PULP AND PAPER SOLAR EFFLUENT TREATMENT AND DETOXIFICATION: PHOTO CATALYTIC DEGRADATION OF METHYLENE BLUE BY NATURAL ULTRA-VIOLET LIGHT CATALYSED BY TITANIUM OXIDE

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Abstract

Pulp and paper mill effluent treatment and detoxification methods have been extensively investigated resulting to varying efficiencies and capital and operational costs. The main toxic component in the mills' effluent is modified lignin, which is difficult to degrade by convectional effluent treatment systems applied by most mills. This study aimed at using natural photo catalytic degradation of methylene blue using anodised pigmented and non-pigmented titanium plates to optimise anodising time and voltage. Titanium plates were anodised at varying voltages and times in a mixture of sulphuric and hydrofluoric acids. Irradiation of aqueous solution of methylene blue was done using varies anodised pigmented and non pigment plates in a batch reactor cell. Absorbance of each photo catalysed solution was determined every five minutes after a dark phase of fourteen minutes using a laser light source. Absorbance was then converted to transmittance, which gave photo catalytic reactivity of plates. The study revealed that photo catalytic reactivity of pigmented titanium plates was higher than nonpigmented. Photo catalytic reactivity also increased with increase in anodising time and voltage. Anodised plate at 200volts for 120 seconds and pigmented with photo catalytic reactivity of 62.325 x 10^{-3} was found to be the best to degrade methylene blue. Application of this optimised plate on Kraft Pulp mill effluent showed reduction in COD, BOD, turbidity, colour and total suspended solids. However effluent pH and electrical conductivity increased. COD, BOD, turbidity and colour removal efficiency improved on introduction of wood ash leachate (electrolyte) in photo catalytic activity. The study recommended the use anodised titanium plates using natural ultra violet energy aid by an electrolyte to treat Kraft pulp and paper mill effluent.

Keywords: pulp and paper, methylene blue, Photo-catalytic degradation, titanium oxide

1. Background

Pulp and paper industry started during ancient times and since then it has remained to be a very important industry in the development of many countries (Hossain and Rao, 2014; Raj *et al.*, 2014). The pulp and paper industry is important as a result of its major roles of paper and paper products in many areas of human activities. It has contributed immensely to gross domestic products of both developing and developed economies over a long period time (FAO, 1998, Kamali and Khodaparast, 2015). The Pulp mill sector utilizes a huge amount of lignocellulosic materials and water during its operations and processes. In the recent past the sector has been faced with ever changing and stringent regulations of its effluent discharge standards with high possibilities for the same to continue in the future. Pulp and paper production has long been recognised as a significant point source of contaminants and toxic components to aquatic life (Gupta, 1994; Sumathi and Hung, 2006; Monte, *et al.*, 2009; Hossain, and Ismail, 2015). Several compounds with varying toxicological significance have been identified in pulp and paper liquid effluent. Effluent from the mills contain chlorinated lignosulphonic acids, chlorinated phenols and chlorinated hydrocarbon among others (Mahida, 1981; Thompson, *et al.*, 2001; Chandra *et al.*, 2007; Mehta, *et al.*, 2014; Barapatre and Jha, 2016).

Treating and detoxifying effluent is a significant challenge to pulp and paper mills, and is an integral part of their operation in order to meet ever changing discharge standards for several pollutants and toxic materials (Kamali and Khodaparast, 2015). Several effluent treatment methods have been investigated extensively and they include use of activated carbon, membrane adsorption, cationic coagulation, polymer addition, ultrafiltration, biological and chemical oxidation, electrochemical, electro-coagulation, photo-catalysis among many more (Hilleke, 1991; Bellew, 1978; Orori, *et at*, 2007; Etiegni, *et al*, 2010; Chandra *et al.*, 2012; Cong, et. al., 2012; Chandra *et al.*, 2013; Hossain and Ismail, 2015, Saez *et al.*, 2013; Zongo *et al.*, 2009; Barapatre and Jha, 2016).

2. Material and Methods

2.1. Study Area

Effluent samples for this study were obtained from Mufindi Paper Mills (MPM) situated in Mgololo valley close to Mafinga town in Mufindi District, Iringa province, in the United Republic of Tanzania. The mill is located about a latitude of 08°55'S and longitude of33°32'E on an altitude of1600 meters above sea level. The area has a mean temperature of 21-25°C (Massawe, *et al*, 2016). MPM produces 35000 metric tonnes of pulp and 28000 metric tonnes of paper, with approximately 70 percent of its rated capacity. The main raw materials for the mill are from pine and eucalyptus plantations owned by company (Sutton and Olomi, 2012). MPM has three Kraft pulping digesters each with a capacity of 40m³. MPM has two fourdrineer paper machines running on different revolutions per minute depending on the paper grade being manufactured. Its main products are packaging materials of various grades and specifications, including Kraft Liner, Sack Kraft, Bag Kraft, Deckle and Grammage (Sutton and Olomi, 2012)

MPM mill has instituted measures to reduce pollution to receiving water by chemical recovery system in which pulping chemicals are recovered through combustion of organics. The mill has not installed a closed white water system, which is very important in the reduction of fibers losses and chemicals. There is need for MPM to install micro-screens on paper machines to cut down fiber loss. The brown coloured combined mill effluent from pulp washing and papermaking sections is passed through trash screens to remove large suspended solids. The screens are designed with effluent volume of 1800m³/hr of 50mm and 15mm manual and mechanical bars spacing respectively. The effluent is passed through a single primary clarifier (turbo circulator) employing an air flotation principle. The clarifier is designed with a flow of 1080 m³/hr with a maximum flow of 1800 m³/hr. The diameter of the clarifier is 43m and 4m peripheral water depth with inlet suspended solid load of 5500kg/day with a total suspended solid removal efficiency of 88-98% (Sutton and Olomi, 2012).

After clarification the supernatant effluent flows into specially designed aeration lagoon fitted with four of 45watt electrically operated surface aerators. The detention time in the aeration lagoon is approximately 7 days. After aeration the supernant effluent flows to settling pond where it takes approximately 5 days. Thereafter the effluent drains slowly through a swamp into river Kigogo Ruaha. River Kigogo Ruaha drains into River Luhuji that drains into River Kilombero, which drains into River Rufiji that into Indian Ocean.

2.2 Anodising and pigmenting of titanium plates

Titanium grade two foil of 0.3mm thick (TiGr2-FL-230-01-02) was obtained from William Gregor Limited shop. The foil was cut into pieces measuring 20mm by 80mm (plates). The plates were degreased in acetone for five minutes and thereafter thoroughly rinsed in distilled water. Before anodizing, each plate was further cleaned by immersing it in a mixture of Nitric acid (1 molar), Hydrofluoric (1molar) and distilled water in a ratio of 13:1:7.5 for 15 seconds and quickly rinsed using a lot of distilled water. Anodizing of titanium was carried out in a one litre cell with varying times and voltages. Anodising time varied from 30, 60, 90 and 120 seconds Anodizing voltage also varied from 60, 80, 100, 120, 140, 160, 180 and 200 volts. Anodising electrolyte was made of double distilled water, sulphuric acidic (18M) and Hydrofluoric (1M) in the ratio of 972:27:1 respectively. The distance between the electrodes and anode was kept at 1cm and was held constant for all anodising reactions. The electrolyte was continuously stirred using a magnetic starrier. Anodized plates were

pigmented using 0.1M solution of copper (II) sulphate electrolyte at 12volts for 5 seconds. The anode was made of copper plate fixed at distance of 3cm from titanium cathode plate. Each plate was pigmented separately using a fresh electrolyte in orders to obtain similar pigmenting results. Annealing of titanium plates was accomplished in a furnace at a temperature of $450^{\circ}C \pm 5^{\circ}C$ for three hours.

2.3 Optimum anodizing conditions

Plate 1 show a fabricated reactor used in this study. Each of the plate was used at a time in the reactor with 60ml of 1.5×10^{-5} M of methylene blue. Optimization of anodizing variables was achieved through a fabricated cell reactor utilising the principle of laser light absorbance by methylene blue. Methylene blue was chosen because of its close chemical structure and bonding to that of lignin, which is the main component found in the pulp paper mill effluent. Two anodizing variables (anodizing voltage and time) were investigated that mainly affect catalytic efficiency of phenyl compounds. The reaction was run for 14 minutes of dark and 46 minutes of UV phase. Absorbance was measured at an interval of 2 minutes during dark phase and 5 minutes during UV phase. The dark phase was important to allow the solution to be homogenous and any adsorption to take place. Absorbance was used to determine the level of degradability of methylene during the experiment. Absorbance was obtained from the concept of laser light intensity before and after going through the solution.



Plate 1: Fabricated reactor unit for optimization of anodised titanium plates

Natural solar ultra violet was used with all experiments carried out between 11.30am and 2.30pm when the UV was between 360-400nm. Absorbance was then converted to transmittance using the Beer Lambert relationship. The best linear relationship between time and transmittance was then determined. The gradient of a linear relationship gave reactivity of each plate that was used to optimise the two variables of interest in the study. Optimised conditions were then used to prepare titanium plates that were used to treat effluent from Kraft mill of Mufindi Paper Mills.

2.4 Effluent treatment efficiency

Plate 2 shows a set-up of photo catalytic effluent treatment unit used in the study. A photo catalytic unit was fabricated with an equal width and length of 24cm and 20cm depth using 4mm clear transparent glass. Twenty four (24) optimized titanium plates measuring 30mm by 80mm were prepared and carefully stuck on a 4mm-thick glass substrate using silicon. Three litres of the effluent was used for each photo catalytic effluent treatment. One side of the stuck titanium plates were held 2cm above effluent surface with a gentle slope ending in the effluent to complete the current flow with the effluent. Using an electric pump (magi-200) a thin layer of effluent was continuously circulated over the plates while exposing it to direct natural ultra violet rays for 6

hours. Regularly the set up was tilted towards direct sun rays for higher light intensity. Effluent from the Kraft pulping mill was subjected to a combination of different photo catalytic effluent treatment combinations. Combined treatments included, photo catalytic alone (PHCALON) and photo catalytic with wood ash leachate as an electrolyte (PHCASH). A control effluent treatment was set by allowing the effluent to circulate over a plain transparent glass (PHOALON). Treated effluent samples were then allowed to settle overnight and the supernant was analysed for colour, turbidity, pH, biochemical oxygen demand, chemical oxygen demand, total solids, total suspended solids and electrical conductivity.



Plate 2: Fabricated photo catalytic effluent treatment unit

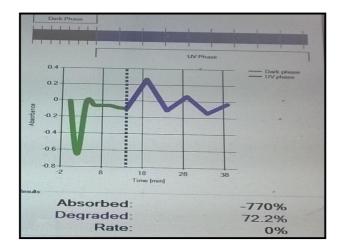
3. Results and Discussion

3.1 Methylene Blue Degradation

Rate of degradation, Absorbance, transmittance of methylene blue gave the reactivity varies titanium anodized pigmented and non pigmented titanium plates. The titanium plate with highest reactivity on methylene blue was then use in treatment of a Kraft pulp and paper mill effluent.

3.2 Absorbance of Methylene Blue

Plate 3, 4, 5, and 6 show selected absorbencies of methylene blue with time. Generally, absorbance decreased for all anodised titanium plates experimented in this study. Absorbance decreased but transmittance increased because some bonds causing colour may have been broken. When more bonds were broken then methylene blue underwent further decolourization. Decrease in methylene blue absorbance is attributed to its degradation by natural UV catalysed by anodised titanium plates, which consequently reduced the ability of the solution to absorb more UV light. The higher the rate of degradation the better the catalytic activity of anodised plates employed.





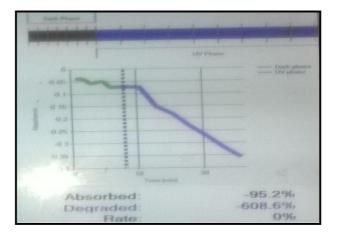


Plate 4: Degradation of methylene Blue with titanium plate anodised at 200 volts for 120 seconds and pigmented

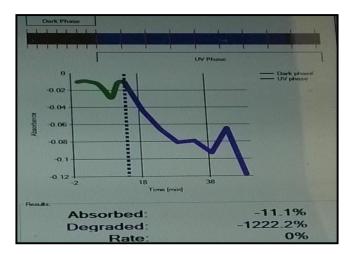


Plate 5: Degradation of methylene Blue with titanium plate anodised at 180 volts for 120 seconds and non-pigmented

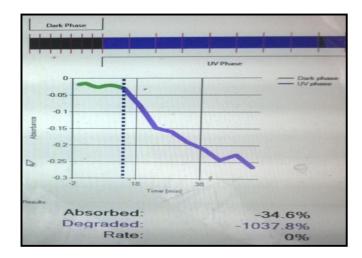


Plate 6: Degradation of methylene Blue with titanium plate anodised at 180 volts for 120 seconds and pigmented

3.3 Transmittance of Methylene Blue

Figure 7 show selected transmittance during methylene blue degradation by natural UV catalyzed by anodized titanium and non pigmented plates. The best relationship between transmittance and degradation time of methylene blue for various plates were linear relationships with values for R-squared ranging from 0.9564 to 0.9802. R-squared values closer to one indicated a very good relationship between transmittance and degradation. The relationship takes the first order reaction equation in which the gradient is the rate of reactivity of anodized titanium plates while transmittance is the intercept and degradation time varying.

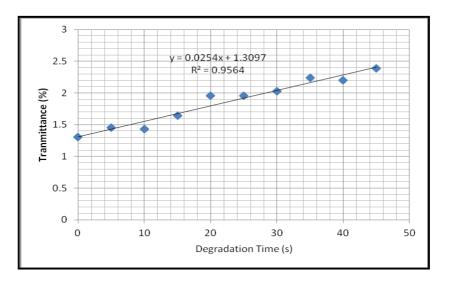


Figure 7: Transmittance of methylene blue using Natural UV catalysed by anodised titanium plate at 160 volts for 120 seconds and non-pigmented

3.4 Degradation Rate of Methylene Blue

Table 1 show means reactivaties of various anodised titanium plates during methylene blue degradation at different using natural Ultra Violet solar radiations. Highest degradation of methylene blue was noted with a plate that was anodised at 200volts for 120 seconds and pigmented using copper solution. The lowest reactivity was noted in non pigmented titanium plates anodised for 30 seconds. There was a significant difference

 $(P \le 0.05)$ among reactivity of plates anodised at different voltages and times. Further there was a significant difference $(P \le 0.05)$ in reactivity between anodised pigmented and non pigmented plates. Furthermore, result indicted that there is significant $(P \le 0.05)$ interaction between anodising time and voltage.

	Reactivity $\times 10^{-3}$								
Volts	30SP	60SP	90SP	120SP	305	60S	90S	120S	
60	2.646	7.291	8.624	9.800	3.170	5.636	6.630	7.800	
80	3.873	9.675	14.528	16.100	3.920	7.870	8.670	10.200	
100	4.799	13.960	23.954	28.890	4.055	9.908	12.600	15.600	
120	6.324	21.765	31.896	39.500	6.332	13.923	17.470	19.200	
140	9.858	24.997	37.320	45.950	8.656	15.389	18.105	21.300	
160	14.285	31.857	42.979	54.840	9.649	16.265	22.135	25.500	
180	16.893	35.786	47.328	58.100	13.796	19.363	22.780	26.800	
200	19.896	38.379	51.936	62.300	12.879	19.703	27.180	29.800	

Table 1: Mean Reactivity of titanium plates anodised at various voltages and time

3.5 Reactivity Trends of Anodized Titanium plates

Further analysis of relationship among reactivity, time and voltage for pigmented and non-pigmented plates is shown on figure 8 for selected plates. The best relationship of reactivity with voltage of titanium anodised and pigmented plates for degradation of methylene blue were logarithmic relationships apart from plated anodised for 30seconds. For all plates with logarithmic trends gave R-squared ranging from 0.9871 to 0.9565. These implied that rate of degradation of methylene blue increases with increase in anodising voltage and time but diminish for pigmented plates.

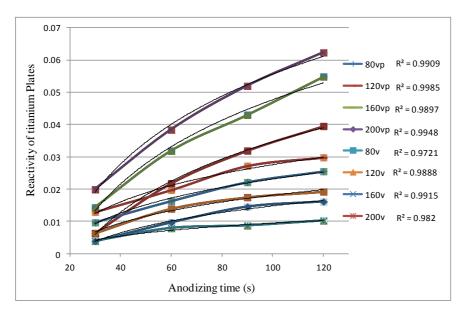


Figure 8: Reactivity trends of selected titanium plates

Only plates anodised for 30 seconds and pigmented showed that the best relationship was linear with R-squared being 0.9818. It therefore imply that better reactivity of plates can be achieved through longer anodizing times. It is also probable that reactivity rate for plates anodised at low voltage for instance that of 60, 80 and 100 volts might follow a logarithmic trend if anodising time was increased beyond the end point time (120 seconds) used

in this study. Reactivity increased with increase in anodising time but the rate slowed as anodising time increased. The best relationship between reactivity and time for non pigmented plates was logarithmic. Obtained R-squared values range between 0.9685 and 0.9685 for all plates tested, which indicates a good relationship. However, a good liner relationship (R-squared of 0.9822) was obtained for anodising time of 30 seconds.

3.5 Effluent Treatment Efficiency

Table 2 shows the treatment efficiency of optimised titanium plate applied in treatment of a pulp and paper mills effluent. Effluent COD reduced by 24.8%, 74.2% and 48.3% for PHOALON, PHCASH and PHCALONE respectively. The obtained COD final values were significantly different ($P \le 0.05$) among all the treatment combinations. Effluent BOD was also reduced by all treatment combinations by 15.3%, 76.7% and 61.6% by PHOALON, PHCASH and PHCALONE respectively. Treated effluent colour increased for PHOALON (16.7%) but reduced by 80.7% and 58.5% for PHCASH and PHCALONE respectively. PHOALON does not involve titanium plates therefore is more of aeration of the effluent without degradation. Therefore, the probable reason for increase in colour for PHOALON could be that lignin compounds were oxidised resulting into more coloured compounds than before treatment. This finding conger with Haslam (1987) assertion that explained why biological degradation of the pulp mill effluent results in increase in effluent colour. Effluent turbidity reduced by over 23.8%, 82.7% and 86.5 by PHOALON, PHCASH and PHCALONE respectively. The final turbidity values for PHOALON, PHCASH and PHCALONE were significantly different (P≤0.05).electrical conductivity reduced of lecheate. PHALON and PHCALONE but increased for PHCASH. The increase in electrical conductivity increased for PHCASH because of dissolved mineral introduced to the effluent by the wood ash Total suspended solids (TSS) reduced by 34.4%, 70.8% and 45.5% for PHOALON, PHCASH and PHCALONE respectively. Total Dissolved Solids reduced for PHOALON (46.5%) and PHCALONE (8.5%) but increased by 19.5% for PHCASH. For PHCASH the increase might have been due to introduction of the wood ash leachate with more chemical constituents. Total Solids (TS) reduced for PHOALON (44.3%) and PHCALONE (15.4%) and increased for (PHCASH)

	Original	PHOALON		PHCASH		PHCALONE	
Properties		Final	Reduction %	Final	Reduction %	Final	Reduction %
COD(mg/l)	824.2	620	24.8	212.4	74.2	426.2	48.3
BOD(mg/l)	352	298	15.3	82	76.7	135	61.6
Colour (Pco)	1200	1400	16.7*	232	80.7	498	58.5
Turbidity(NTU)	63	48	23.8	11	82.5	8.5	86.5
EC (µS/cm)	1085	812	25.2	1420	30.9*	628	42.1
pН	7.06	7.02	0.6	8.2	16.1*	7.12	0.8*
TSS(mg/l)	154	101	34.4	45	70.8	84	45.5
TDS(mg/l)	673	360	46.5	804	19.5*	616	8.5
TS(mg/l)	827	461	44.3	849	2.7*	700	15.4

Table 2: Effluent treatment efficiency by	PHOALON	PHCASH and PHCALONE
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* Percent increase

4. Conclusions and Recommendations

The study revealed that photo catalytic reactivity of pigmented titanium plates was higher than non-pigmented titanium plates. Titanium plates anodised at various voltages and times had different photo catalytic reactivity. Reactivities of titanium plates anodised increased as anodising time and voltage increased. The study revealed that a pigmented plate and anodised at 200volts for 120 seconds with photo catalytic reactivity of 62.325×10^{-3} was the best to degrade methylene blue. The plate was then used to treat and detoxify Kraft pulp and paper mills

effluent. The study revealed that effluent treatment efficiency was higher for photo catalytic aided by wood ash leachate compared with photo catalytic alone using anodised pigmented titanium plates. However, effluent treatment efficiency was low for photo degradation alone for most physical chemical characteristics such as COD, BOD, colour and turbidity. Percent electrical conductivity, pH TDS and TS increased for photo catalytic aided by wood ash leachate. Therefore, it was recommended that application of photo catalytic aid by wood ash leachate in treatment of Kraft pulp and paper mill effluent is viable and can be applied.

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