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Pulp and Paper Industry Effluent Decolourization Kinetics with Ozone and Titanium Dioxide

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Abstract

Ozone, a potential oxidant has become the most important innovation for ultimate treatment of all types of organic / inorganic impurities in water and waste water by oxidation process. It can be safely and effectively used for the decolourization of effluents from pulp and paper industry. The pulp mill of paper industry is a water intensive and producing large volume of effluents containing different organic and inorganic substances which include residual ionic species, ligneous fragments of organic solids etc. The pollutants in the effluent should be removed before their discharge to water sources. An attempt has been made to study the impact of catalytic amount of TiO_2 on the ozonation of coloured effluent with the variation of pH, temperature, catalyst and ionic strength. Again, the decolourization kinetics of post oxygen stage effluent of pulp and paper industry using bamboo and hardwood (20: 80) as furnish has been studied at temperature range 25-50^oC using laboratory generated ozone. The ozonation reactions follow a pseudo first order disappearance of colour and the rate constant increases with increase in ozone concentration.

Keywords - *Ozone, Colour, Effluent, Kinetics, Pulp mill, Catalyst, Wood*

I. INTRODUCTION

The planning, designing, construction and operation of waste water treatment facilities are complex problems. These involve political, social and technical issue. Therefore, besides meeting the effluent quality requirements, a waste water treatment and disposal system must also satisfy many other environmental conditions. A pulp and paper industry effluent contains both inorganic and organic pollutants in their waste water. The purpose of waste water treatment is to destroy these contaminants in the effluents which are discharged into the streams. Oxidative decomposition is the easier and greener method for the treatment of pulp and paper industry effluent. Among the oxidative methods ozonation is the best method to treat the effluent in side plant. It is observed that ozonation reaction of pulp and paper industry effluents is enhanced in presence of catalytic TiO_2.It is capable of decomposing colouring substances, humic acid materials, tannins, lignin degraded products etc. at a faster rate without generating any toxic by-product[1-5]. Although ozonation is a very good choice for the physical and chemical treatment of effluents released from pulp and paper industry, the exact mechanism and kinetics of ozone induced decolourization have not yet studied systematically. In the present work an attempt has been made to study the kinetics of ozone induced decolourization in presence of TiO_2 as catalyst using post oxygen (PO) stage effluent generated from a pulp and paper industry. ***Rajeswari et al.*[2009]** reported on TiO_2 based heterogeneous photocatalytic treatment of pesticide carbendazim combined with ozonation for carbendazim degradation. A batch annular photo reactor has been used for carrying out the combined process and influence of TiO_2 concentration; ozone dose and pH are investigated. Their result shows that removal rate increased with increase in ozone dose up to 0.48g/h and decreased above 1 g/l of TiO_2. At optimum pH of 6 with 1 g/l TiO_2 and with 0.48 g/h ozone dose, 88% COD removal is achieved in 3 hours by combined photolytic ozonation process. Present investigation is carried out for the improving catalytic ozonation with the application of TiO_2, which is easily available in the market with miserable price[6]. ***Parveen Kumar et al.*** (**2011**) worked on the advanced photocatalytic oxidation of the pulp and paper industry effluent (primary clarified and bio treated) with UV/TiO_2 and $UV/TiO_2/H_2O_2$ treatment processes for environmental load reduction. The photo-oxidation experiments are performed under UV radiation in a slurry-type of reactor with optimized treatment conditions i.e. pH 7.0, 0.5 g/l of TiO_2 and 15 mM/L of H_2O_2 for 4 hours[7]. ***Thiruvenkatachari et. al.*** (**2008**) reported that titanium dioxide exposed to sunlight becomes photoactive, the surface of the catalysts generates free electrons, and valance band holes form. Water encounters the valance holes and the water oxidizes to form hydroxyl radicals. Hydroxyl radicals are non-selective, strong oxidizers and very reactive[8]. ***Konstantinou et al.* (2004)** reported that oxygen from the air and dissolved in the water can accept the free electrons on the surface of photo activated TiO_2 generating the radical anion, O^{2-}. The anions can further oxidize the organic compounds[9]. ***Daneshvar et. al.*** (**2003**) reported that many of the reactions occurring on the surface of titanium dioxide lead to the breakdown of the dyes making it an efficient photo catalyst. There are many parameters that control the extent of oxidation including pH, concentration of the organic compounds and TiO_2, and the presence of reagents[10]. ***Pekakis et.al.*(2006)** reported on the oxidative degradation of an actual textile dye house wastewater was investigated by means of photo catalysis in the presence of TiO_2. The UV-induced photo catalytic oxidation over TiO_2 suspensions was capable of decolorizing the effluent completely, as well as reducing chemical oxygen demand (COD) sufficiently (COD reduction generally varied between about 40% and 90% depending on the operating conditions) after 4 hours of treatment. Two crystalline forms of TiO_2, viz. anatase and rutile, were tested for their photo catalytic activity and anatase was found to be more active than rutile[11]. The organics studied did not adsorb significantly either in wastewater or in phosphate-buffered water. The catalysts did not modify the rate of the hydroxyl-mediated ozonation with respect to the homogeneous value. The mode of action of metal oxide catalysts would be an enhanced generation of oxidant species from the catalytic decomposition of ozone[12]. All catalysts increased the efficiency in the production of hydroxyl radicals from ozone.

II. MATERIAL AND METHODS

The chemicals used are of reagent grade. Ozone is generated by using pure oxygen gas in an ozonator [Model number (CD-500)] which produces ozone by electric discharge principle. For Ozone determination, the iodometric standard titration method has been followed. The sample is collected in a 250 ml volumetric flask containing 10 ml of 0.1 N H_2SO_4 and 20 ml of 20 % KI solution. A blank is also set up and the titrations are carried out using 0.005N sodium thiosulphate solution. The ozone concentration applied has been calculated from the graph of standard concentration at different flow rate. The experiments are performed by following the disappearance of colour in the effluent at different reaction time after passing the ozone at fixed flow rate. The reduction in colour (in Platinum Cobalt Unit) concentration are determined spectro-photometrically at 465 nm after centrifuging the solution. Experiments are carried out by passing the O_3 at a fixed flow rate into a reaction flask of one liter capacity with 500 ml of effluent after adjusting the pH to 9.5.The amount of O_3 passing to the solution was calculated from a standard curve done earlier. Aliquots are withdrawn at regular intervals and the reaction has been quenched by ice. The intensity of colour has been determined after centrifuging. The measurement of the colour of the supernatant liquid is done by a UV-VIS spectrophotometer [Model Shimadzu-1700] at 465 nm. TiO_2 salts are generally springy soluble in water, so at the time of preparing catalyst solution one ml of hot diluted sulphuric (4N) was added for total solubility of the salt. From the stock solution require amount of samples were used for the catalytic study.

III. RESULT AND DISSCUSSION

Stoichiometric experiments were performed by taking $[O_3] > [Colour]$, while maintaining other conditions constant by measuring the colour concentration spectro-photometrically by calculating the disappearance of colour from 500ml effluent at different time intervals i.e. [colour] = 2000 PCU, $[O_3]$ =1.78 gm/lit. and pH=9.5 or by passing excess of O_3 over colour. The unreacted O_3 after the completion of reaction was estimated. In the run, readings were taken after long intervals until constancy in the leftover O_3 was reached i.e. 100 % of completion of the reaction. Then the oxidant concentration consumed or involved, $[O_3]$, for the completion of the reaction with respect to known concentration of the colour was calculated, from which the stoichiometric ratio of [colour] to $[O_3]$ was found out for the overall reaction. The results of stoichiometric experiment conducted with effluent containing an excess of O_3 over that of [colour] at a fixed pH of 9.5 revealed that 1.0 mg dm^{-3} of $[O_3]$ is required for the reduction of 1.0 mg dm^{-3} of [colour] to give the colourless product. The rate of reaction is observed from the graph [% of colour reduction vs. Time] which is presented below. In the graph, the colour reduction percentage gradually increases by the increasing of reaction time with certain interval then remains constant, which indicates the reaction follows first order rate law as shown in in Fig.1.

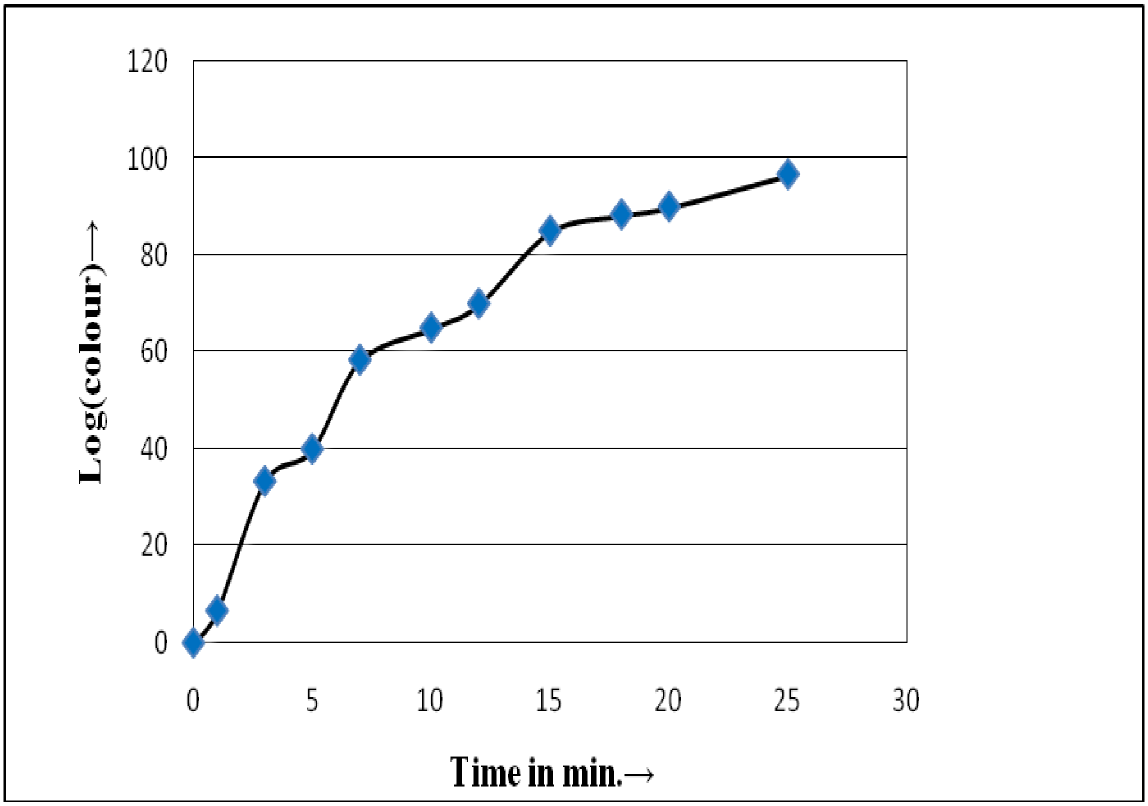

Fig 1: Stoichimetric graph for decolourization of pulp and paper industry PO-stage effluent on ozonation in presence of TiO_2catalyst

A. *Effect of Colour concentration on $k_{1(obs)}$*

The pseudo first order rate constants measured from the kinetic runs ($k_{1(obs)}$) at different initial concentration of the [colour] are presented in Table 1. Data show that the $k_{1(obs)}$ values remain unchanged with the increase in [colour] as measuring the colour concentration. The disappearance of colour is measured at different colour concentration by applying same ozone dose and at same pH which is shown bellow in fig. 2 to 5. The pH is adjusted by adding either dilute H_2SO_4 or by adding dilute NaOH solution as per requirement. The colour concentration is adjusted by proper dilution with water. The reaction follows perfectly pseudo-first order kinetics. The pseudo first order [colour] disappearance is perfectly satisfied for at least two half lives in all runs performed in aqueous conditions. However, the pseudo first order rate constant is not altered significantly when concentration of [Colour] is used for study.

TABLE 1: Effect of [Colour] on reaction rate in presence of catalytic TiO_2 with condition: $[O_3]$ = 1.78g/lit, pH =9.5, Temp=30°C

Sl. No.	Initial Colour(PCU)	k_{1obs} Sec^{-1}
1	1000	0.002303
2	1500	0.002178
3	2000	0.002571
4	2500	0.002303

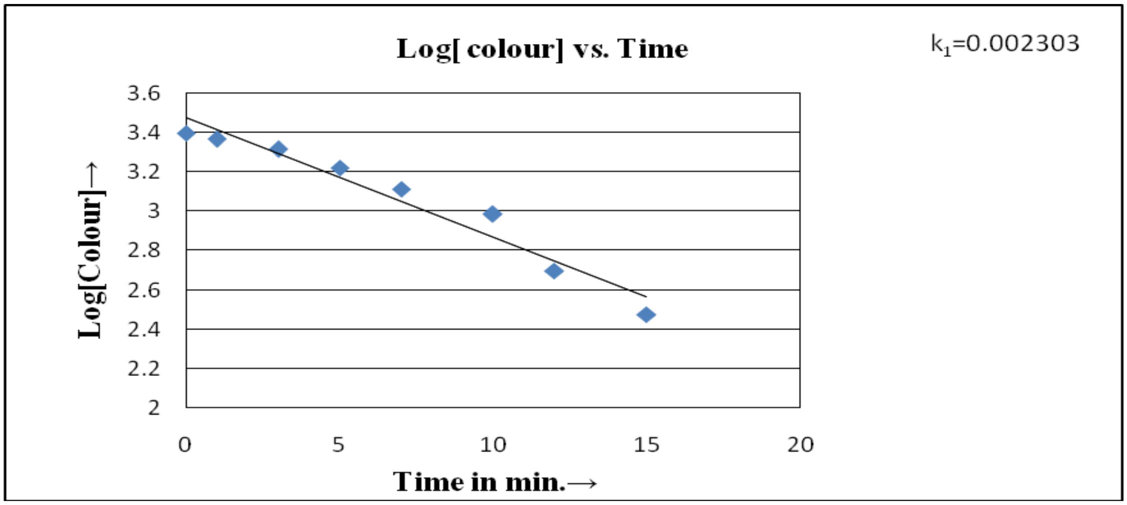

Fig 2: Kinetic plot of pulp and paper PO-stage effluent colour reduction on ozonation in presence of catalytic TiO_2
Condition: Initial colour of the effluent=2500PCU, $[O_3]$ = 1.78g/lit, pH =9.5, Temp=30°C

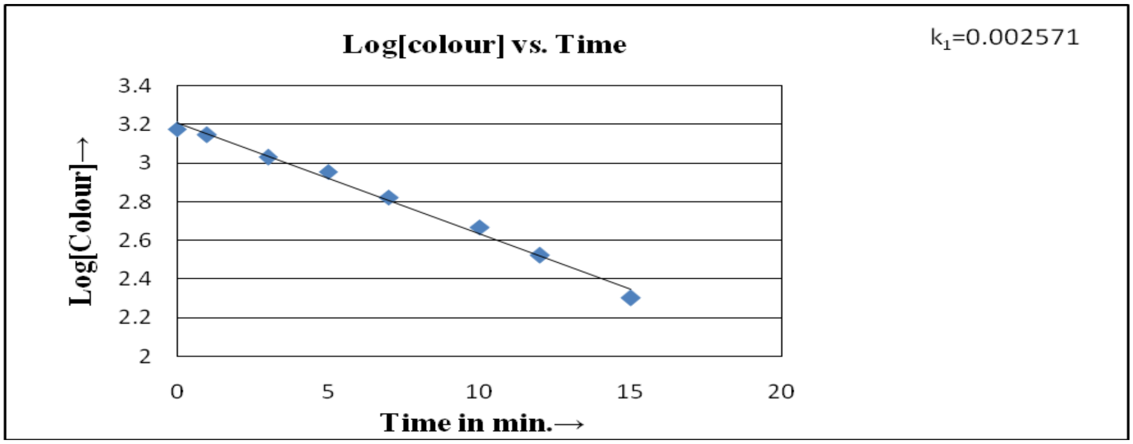

Fig 3: Kinetic plot of pulp and paper PO-stage effluent colour reduction on ozonation in presence of catalytic TiO_2.
Condition: Initial colour of the effluent=2000PCU, $[O_3]$ = 1.78gm/lit, pH =9.5, Temp=30°C

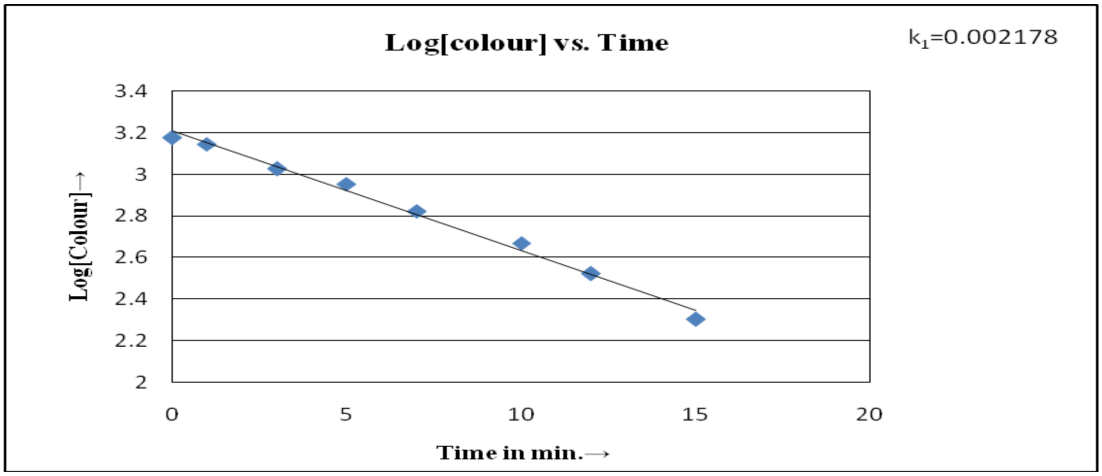

Fig 4 : Kinetic plot of pulp and paper PO-stage effluent colour reduction on ozonation in presence of catalytic TiO_2
Condition: Initial colour of the effluent = 1500, PCU, $[O_3]$ = 1.78gm/lit, pH =9.5, Temp=30°C

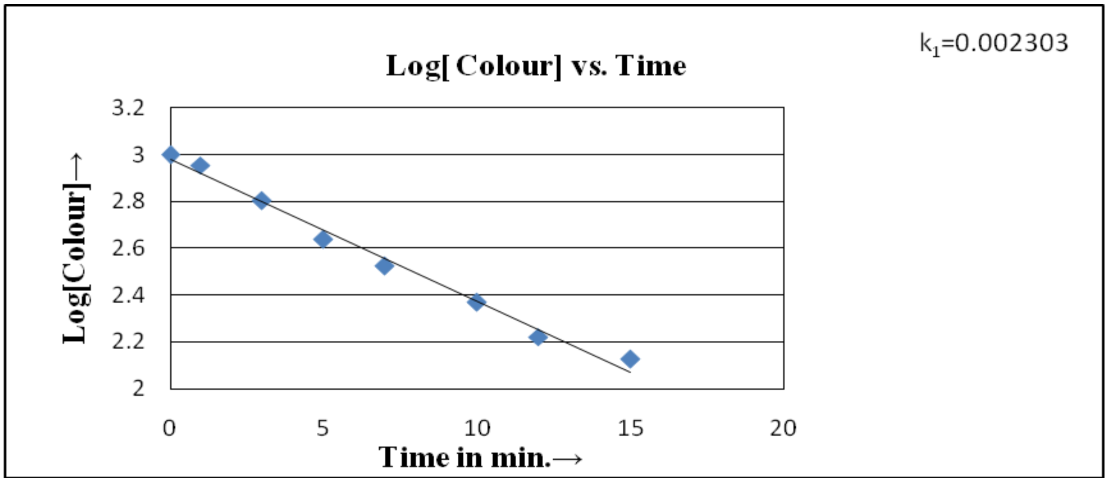

Fig 5: Kinetic data of pulp and paper PO-stage effluent colour reduction on ozonation in presence of catalytic TiO_2 Condition: Initial colour of the effluent=1000PCU, $[O_3]$=1.78g/lit, pH=9.5,Temp=30°C

B. *Rate of disappearance of colour with ozone variation*

Experiments are conducted with application of different ozone dose. The disappearance of colour is with different ozone dose shows that with the increasing ozone dose the rate of decolourization increases. The disappearance of colour is followed a pseudo first order kinetics for at least 90% completion of the reaction in the present work. Under the condition of [ozone] < [colour], a curve is obtained when plotted against log [oxidant] vs. Log $k_{1(obs)}$ presented in Fig.6. Which indicates the rate may be a fractional order.

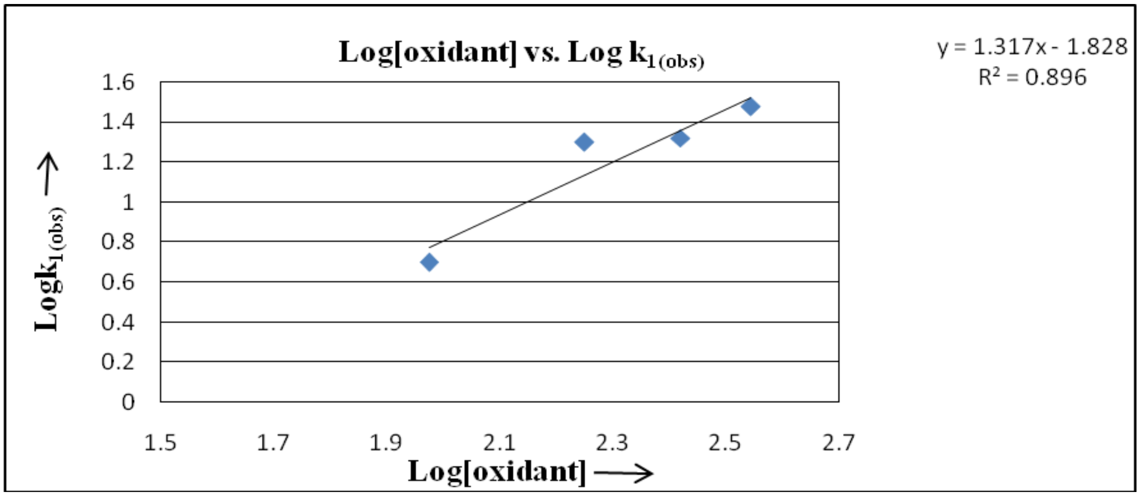

Fig 6: Plot between Log [oxidant] vs. Log$k_{1(obs)}$

C. *Effect of varying the catalyst on $k_{1(obs)}$*

The disappearance of colour is also observed at maintaining different catalyst dose to the post oxygen stage effluent. The pH is adjusted by adding either dilute H_2SO_4 or by adding dilute NaOH solution as per requirement. The observed pseudo first order rate constant [$k_{1\ (obs)}$] are influenced by different dose of catalytic application. The plot between Log(catalyst) vs. Log$k_{1(obs)}$ is also a straight line slope shown in Fig-7.

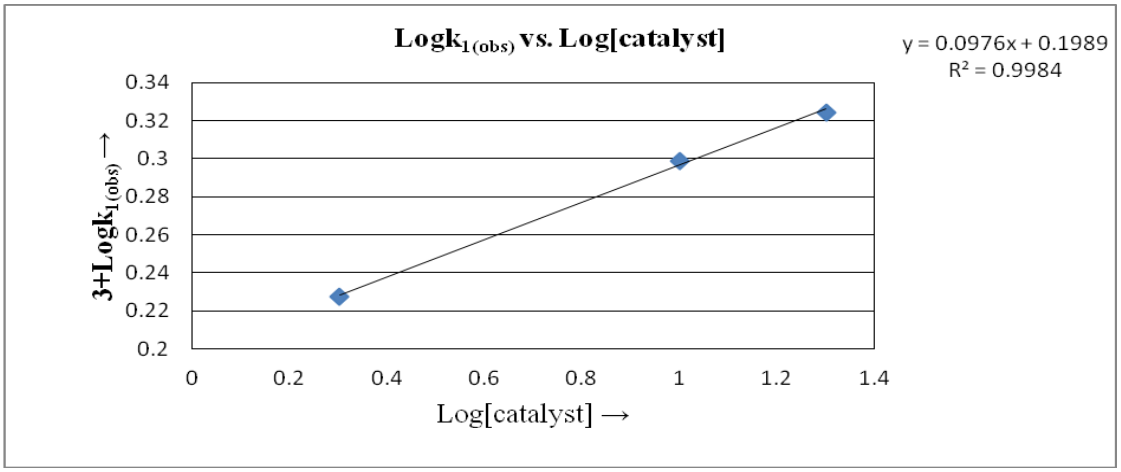

Fig 7: Plot **between Log(catalyst) vs. $Logk_{1(obs)}$**

D. Effect of varying the pH on $k_{1(obs)}$:

The disappearance of colour is also observed at maintaining different initial pH of the post oxygen stage effluent with the application of catalytic TiO_2. The pH is adjusted by adding either dilute H_2SO_4 or by adding dilute NaOH solution as per requirement. The observed pseudo first order rate constant $[k_{1(obs)}]$ are influenced by different pH. The rate constant is higher at lower and higher pH. This means that at higher pH of greater than 10 and at lower pH less than 5 the decolourization of pulp and paper industry effluent with ozone is better. At neutral pH the decolourization efficiency with ozone is lower. This is shown in the Table 2.

TABLE 2. Effect of pH on reaction rate with condition: [Colour] = $2x10^3$PCU, $[O_3]$= 1.78g/lit, Temp=30°C

Sl. No.	pH	k_{1obs} sec^{-1}
1	4.5	0.0023413
2	5.0	0.002111
3	7.0	0.001612
4	8.0	0.0016121
5	9.5	0.0019959
6	10.5	0.0025716

E. Effect of variation in temperature on $k_{1(obs)}$ values:

Temperature plays significant role in the TiO_2 catalysed ozonation reaction of effluents. The reaction runs are carried out at different temperatures (35,40,45^{0}C) with the application of different dose of TiO_2 catalyst. For maintaining the initial temperature ,the effluent is heated up to the temperature and taken for conducting the ozonation.From the data, the effect of temperature on the reaction rate can be identified and also to compute the net activation parameters pertaining to the reaction. It is observed that increase in temperature the rate of decolourization of effluents increases on ozonation. Plot of log $k_{1(obs)}$ vs. 1/T are perfectly linear (Fig.8). From the slope of the plots, various net activation Arrhenius parameters are computed at 30^{O}C for the reaction of colour compound with $[O_3]$ are: Ea = 27.1KJ mol $^{-1}$, ΔH^+ = 24.65JK^{-1}mol $^{-1}$, ΔS^+ = -173.3 JK^{-1}mol $^{-1}$, log A =1.95.

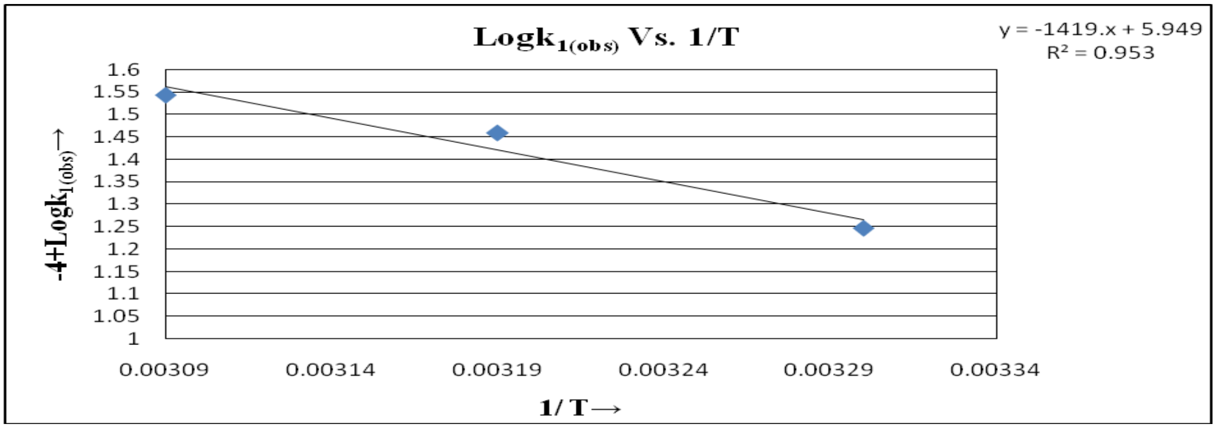

Fig 8: Plot between, Logk$_{1(obs)}$ vs. 1/T

F. The mechanism of catalytic ozonation by using Ti (IV)

$$[\text{Colour}] \overset{K_a}{\rightleftharpoons} [\text{Colour}]^- + H^+$$

$$O_3 + \text{Ti(IV)} \overset{K}{\rightleftharpoons} O_2^* + O^*$$

$$O^* + [\text{Colour}] \overset{K_1}{\rightleftharpoons} [\text{Complex}] \xrightarrow[\text{Slow}]{k_1} \text{Oxidation Products}$$

or

$$O_2^* + [\text{Colour}] \overset{K_2}{\rightleftharpoons} [\text{Complex}] \xrightarrow[\text{Slow}]{k_2} \text{Oxidation Products}$$

SCHEME-1

Rate Calculation

Rate = k_1[Complex]

$$[\text{Complex}] = \frac{k_1[O^*][\text{Colour}]}{1+K_1[\text{Colour}][O^*]}$$

But, $O^* = K[O_3][\text{Ti(IV)}]$

$$[\text{Complex}] = \frac{KK_1[O_3][\text{Ti(IV)}]}{1+KK_1[\text{Colour}][O_3][\text{Ti(IV)}]}$$

Putting the value of [Colour] in the above equation

$$-\frac{d[\text{Colour}]}{dt} = \frac{KK_1k_1[O_3][\text{Colour}][\text{Ti(IV)}]}{1+KK_1[\text{Colour}][O_3][\text{Ti(IV)}]}$$

From the rate law,

$$\frac{1}{\text{Rate}} = \frac{1}{KK_1[O_3][\text{Colour}][\text{Ti(IV)}]} + \frac{K_2}{K_1k_1}$$

CONCLUSION

From the above research work it is clearly concluded that the catalytic application of TiO_2 gives a gives better result for colour reduction during ozonation. The effect of temperature & pH, takes a significant role on the rate of colour reduction. The detailed rate equations are given in scheme-1 and the rate law also calculated

REFERENCE

[1] J W Chen, C Hui, T Keller & G Smith., Catalytic ozonation in aqueous system. Water-1976:I. Physical chemical waste water treatment., Published by- American Institute of chemical engineers.,73(166) : 206-212,1997.

[2] A Enescia, L Andronic, A Duta & S Manolache., Optical properties and chemical stability of WO_3 and TiO_2 thin films photo catalysis., Romanian Journal of Information science & technology., 10(3): 269-277,2007

[3] U G Akpan & Hameed., Parameters affecting the photo catalytic degradation of dyes using TiO_2-based photocatalysts: A review., Journal of hazardous materials.,170:520-529,2009

[4] G Laer, M N Chong, B Jin & A Lopez., An integrated MBR-TiO2 photocatalysis process for the removal of carbamaze pine from simultated pharmace utical industrial effluent., Bioresource technology.,102:7012-7015, 2011.

[5] P K Bhaba, K Vaithyanathan, M Dillipkumar and C B Ahmed., Electrochemical treatment of pulp and paper effluent using RuO_2/ TiO_2/Ti-electrode., Ippta Journal.,16(1):17-20, 2004.

[6] R Rajeswari & S Kanmani., TiO_2-based heterogeneous photo catalytic treatment combined with ozonation for carbendazim degradation.,

[7] K Praveen, K Satish, N K Bhardwaj & A K Choudhary., Advanced oxidation of pulp and paper Industry Effluent., International Conference on Environmental & Engineering., 15:170-175, 2011.

[8] R Thiruvenkatachari & S Vigneswaran.,. A review on UV/TiO_2 & lt;sub >2</sub> photocatalytic oxidation process , Journal Review, Korean Journal of Chemical Engineering, 25(1): 64-72, 2008.

[9] I K Konstantinou & T A Albanis., TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigation: A review., Applied Catalysis B: Environmental., 49(1): 1-14, 2004.

[10]N D Daneshvar, Salari,, Photocatalytic degradation of azo dye acid red 14 in water: investigation of the effect of operational parameters. Journal of Photochemistry and Photobiology & Chemistry., 157(1): 111-116,2003.

[11] P A Pekakis, N P Xekoukoulotakis & D Mantzavinos., Treatment of textile dyehouse wastewater by TiO_2 photocatalysis., ***Water research***, **40** : 1276–1286, 2006.

[12] R Rosal, S Gonzalo, J Santiago, A Rodriguez, J Antonio, P Melon & E G Calvo., Kineties and mechanism of catalytic ozonation of aqueous pollutants on metal oxide catalysts., Ozone:Science and Engineering.,33(6):434-440,2011.

[13] Iranian Journal of Environmental Health Science &Engineering., 6(2):61-66,2009.