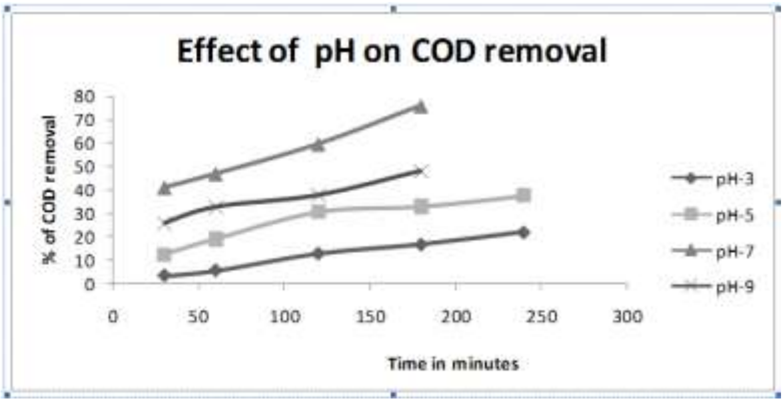


Figure .3. Effect of pH on the removal of COD

The sample of the bleach effluent was taken and photocatalysis was carried out under optimum conditions of pH, catalyst dosage, H_2O_2 concentration and contact time and the sample was analyzed for the removal of AOX. The initial AOX concentration of the untreated bleach effluent sample was found to be 1.60 mg/l. The photocatalytic treatment of untreated bleach effluent sample was carried at an optimum catalyst dosage and H_2O_2 concentration for 4 hours and the AOX removal efficiency was calculated.

AOX measurements were made after pretreatment (Presto Filtration Unit) with activated carbon adsorption using ECS -120 AOX Analyser with ES- Boat water Module. The optimum catalyst dosage and H_2O_2 concentration was found to be 1 g/L and 1.2 mL/L. The experimental results are presented in Table 4.10. The degradation efficiencies are illustrated in Fig. 4. The UV photocatalytic process is more favoured than the UV photolytic degradation process in the removal of AOX. The AOX concentration goes through a minimum when the concentration of TiO_2 and H_2O_2 increase at constant pH and UV intensity (Mehmet Ugurulu *et al.*, 2009). The toxic effects of AOX range from carcinogenicity, mutagenecity to very acute and chronic toxicity.

The increase in the AOX concentration observed with only UV photo catalysis could result from the possible reaction of Chlorine molecules in the medium with degraded organic fragments reflecting the effect of UV photocatalysis. However, by adding H_2O_2 and increasing the concentration of H_2O_2, AOX concentration gets decreased. The maximum AOX removal efficiency was found to be 31%.

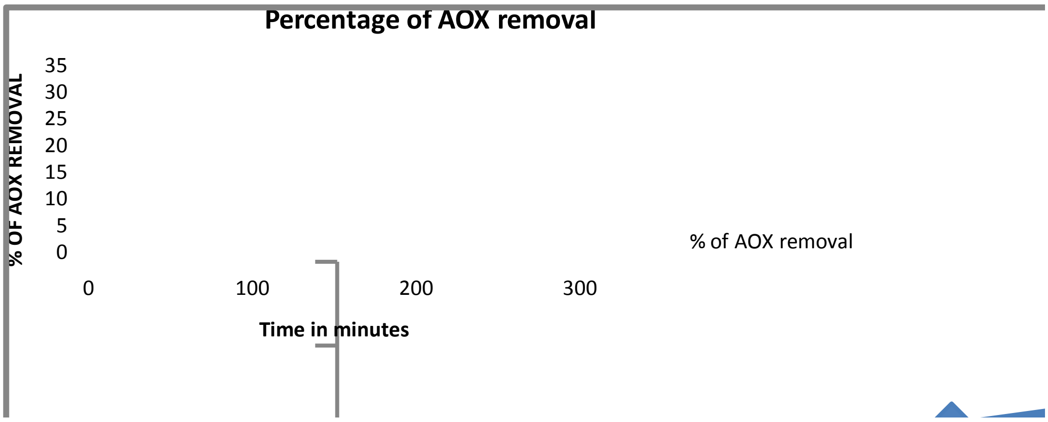


Figure .4. Effect of contact time on the removal of AOX

The graphical method was used to find the initial kinetic rate constant (k) of the Ultra violet/Hydrogen peroxide process photocatalysed by Titanium dioxide for the removal of Organics from the bleach effluent sample. Rate constant derived from the pseudo-first-order kinetics was used to find the degradation of organic compounds. In order to find the initial rate of degradation, a plot of time vs ln (COD_0 /COD) was made. Using the exponential equation it was found to be best fit for the degradation with R^2 values of 0.923. Hence, the rate of degradation of this wastewater followed the first order kinetics.

The kinetic rate constant (k) was found to be 0.002. Khare *et al.*, (2004) observed that the plots were found linear for disperse dyes, which suggests that the COD removal reaction follows pseudo-first order kinetics. The kinetic results are shown in figure 4.10, which produce a single straight line. Therefore, the degradation of bleach effluent from the pulp and paper Industry follows a first order kinetic model. According to the degradation rate constant, obtained by plotting the graph between the time and the rate degradation it was found that the UV photocatalytic degradation processes are more effective than the UV photolytic degradation process for the treatment of paper–mill effluents.

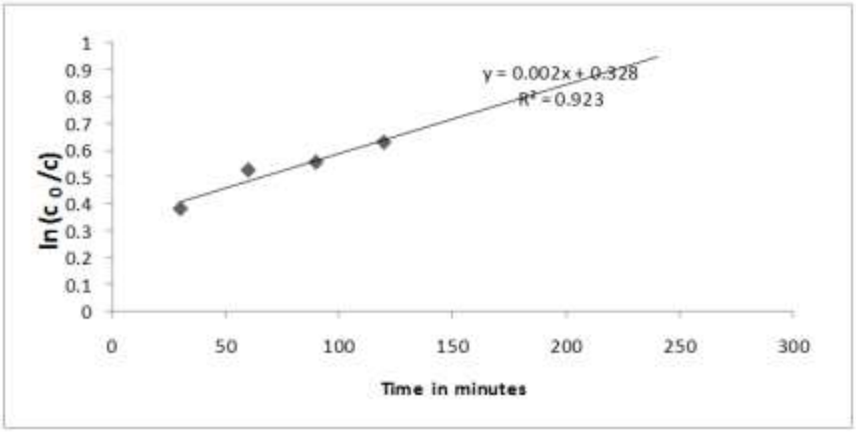


Figure 5.Determination of Kinetic Rate constant

IV. Conclusions

Degradation of bleach effluent from pulp and paper industry wastewater is effective using Ultra violet/Hydrogen peroxide process photocatalysed by Titanium dioxide.At optimum conditions the maximum COD removal efficiency of 76 % and colour removal efficiency of 78%was achieved after 4 hours treatment at a pH of 7 in the Ultra violet/Hydrogen peroxide process photocatalysed by Titanium dioxide. The maximum AOX removal efficiency of 31 % was achieved after 4 hours treatment. The photocatalytic process can be considered a suitable alternative to the removal of organics and colour from the bleach effluent of pulp and paper Industry.

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