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ABSTRACT

Wastewater from pulp and paper mills entails diversity of recalcitrant pollutants and toxins, which compels search for cost effective and efficient treatment technologies. This study evaluated the efficiency of treating a real Kraft pulp and paper mill effluent by photocatalytic using Cu-TiO₂/sunlight. The study first established that the most photoactive titanium dioxide piece of foil was one anodized at 200 V for 120 s and copper-doped. Four possible novel effluent treatment techniques were investigated including; photocatalytic combined with photovoltaic (PHCPVC); photocatalytic combined with wood ash leachate (PHCASH); photocatalytic alone (PHCALON); and photo-treatment without Cu-TiO₂ foils (PHOALON). It was revealed that PHCPVC was the most effective in reducing BOD, COD, color, TSS, TDS, and turbidity of real Kraft pulp mill effluent by an average of 82.1%, 68.6%, 78.5%, 68.2%, 54.4%, and 68.8% respectively. PHCPVC reduced several elemental constituents in the effluent to within internationally acceptable limits.

INTRODUCTION

Wastewater from pulp and paper processing industries pose varieties of problems to the receiving environment if not treated to the required discharge guidelines (Chandra et al., 2018; Kamali et al., 2019; Zainith et al., 2019). Processing of wood into pulp and its conversion into paper consumes huge amounts of fresh water, subsequently releasing enormous amounts of wastewater into the environment. The wastewater contains toxic and very complex recalcitrant organic and inorganic pollutants (Singh and Chandra, 2019). The industry has long been recognized as a significant point source of toxic contaminants of aquatic ecosystems (Hossain and Ismail, 2015). Compounds of varying toxicological significance have been identified in the pulp and paper effluents (Mehta, 2014). The wastewater contains toxins such as furans, terpenes, resin acid, chlorinated lignosulphonic acids, chlorinated resin acids, chlorinated phenols and chlorinated hydrocarbon (Barapatre and Jha, 2016).

The treatment of pulp and paper mill wastewater for the removal of pollutants and toxins has been extensively investigated. Methods for the treatment of pulp and paper mill wastewater include the use of activated carbon, membrane adsorption, cationic coagulation, polymer addition, ultrafiltration, biological and chemical oxidation, electrochemical and electrocoagulation (Hossain and Ismail., 2015; Sáez et al., 2013; Zainith et al., 2019). However, most of these effluent treatment methods do not easily and fully meet the required standards for discharge of effluent into the environment. More often, biological effluent treatment methods, such as aerated lagoons and activated sludge systems rarely cause any significant reduction in chlorinated phenyls and related compounds. Instead, these systems aggravate the problem by oxidizing lignin derivatives to more toxic forms. Moreover, most of these treatment systems are non-destructive because they transfer non-biodegradable matter into sludge (Kamali et al., 2019). Consequently, undegraded sludge gives rise to other forms of pollution that require extra treatments (Brink et al., 2018; Catalkaya and Kargi., 2008).

Wastewater treatment system such as electrochemical wastewater treatment, especially when combined with an electrolyte, has shown higher pollutant removal efficiency (Lazare Etiégni et al., 2010). Electrocoagulation could be a viable effluent treatment for pulp and paper mill. But one major concern in the use of electrochemical is the cost of energy, which is often high in conjunction with huge amount of wastewater released by the mills. The concern of lower energy cost is thus driving research towards cheaper electrochemical methods. Therefore, there is a need to devise an effluent treatment method that would comply with effluent discharge requirements, whereas employing cheap renewable energy sources (Kamali et al., 2019). Additionally, the treatment technique should either mineralize completely pollutants and toxicants or reduce them into less harmful ones, without generating secondary wastes (Crini and Lichtfouse., 2019; Kabra et al., 2004).

Photocatalytic has an excellent potential to treat the pulp and paper mill effluent owing to its versatile mechanism to degrade several organic compounds (Zawadzki et al., 2018). Photocatalytic has the ability to mineralize completely a wide range of organic compounds present in most wastes (Kamali et al., 2019). Subsequently, photovoltaic treatment could achieve coagulation and mineral removal. Photocatalytic treatment can achieve a reduction in toxicity and pollution abatement while employing a cheap, abundant and renewable solar energy source (Bajpai, 2017; Hossain and Ismail, 2015). Additionally, the mineralization of effluent components by photocatalytic technology would reduce the risks of bioaccumulation of the toxicants in the effluent because they move up the food chain (Kabir et al., 2015).

Photocatalytic processes are emerging waste treatment methods with a major advantage of mineralizing components of the waste (Amor et al., 2019). Photocatalytic in the presence of titanium dioxide is relatively cheap, non-toxic, photolytically and chemically stable; the catalyst is reusable and easy to modify and photogenerated holes are highly oxidizing (Haque et al., 2005). Photocatalytic mechanisms of several metals have extensively been investigated and documented. For instance, when a light photon strikes a titanium surface, an electron is released from the valence band to the conduction band, leaving a positive charge (hole) behind on titanium dioxide. The hole can either directly oxidize any adsorbed pollutant or leads to the production of hydroxyl radical. The hydroxyl radical would quickly, without any selectivity oxidize any organic pollutant. The electron produced earlier is instantaneously adsorbed by an oxygen molecule to produce a superoxide ion, which prevents any electron-hole recombination. The superoxide ion produced can also participate in degradation of contaminants (Li et al., 2019).

In light of the aforementioned challenges facing the pulp and paper industry to comply with effluent discharge standard guidelines into the environment, it is of great interest to investigate the efficiency of photocatalytic treatments of Kraft pulp and paper mill effluent. In this paper, we report on a study conducted to determine the best anodizing time and voltage for titanium foils with the highest photoactivity and their effect on copper-doping. We also report on the efficiency of treating the real Kraft pulp and paper mill effluent by various combinations of photocatalytic using the most photoactive titanium dioxide foils in the presence of sunlight.

MATERIALS AND METHODS

Effluent samples

Pulp mill effluent (PME) and biologically treated combined pulp and paper mill effluent (BPPME) samples were procured from Mufindi Paper Mills (MPM) Ltd. The mill manufactures 35,000 tonnes of Kraft pulp and 28,000 tonnes of paper annually. The wood raw materials for the mill constitute Pinus patula, Pinus elliottii and Eucalyptus saliga. The mill has three Kraft cooking digesters, each with a capacity of 40 m³ and two Fourdrinier paper machines. The mill has a Kraft chemical recovery system, which has significantly reduced the pollution load from the Kraft pulping section. The effluent from the mill is passed through trash screens and clarification before it enters the aeration and stabilization ponds. From the stabilization pond, the wastewater flows through a swamp into River Kigogo-Ruaha, a tributary of River Luhuji that drains into River Kilombero enroute to the Indian Ocean.

Anodizing and doping of titanium foils

Titanium grade two foil of 0.3 mm thickness (TiGr2-FL-230-01-02) was purchased from William Gregor Limited Shop. The foil was cut into small pieces measuring 20×80 mm. They were degreased by immersing them in acetone for five minutes and then thoroughly rinsed with distilled water. Any oxide on the surface of the foils was etched off by dipping them in a mixture of nitric acid (1 M), hydrofluoric acid (1 M) and distilled water in a ratio of 13:1:7.5 for 15 s and

quickly rinsing them with double-distilled water. Anodizing was performed in a one-liter cell using an electrolyte made of double-distilled water, sulfuric acid (18 M) and hydrofluoric acid (1 M) at a ratio 972:27:1. Anodizing time was varied from 30, 60, 90, 120, and 150 s, and the voltage was varied from 60, 80, 100, 120, 140, 160, 180 and 200 V. During anodizing, the distance between an aluminum cathode (50 cm²) and titanium anode was kept constant at 2 cm. The electrolyte was continuously stirred at 120 rpm using a magnetic stirrer. Four pieces of foils were anodized for each set of time and voltage. After anodizing, half of the anodized foils were doped using copper (II) sulfate (0.1 M) electrolyte at 12 V for five seconds. During doping, the copper anode (24 cm²) was fixed at a distance of 2 cm from a titanium cathode foil. In order to attain similar output, each titanium foil was separately doped using a fresh electrolyte. Both doped and non-doped foils were then annealed in a furnace at a temperature of $450^{\circ}C \pm 5^{\circ}C$ for 3 h.

Photoactive titanium dioxide

The most photoactive foil was determined by exposing Methylene Blue (MB) to sunlight in the presence of titanium dioxide foils, which were anodized at varying time and voltage. MB was employed to determine the most photoactive titanium dioxide foils because of its phenyl base with many bonds, which resemble that of lignin derivatives. Lignin derivatives are the most abundant components of the pulp and paper mill wastewaters (Buzzini and Pires, 2007). A sketch of a photocatalytic cell for determining the most photoactive titanium dioxide foil reactions is shown in Fig. 1. One titanium dioxide piece of foil was used in the cell at a time with 60 ml of MB (1.5×10^{-5} M). All reactions were allowed to run for 14 and 46 min in the dark and direct sunlight phase, respectively. All experiments were performed between 11.00 am and 3.00 pm when the ultra violet (UV) intensity of sunlight was high (360 to 390 nm). Absorbance was measured at an interval of two and five minutes during the dark and sunlight phase, respectively.

Absorbance data was obtained from the concept of laser light intensity before and after going through the solution, according to Mathews et al., 2009. Transmittance was determined from absorbance data using the Beer-Lambert relationship as applied in Chaouch, et al., 2018. Photoactivity of each titanium dioxide piece of foil was equivalent to the gradient of the linear regression of transmittance and sunlight exposure time. The efficiency of each titanium dioxide piece of foil was based on the level of photoactivity. Anodizing time and voltage that resulted in the most photoactive piece of foil were considered to be the best anodizing conditions. The best anodizing conditions were then used to prepare titanium dioxide pieces of foil that were applied to treat the real Kraft pulp and paper mill effluent.

Efficiency of effluent treatment

A photocatalytic effluent treatment reactor was made using a 4 mm thick clear transparent glass with equal width and length of 24 cm and a depth of 20 cm as shown in Fig. 2. Twenty-four most photoactive and copper-doped titanium dioxide foils $(30 \times 80 \text{ mm})$ were fixed on a 4-mm-thick glass. One edge of the stuck titanium foils was held 2 cm above the effluent surface with a gentle slope, gradually ending in the effluent on the opposite end. For photovoltaic treatment, two 5-mm-thick aluminum electrodes connected to a 12 V photovoltaic solar panel were used. The electrodes (22 \times 19 cm) were firmly secured in the effluent at a distance of 2 cm from each other. Three liters of the effluent were used for each photocatalytic treatments. An electric pump (magi-200), continuously circulated a thin layer of effluent over the pieces of foil, while exposing it to sunlight for 8 h.

Effluent from MPM pulping mill (PME) and discharge of a biological treatment system into the environment (BPPME) were subjected to photocatalytic effluent treatments including photocatalytic and photovoltaic treatment (PHCPVC), photocatalytic alone



Fig 1. Sketch of photocatalytic cell for determining the most photoactive titanium dioxide foil.



Fig 2. A sketch of the fabricated sunlight photocatalytic effluent treatment reactor.

(PHCALON) and photocatalytic with wood ash leachate as an electrolyte (PHCASH). While a control treatment was set by allowing effluent to circulate over a plain transparent glass in the presence of sunlight (PHOALON). Effluent samples were collected thrice and replicated three times during each photocatalytic treatment. Physicochemical characteristics of the effluent before and after (supernatant) treatments were performed according to American Public Health Agency standard methods for the analysis of wastewater (APHA, 2005). Effluent elemental analyses were performed by an inductively coupled plasma-mass spectrometry (ICP-MS) 9000 series.

DATA ANALYSIS

The Statistical Package for Social Sciences (SPSS Version 23.0) was used for all analyses. Linear regression analysis was employed to fit the best model for determining photoactivity of each titanium dioxide foil. Two-way factorial ANOVA was used to determine any significant difference in photoactivities with varying anodizing time and voltage and also between copper-doped and nondoped titanium dioxide foils. The photocatalytic efficiency of effluent treatment experiments (effluent physicochemical parameters) were designed in 2 × 4 factorial with two treatment levels (PME and BPPME) and four effluent treatment methods (PHCPVC, PHCALON, PHCASH, and PHOALON) as factors. Physicochemical data of the effluent were subjected to univariate analyses to determine any significant differences in the effluent treatments. Whenever significant differences were discerned, separation of means was performed using Tukey post-hoc tests.

RESULTS AND DISCUSSION

Photoactivity of titanium dioxide foil

Absorbance of MB against sunlight exposure time for selected titanium dioxide foils is shown in Fig. 3. Titanium dioxide foils anodized at a higher voltage and for long periods displayed relatively higher MB absorbance. Absorbance of MB showed an inverse relationship with respect to sunlight exposure time for different titanium dioxide foils. Absorbance of MB decreased owing to the breakdown of bonds, leading to its respective mineral states such as carbon dioxide, water, and hydrochloric acid as reported (Akpan and Hameed 2009). The breakdown may have occurred through the excitation of oxygen molecules from MB by visible light via the electrons from the titanium dioxide conduction band. Breakdown of MB occurred through the supper oxygen radical created by the interaction of titanium dioxide and sunlight (Gray et al., 2018). Therefore, going by this



Fig 3. Percent absorbance against sunlight exposure time for selected titanium dioxide foils (V-voltage and non-doped; VD-voltage and doped).

assertion, the decrease in MB absorbance was owing to its photocatalytic breakdown by titanium dioxide holes, superoxide radicals or electrons released from titanium dioxide (Gopalakrishnan et al., 2018).

Most titanium dioxide foils showed a rapid initial decrease, followed by a gradual decline in absorbance with increasing sunlight exposure time. It is probable that the initial rapid decrease in absorbance was attributable to a high initial concentration of oxygen molecules released from MB. This, in turn, resulted in a high concentration of very reactive superoxide radicals to react with MB. Despite, the increase in sunlight exposure time, the concentration of supper oxygen radical diminished due to the decrease in oxygen molecules in solution, which subsequently led to a decrease in the rate of absorbance. These findings concur with a previous study on simultaneous removal of MB and hexavalent chromium from water using TiO₂/Fe(III)/H₂O₂/sunlight (Djellabi et al., 2017). However, that study differed from the current study because titanium dioxide particles were employed, whereas in the current study titanium dioxide foils were used. Similar findings in a study involving enhanced photocatalytic activity for hydrogen generation and degradation of MB, in which the reaction was rapid at the initial stage (Kokane, et al., 2014). Similar trends in absorbance with increasing artificial UV irradiation time were observed by (Mathews et al., 2009) while studying the influence of annealing temperature on the structural, optical and photocatalytic properties of titanium dioxide nanotubes.

The MB absorbance decreased at a higher rate for

copper doped foils compared with non-doped foils. This concurs with the classical theory of doping of metals, where doping has been found to increase the UV absorption band of metals. For that reason, the rate of MB absorption increased due to increased absorption due to copper doping as opposed to non-doped titanium dioxide foils. Increased absorption rates of MB in a study that investigated the effect of doping titanium dioxide with various metals (Kokane et al., 2014).

Transmittance of MB against sunlight exposure time in the presence of non-doped titanium dioxide foils at varying anodizing voltages for 120 s is shown in Fig. 4. There were a significant positive linear relationships between transmittance and exposure time for various non-doped foils (R^2 value = 0.9564 to 0.9802, P<0.05). These findings were consistent with a previous study on sol-gel synthesis of photoactive zirconia-titania from metal salts, which was investigating the photocatalytic properties of MB (Shao et al., 2014). Similarly, (Zulmajdi et al., 2017) also observed a first-order relationship between transmittance and exposure time during photocatalytic degradation of MB. The transmittance of MB against sunlight exposure time catalyzed by copper doped titanium dioxide anodized at selected voltages for 120 s is shown in Fig. 5. There was also a significant positive linear regression between transmittance and exposure time of MB for various copper doped foils (R^2 value = 0.8565 to 0.9625, P<0.05). These findings were consistent with a previous study on basic blue dye decolorization using doped titanium nano-particles (Giwa et al., 2012).

Photocatalytic activities of copper-doped and non-



Fig 4. Percent transmittance against sunlight exposure time in the presence of non-doped titanium dioxide foils, anodized at selected voltages for 120 s (V-voltage and non-doped foils).



Fig 5. Percent transmittance against sunlight exposure time in the presence of doped titanium dioxide foils, anodized at selected voltages for 120 s (VD-voltage and doped foils).

doped titanium dioxide foils anodized at varying times and voltages are shown in Table 1. Foils anodized at higher voltages and longer times displayed relatively higher photoactivity compared with those anodized at lower voltages and shorter times. The highest photodegradation of MB was catalyzed by a copper-doped titanium dioxide foil that was anodized at 200 V for 120 s. A titanium dioxide foil anodized at 200 V for 150 s attained lower photoactivity compared to one anodized at 200 V for 120 s. The lowest photoactivity was attained by a non-doped titanium dioxide foil anodized at 60 V for 30 s. There was also a significant difference (P<0.05) between photo-activities of foils anodized at various voltages and times. Anodizing of titanium at higher voltages and for longer periods often lead to rougher surfaces and deeper pores respectively (Ainuddin and Sulaiman., 2017). On the other hand, (Rasalingam et al., 2015) reported that higher titanium dioxide porosity resulted in higher photoactivity. For these reasons, a combination of longer anodizing time and a higher voltage results to rougher and deeper pores, thus higher titanium dioxide photoactivity. This could be the reason for higher photoactivity of foils anodized at higher voltages and longer times. Even though, a combination of very long anodizing period and a high concentration of an electrolyte of a strong acid, would etch off the dioxide layer thus resulting in low photoactivity (Chrcanovic and Martins., 2014).

Photoactivity variance analysis revealed a significant difference (P< 0.03) between copper-doped and non-doped titanium dioxide foils. The photoactivity of copper-doped titanium dioxide foils was relatively higher compared with that of non-doped foils. Doping extends the photoresponse of titanium dioxide to the visible region of sunlight, subsequently increasing its

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photo-electrochemical properties and consequently increasing its activity as a catalyst for hydrogen generation. Similar findings were reported in a study on the photocatalytic degradation of MB by poly-O-phenylene diamine-modified titanium dioxide nanocomposites. In that study, the titanium dioxide nanocomposites exhibited a higher photoactivity compared with titanium dioxide (Yang et al., 2017). The increased photoactivity of copper-doped compared with non-doped sol-gel manufactured thin films of titanium dioxide during artificial UV degradation of MB has also been shown elsewhere (Carvalho, et al., 2010). Faster decolorization of Congo-red dye by 3% copper-doped compared with non-doped titanium dioxide particles were also observed by (Zuas and Budiman., 2013). Increased photoactivity of titanium nanoclusters doped by copper. Therefore, the most photoactive titanium foil was that anodized at 200 V for 120 s and copper-

doped which was reposted in (Ahmed, 2015) also reported. Therefore, several pieces of copper doped titanium dioxide foils were prepared using these conditions and subsequently used to treat the real Kraft pulp and paper mill effluent.

Photocatalytic treatment efficiencies of the real kraft pulp and paper mill effluent

Biochemical oxygen demand, chemical oxygen demand, and color: Photocatalytic reduction efficiencies for effluent BOD, COD, and color are shown in Table 2. The Initial MPM BOD was high for PME but decreased after mechanical and biological treatments (BPPME). Mechanical and biological treatment system employed by MPM resulted in a BOD removal efficiency of 43.1%. The BOD removal efficiency for MPM effluent treatment system was low compared with the industry average of over 80% (Aleya et al., 2019). These findings coincide with

Table 1. Photoactivit	y of titanium	n dioxide foils	anodized at	t various v	voltages and	l times.
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		Anodizing time (s)							
	Anodizing voltage (volts)	30	60	90	120	150			
	60	3.17 ± 0.1	5.64 ± 0.2	6.63 ± 0.3	7.80 ± 0.8	8.30 ± 0.8			
ils	80	3.92 ± 0.3	7.87 ± 0.7	8.67 ± 0.4	10.20 ± 0.5	11.60 ± 0.5			
fo	100	4.05 ± 0.2	9.91 ± 09	12.60 ± 0.9	15.60 ± 0.9	16.20 ± 0.8			
bed	120	6.33 ± 1.0	13.92 ± 0.7	17.47 ± 1.1	19.20 ± 1.1	19.60 ± 0.9			
lop	140	8.66 ± 0.5	15.39 ± 0.8	18.11 ± 0.7	21.30 ± 0.7	22.90 ± 1.0			
-uc	160	9.65 ± 0.7	16.26 ± 0.9	22.14 ± 0.8	25.50 ± 1.5	26.50 ± 1.7			
ž	180	13.80 ± 0.4	19.36 ± 1.2	22.78 ± 0.8	26.80 ± 1.2	28.30 ± 1.1			
	200	14.88 ± 1.2	19.70 ± 1.4	27.18 ± 0.8	29.80 ± 1.1	29.60 ± 1.7			
	60	2.65 ± 0.1	7.29 ± 0.4	8.62 ± 1.0	9.80 ± 1.0	11.60 ± 0.9			
oils	80	3.87 ± 0.5	9.67 ± 0.5	14.53 ± 0.4	16.10 ± 0.6	16.40 ± 0.7			
d fe	100	4.80 ± 0.7	13.96 ± 0.4	23.95 ± 0.9	28.89 ± 0.7	29.80 ± 1.1			
be	120	6.32 ± 0.6	21.76 ± 0.5	31.90 ± 1.5	39.50 ± 2.3	40.30 ± 2.2			
op-	140	9.86 ± 0.8	25.00 ± 1.0	37.32 ± 1.3	45.95 ± 1.8	47.90 ± 2.5			
per	160	14.28 ± 0.5	31.86 ± 1.7	42.98 ± 1.5	54.84 ± 2.1	56.90 ± 2.4			
ldo	180	16.89 ± 0.5	35.79 ± 1.1	47.33 ± 1.8	58.10 ± 2.2	58.80 ± 2.1			
U	200	19.90 ± 07	38.38 ± 0.7	51.94 ± 1.7	62.30 ± 1.8	61.50 ± 1.7			
Photoactivity (× 10 ⁻³); Mean ± Standard Deviation									

Table 2. Photocatalytic reduction efficiency for COD, BOD and color.

Effluent	Parameters	BOD (mg/L)		COD (mg/L)		Color (PCU)	
treatments	Effluent types	PME	BPPME	PME	BPPME	PME	BPPME
	Initial	352.2 ± 6.3	200.5 ± 7.7	855.0 ± 18.0	558.2 ± 16.4	1200.1 ± 48.8	1613.8 ± 56.8
	Final	298.3 ± 6.5	174.8 ± 6.4	642.79 ± 18.2	544.6 ± 11.5	1400.1 ± 39.7	2012.2 ± 61.2
PHOALON	Reduction (%)	15.3	12.8	24.82	6.1	16.67	24.90
PHCALON	Final	135.4 ± 5.4	112.2 ± 5.8	442.7 ± 19.2	401.6 ± 11.8	497.6 ± 24.7	1251.0 ± 45.8
	Reduction (%)	61.6	44.0	48.2	28.1	58.5	22.4
PHCASH	Final	82.5 ± 5.4	96.7 ± 5.0	220.8 ± 14.7	294.0 ± 14.3	231.5 ± 12.5	732.2 ± 31.2
	Reduction (%)	76.6	51.8	74.18	47.3	80.7	54.6
PHCPVC	Final	51.1 ± 3.7	69.0 ± 3.7	185.1 ± 12.5	230.4 ± 13.5	211.3 ± 15.5	408.89 ± 27.1
	Reduction (%)	85.5	65.6	78.4	58.7	82.39	74.62
Red – Reduction; * increase;							

that reported for aeration and stabilization ponds for an integrated Kraft pulp and paper mill in Kenya with a BOD removal efficiency of 50.8% (Situma et al., 2002). A number of factors affect pulp and paper wastewater treatment performance by lagoons, such as influent, design and environmental characteristics (Aleya et al., 2019).

The BOD variance analysis exhibited significantly different (P<0.05) BOD reductions between PME and BPPME by the four effluent treatment methods. The PHCPVC effluent treatment attained the highest BOD removal efficiency, followed by PHCASH treatment, then PHCALON treatment and finally PHOALON treatment for both PME and BPPME. The findings were different from a similar study by (Kumar et al., 2011) who used a Kraft pulp mill bleach plant effluent using artificial UV with titanium dioxide particles. In Kumar and collaborators', they found a low BOD removal efficiency of 34.1% and 42.9% with clarified and biologically treated effluent, respectively. PHCPVC treatment attained the highest BOD reduction for both PME and BPPME owing to photocatalytic degradation and photovoltaic coagulation of easily biodegradable components of the effluent. Additionally, the photovoltaic aided in the coagulation of biological constituents of the effluent.

Additionally, high BOD removal efficiency by PHCPVC was owing to enhanced production of very reactive hydroxyl radicals from photovoltaic system as was observed in some studies elsewhere (Espinoza, Romero, Villegas, Cornejo-Ponce, and Salazar, 2016; Pérez, Garcia-Segura, El-Ghenymy, Nava, and Brillas, 2015). PHCALON treatment resulted in a low BOD removal efficiency because it involved only photocatalytic mineralization of organic materials without coagulation. The BOD removal efficiency obtained by PHCALON treatment for BPPME, compared closely with a previous study by (Amat et al., 2005), using titanium dioxide nanotubes with an artificial UV source. This study reported photodegradation of easily biodegradable materials of 47%. However, the study conditions were different from the current study because it involved the treatment of simulated board paper mill effluent using artificial UV source catalyzed by titanium dioxide nanotubes (Amat et al., 2005). In another study of pulp and paper mill effluent treatment using synthesized nano-sized titanium dioxide with solar light, the effluent biodegradability index was noted to increase significantly. In the same study, BOD reduction was 54.3%, which was close to that attained by PHCASH and PHCALON treatment for BPPME in the current study (Ghaly et al., 2011).

COD of PME was very high compared with discharge point into the environment (BPPME) resulting in a COD removal efficiency of 34.7% by the MPM's effluent treatment system. The PME COD was high owing to the fact that the paper mill has no internal pollution measures such as a whitewater closure system. COD reductions variance analysis was significantly different (P<0.05) for all photocatalytic treatments for both PME and BPPME. PHCPVC treatment was the most efficient in reducing COD for both PME and BPPME, followed by PHCASH, then PHCALON and finally PHOALON. PHCPVC treatment was the most efficient for COD the reduction, probably because of the adsorption of the effluent chemical constituents in the titanium dioxide holes created by sunlight. Additionally, the chemical constituents of the effluent were ionized by electrons released from the titanium dioxide and aluminum plates by photovoltaic treatment leading to effective mineralization. The COD removal efficiency by PHCASH treatment was higher than PHCALON treatment for both PME and BPPME. This was so because, in the PHCASH treatment, the photocatalytic mechanism was supported by photovoltaic via the ions that were introduced from wood ash leachate, whereas during the PHCALON treatment, no supporting ions were introduced.

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In a similar study by Kumar et al. (2011), COD reduction of clarified and biologically treated Kraft pulp bleach plant effluent was 46.8% and 57.8%, respectively. While PHCALON treatment being closest in principle to that of (Kumar et al., 2011), resulting in almost the same COD removal efficiency for PME. Conversely, PHCALON treatment resulted in a very low COD removal efficiency (17.3%) after biological treatment (BPPME). The variation in COD reduction could be owing to different UV source and period of application and effluent compositions in the two studies. In the study by (Kumar et al., 2011), artificial UV source was applied for four hours with titanium dioxide particles to treat clarified and biologically treated Kraft pulp bleach plant effluent. In a previous study by (Herrmann, 1999) involving a highly loaded industrial wastewater with an initial COD of 800,000 mg/L, which was diluted 1000 times then subjected to photodecomposition catalyzed by titanium dioxide particles, a very high COD removal efficiency was obtained. The results indicated that COD reduced by 95% after adsorption in a dark phase for one hour followed artificial UV irradiation for four hours. This COD removal efficiency (95%) was very high compared with 78.4% achieved by PHCPVC treatment, which was the most efficient in the current study. The probable reason being

that artificial UV with constant output of photons was employed in Herrmann's study whereas in the current study sunlight was employed with a varying output of photons. The varying output of photons results in a low concentration of reactive hydroxide radicals, consequently low COD removal efficiency. COD removal by PHCALON treatment was lower than the PHCPVC and PHCASH treatments due to the extra ions introduced from aluminum foils through photovoltaic treatment and wood ash leachate, respectively. These findings were consistent with the cognate study on photocatalytic removal of diazinon insecticide using zinc oxide nanocrystals with the addition of copper and zinc ions. The result revealed that the removal efficiency of diazinon insecticide increased with the addition of copper and zinc ions (Seyed-Dorraji, et al., 2009).

The initial color of effluent from MPM's Kraft pulp mill (PME) was darkish brown (1200 PCU). The effluent color increased through the biological treatment system to discharge point (BPPME) into the environment (1600PCU). The color increase by the biological effluent treatment could either be attributed oxidization of lignin fragments or decomposition of the biological components of the effluent (Haslam, 1988). PHCPVC and PHCASH treatments were the most efficient for the removal of effluent color, followed by PHCALON for both PME and BPPME. Color reduction variance analysis revealed that all photocatalytic treatments exhibited significantly different (P<0.05) color reductions for both PME and BPPME. Conjugated lignin derivatives and the presence of some extractives are the main color causing components in pulp and paper mill effluent. The reduction in the effluent color could be owing to photodegradation of these high molecular weight components (such as lignin derivatives) either to low molecular compounds through mineralization by a superoxide, hydrogen peroxide or an electron released from the titanium dioxide valance band. Additionally, PHCPVC treatment resulted in higher color removal efficiency than other treatments because of electrocoagulation by photovoltaic.

Similar findings on the photocatalytic treatment of a bleach plant effluent catalyzed by titanium dioxide particles were reported by (Kumar et al., 2011). In their study, the effluent color reduced by 75.3% and 79.4% for a primary-clarified and bio-treated bleach plant effluent, respectively. The color removal reported by (Kumar et al., 2011), was lower than that obtained by PHCPVC (82.4%) and PHCASH (80.7%) treatments in the current study. However, the

variation in color reductions efficiency might also be owing to differences in mill conditions, effluent type, effluent volume and the form of the titanium dioxide employed. Moreover (Kumar et al., 2011), used titanium dioxide particles, with a higher surface area per unit volume of effluent than the titanium dioxide foils used in the current study. However, the main detriment of using titanium dioxide particles in the treatment of wastewater is the difficulties associated with handling and reclaiming the particles after use. The titanium dioxide particles require separation from the supernatant effluent preferably application membranes after treatment (Thiruvenkatachari et al., 2008).

In contrast to the other photocatalytic treatment methods, PHOALON treatment ended up with higher effluent color after treatment for both PME and BPPME. PHOALON treatment was typically effluent aeration because the effluent was circulated over a transparent glass in the presence of solar without titanium dioxide foils (no catalysis). For that reason, PHOALON treatment consisted of effluent oxidation without photocatalysis. These findings concur with a previous study reported that treatment of pulp and paper mill effluent by aerobic methods, more often than not lead to polymerization of low-molecular to higher molecular weight lignins fragments, thus color increase (Ferrer et al., 1991).

Total suspended solids, total dissolved solids, and turbidity

The photocatalytic effluent treatment efficiencies for TSS, TDS, and turbidity are shown in Table 3. PHCPVC treatment was the most efficient for the reduction of TSS followed by the PHCASH treatment, then PHCALON treatment and finally the PHOALON treatment for both PME and BPPME. Variance analysis of TSS reduction was significantly different (P<0.05) by all effluent treatments for both PME and BPPME. Electrocoagulation by photovoltaic played a major role in the removal of suspended material from both effluents. This occurred via the release of electrons from the titanium dioxide (via photocatalytic) and aluminum electrodes (via photovoltaic). These led to the neutralization of the repulsive forces between suspended materials leading to agglomeration and final clarification of the effluent. PHCALON treatment with only photocatalytic mechanism was less effective than PHCASH treatment in the removal of suspended solids. Efficiency of removal of suspended solids by photocatalytic improved with the introduction of wood ash leachate, which contained several ions. Therefore, PHCASH treatment resulted in

Effluent	Parameters	TSS (mg/L)		TDS (mg/L)		Turbidity (NTU)	
treatments	Effluent types	PME	BPPME	PME	BPPME	PME	BPPME
	Initial	154.11 ± 3.5	108.74 ± 3.6	673.44 ± 15.8	219.88 ± 9.7	827.55 ± 24.2	328.62 ± 16.7
PHOALON	Final	101.18 ± 3.5	92.14 ± 2.6	360.33 ± 12.5	172.63 ± 6.8	461.51 ± 18.2	265.26 ± 15.8
PHOALON	Reduction (%)	34.35	15.27	46.49	21.49	44.23	19.12
PHCALON	Final	84.17 ± 2.7	87.3 ± 2.0	310.56 ± 12.6	156.25 ± 7.1	394.72 ± 15.3	243.63 ± 12.3
	Reduction (%)	45.39	19.72	53.89	28.94	52.3	25.71
DUCACH	Final	44.91 ± 1.9	54.19 ± 2.8	804.33 ± 18.4	331.13 ± 11.2	849.24 ± 24.3	383.74 ± 15.9
РПСАБП	Reduction (%)	70.86	50.17	19.44*	50.60*	2.62*	17.01*
PHCPVC	Final	34.01 ± 2.7	45.26 ± 2.6	253.00 ± 10.1	118.13 ± 8.2	287.01 ± 11.8	163.26 ± 7.7
	Reduction (%)	77.93	58.38	62.43	46.28	65.32	50.22
Red – Reduction; * increase;							

Table 3. Photocataly	vtic treatment efficiencie	s for TDS, TSS	and turbidity.
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higher removal efficiency of suspended solids than PHCALON treatment, mainly because of enhanced coagulation by ions introduced from wood ash leachate. (Zahrim et al., 2007) reported similar findings during the treatment of pulp and paper mill effluent by the photo-Fenton process using artificial UV light. The study reported a high TSS reduction (87.0%) compared with that attained by PHCPVC (77.9%) and PHCASH (70.7%) treatments. Higher reduction in suspended solids removal in the photo-Fenton study could be attributed to the high concentration of iron ions and use of artificial UV with a constant output of photons, whereas in the current study where sunlight with varying output of photons.

The TDS removal efficiency for MPM mechanical and biological treatment system was 67.4%. The TDS at the discharge into the environment was within the required international discharge limits of 1200 mg/L. TDS variance analysis depicted a significant difference (P<0.05) in changes by all the effluent treatments for both PME and BPPME. Further analysis also revealed that there was a significant (P<0.05) interaction between TDS changes with the effluent type (PME and BPPME). This implied that the application of any photocatalytic and photovoltaic effluent treatment for either PME or BPPME would result in a significantly different effect on the TDS removed. PHCPVC treatment was the most effective for the reduction of TDS, followed by PHCALON treatment and finally PHOALON treatment for both PME and BPPME. PHCPVC was the most efficient owing to the removal of effluent ions by depositing them on the aluminum cathode. Nonetheless, PHCASH treatment increased TDS for both PME and BPPME because of the wood ash leachate used as an aiding electrolyte, which consists of high content of dissolved solids. Studies have shown that wood ash leachate contains a variety of ions and when used as an electrolyte leads to a higher amount of dissolved solids. Similar findings were reported in an electrocoagulation treatment of paperboard factory and pulp and paper mill effluents using wood ash leachate and rock phosphate used as assisting electrolytes (Orori et al., 2010).

Effluent turbidity was high at the discharge point (BPPME) compared with pulp mill effluent (PME), which was a result of degraded materials during biological treatments. The MPM's biological and mechanical effluent treatment systems resulted in turbidity removal efficiency of 10.4%. PHCPVC was the most efficient in reducing effluent turbidity followed by PHCASH, PHCALON and finally PHOALON for both PME and BPPME. The turbidity variance analysis showed a significant difference (P<0.05) in turbidity reduction by all photocatalytic treatments for both PME and BPPME. There was also a significant interaction (P<0.05) in turbidity reductions between photocatalytic effluent treatments and effluent type.

PHCPVC was the most efficient for turbidity reduction because of electrocoagulation through photocatalytic mechanism. Electrons released from titanium dioxide and aluminum electrodes assisted in the reduction of zeta potential between effluent particles, leading to coagulation and finally settlement (Shim et al., 2014). This mechanism may have occurred in the PHCASH treatment but was highly enhanced by the introduction of more ions from wood ash leachate used as an aiding electrolyte. Additional ions from electrolytes are known to increase the surface area for the attraction of opposite charges by suspended materials. During electrochemical effluent treatment, the addition of an electrolyte aids to neutralize repelling forces, causing particles to coalesce and settle. The inclusion of more ions considerably reduces the "zeta potential" of particles, leading to higher turbidity reduction (Chang and Liu, 2007). Previous studies on pulp and paper mill effluent treatment by electrocoagulation

have reported high turbidity removal with the addition of electrolytes. For instance, in a study on an integrated pulp and paper mill effluent treatment by electrocoagulation supported by wood ash leachate as an electrolyte (with more ions from wood ash leachate as an aiding electrolyte), a turbidity removal efficiency of 94.7% was obtained compared with 79.3% electrocoagulation treatment supported calcium ions (with fewer ions from calcium sulfate as aiding electrolyte) (Orori et al., 2005).

Electrical conductivity, pH, phosphates and nitrates

The photocatalytic effluent treatment reduction efficiencies for EC, pH, phosphates, and nitrates are shown in Fig. 6. The EC changes variance analysis was significantly different (P<0.05) among all the effluent treatments for both PME and BPPME. There was a significant (P<0.05) interaction in the EC changes between photocatalytic effluent treatments and effluent types. The PHCPVC treatment was the most efficient in EC reduction followed by the PHCALON treatment. The PHOALON treatment reduced EC by an average of 20.6% for both PME and BPPME. Notwithstanding, PHCASH increased EC of PME (31.0%) and BPPME (62.3%). The increase in EC by the PHCASH treatment was mainly because of additional ions from wood ash leachate. Wood ash leachate has numerous ions that resulted in effluent higher conductivity after treatment by PHCASH. Previous studies have reported that wood ash leachate contains a variety of ions (Etiegni and Campbell, 1991).

The initial pH of PME and BPPME were 7.06 and 7.61, respectively. MPM effluent discharge pH was within



Fig 6. Photocatalytic effluent treatment efficiencies for EC, pH, phosphates and nitrates.

the standard limit of the World Health Organization, ranging from 6.5 to 8.5 for the release of the effluent into the environment (Chapman and Kimstach, 1992). There were relatively insignificant changes in pH after treatment by PHCPVC, PHCALON, and PHOALON for both PME and BPPME. The PHCASH treatment increased the pH for both PME and BPPME because of the addition of wood ash leachate. Wood ash contains a variety of elements in small amounts such as sodium, magnesium, and calcium in the form of oxides/phosphates/oxalates and in the presence of water they form an alkaline solution, which leads to a higher pH (Demeyer et al., 2001). Variance analysis of pH changes was not significantly different (P < 0.05) among all the effluent treatments for both PME and BPPME. There was also no significant interaction (P < 0.05) in the pH changes between effluent treatments and for both PME and BPPME.

The initial nitrates concentration for PME and BPPME were 5.9 mg/L, and 4.5 mg/L respectively. The final nitrates concentration at the discharge point into the environment was within the minimum permissible limit by WHO of 20 mg/L (Chapman and Kimstach, 1992). Nitrates variance analysis showed a significantly different (P<0.05) in nitrates concentration changes by all effluent treatments for both PME and BPPME. There was a significant (P<0.05) interaction in nitrates concentration changes between effluent treatments and the type of effluents. PHCPVC was the most effective for the reduction of the nitrates concentration, followed by PHCALON and then PHOALON treatments. However, PHCASH treatment increased the nitrates concentration in the supernatant effluent for PME (32.8 mg/L) above permissible international limits for discharge. The increase in nitrates concentration by PHCASH treatment was owing to the introduction of some nitrate from the wood ash leachate. This was consistent with findings reported in the electrochemical treatment of an integrated pulp and paper mill effluent in Kenya that used wood ash as a supporting electrolyte (Etiégni et al., 2007).

The initial phosphates concentration for PME and BPPME was 0.488 mg/L and 0.362 mg/L, respectively. The phosphates concentration decreased with MPM effluent treatment, leading to 29.5% removal efficiency. Variance analysis showed a significant difference (P<0.05) in the reduction of phosphates concentration by all the effluent treatments for both effluent types. There was no significant (P<0.05) interaction in the reduction of phosphates between photocatalytic treatments and effluent types. The PHCPVC treatment was the most

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efficient for the removal of phosphates by 39.8% and 27.5% for PME and BPPME respectively.

Elemental concentrations

Elemental concentrations in untreated and photocatalytic treated PME and BPPME are shown in Table 4. There was a significant decrease in most elemental constituents after PHCPVC and PHCALON treatment of the effluent compared with untreated effluent for both PME and BPPME. Even though, there was a significant increase in the aluminum concentration in the PHCPVC-treated effluent for both PME and BPPME. This increase was owing to the sacrificial aluminum electrodes employed during photovoltaic treatment.

There was a significant increase in concentrations of most elements after PHCASH treatment compared with the untreated effluent for both PME and BPPME. However, PHCASH treatment resulted in a decrease in the iron, magnesium and manganese concentrations compared with untreated effluent for both effluent types. The increase in various elements

Table 4. Elemental concentrations in untreated and photocatalytic treated PME and BPPME.

Element	Effluent	Untreated PHCPVC		PHCALON	PHCASH	PHOALON
Element	Enluent	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)
C:1	PME	9.3	2.6	4.7	32.3	10.1
Silver	BPPME	10.7	3.6	8.9	26	10.4
A 1 ·	PME	362.7	12,124.80	182.7	79,366.70	293.5
Aluminum	BPPME	352.7	9,187.20	460.6	50,350.00	439.2
P	PME	41	12.8	20.7	4,140.00	44.5
Boron	BPPME	41.7	14.1	34.7	1,770.00	49.7
0.1.1	PME	12,933.30	5,593.80	6,516.30	7,393.30	16,032.70
Calcium	BPPME	18,600.00	6,299.40	15,500.00	9,880.00	17,147.10
C 1 ·	PME	27.3	7.6	13.8	51	22.7
Cadmium	BPPME	32	10.8	26.7	70.5	21.2
C 1 1	PME	21	5.7	10.6	57.3	20.8
Cobalt	BPPME	24.3	8.2	20.3	51	29.7
<u> </u>	PME	22	6.1	11.1	44.7	23.9
Chromium	BPPME	25.3	8.6	21.1	39.3	19.5
	PME	21	5.8	10.6	151.3	22.8
Copper	BPPME	22.7	7.7	18.9	93.3	22.1
-	PME	844.3	234.6	425.4	60	916.1
lron	BPPME	117.7	39.9	98.1	83.3	104.8
	PME	40.7	11.3	20.5	148.3	38.4
Gallium	BPPME	43.3	14.7	36.1	99.5	42.3
	PME	1,910.00	530.7	962.3	12,766.70	2,072.40
Iodine	BPPME	4,910.00	1,662.90	4,091.70	9,433.30	5,290.50
	PME	5,770.00	1.603.30	2,907.20	7.83.333.30	6,260.50
Potassium	BPPME	5,410.00	1.832.30	4,508.30	7.12.000.00	6,127.80
	PME	16	4.4	8.1	13.7	9.7
Lithium	BPPME	9	3	7.5	19	8.8
	PME	3,093,30	859.6	1,558.50	883.7	3,356.30
Magnesium	BPPME	2,953.30	1.000.20	2.461.10	2,633,30	3,081.40
	PME	11	3.6	5.5	2	21.9
Manganese	BPPME	12	3	7.5	9.5	8.8
	PME	69,400.00	19,284.40	34,966.50	5,68,333,30	69,299.00
Sodium	BPPME	49,333.30	16,708.20	41.111.10	3,32,000.00	45,132.20
	PME	479.3	133.2	241.5	5.623.30	520.1
Phosphorous	BPPME	374.3	126.8	311.9	4,580.00	296.5
	PME	171.7	47.7	86.5	661	98.6
Lead	BPPME	240	81.3	200	537.7	254.2
	PME	2,843.30	790.1	1.432.60	3,72,000.00	2,985.00
Sulfur	BPPME	5,563.30	1,884.20	4,636.10	58,666.70	4,427.90
	PME	28.3	7.9	14.3	67.3	30.7
Zinc	BPPME	29.3	9.9	24.4	54.7	38.6

after PHCASH treatment was attributed to wood ash leachate, which has been reported to contain several elements (Etiegni and Campbell, 1991). PHOALON treatment had no significant impact on the elemental concentrations compared with that of untreated effluent for both PME and BPPME. After photocatalytic treatments, most of the elemental concentrations for both PME and BPPME were within the minimum WHO discharge standards (Chapman and Kimstach, 1992).

CONCLUSIONS AND RECOMMENDA-TIONS

The photoactivity of titanium dioxide foils increased with increasing anodizing time and voltage. Photoactivities of copper-doped titanium dioxide foils were relatively higher than non-doped foils. A copperdoped titanium dioxide foil with a photoactivity of $62.3 \times 10-3$ was the most photoactive. Treatment of Kraft pulp and paper mill effluent by photocatalytic with copper-doped titanium dioxide showed an excellent application potential. Photocatalytic using titanium dioxide with photovoltaic (PHCPVC) was the most efficient to treat real Kraft pulp and paper mill effluent followed by photocatalytic aided by wood ash leachate as an electrolyte (PHCASH). Photocatalytic in the presence of titanium foils (PHCALON) and photo treatment without titanium dioxide foils (PHOALON) were second and least efficient, respectively. PHCPVC treatment reduced the BOD, COD, color, TSS, TDS, and turbidity of PME and BPPME by an average of 82.1%, 68.6%, 78.5%, 68.2%, 54.4%, and 68.8%. The concentrations of most elements in the PHCPVC treated effluent were also within the WHO minimum standard guidelines for discharge into the environment. Even though PHCASH was the second most efficient treatment, it increased TDS, pH, and EC for both PME and BPPME. The study also revealed that photocatalytic effluent treatment efficiency can be improved with the addition of wood ash leachate as supporting electrolyte. The study recommends treatment of Kraft pulp and paper mill effluent by photovoltaic with photocatalytic by solar catalyzed by copperdoped titanium dioxide foils. However, toxicological studies should be performed to understand the effects of these treatments on aquatic ecosystems

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DISCLOSURE OF INTEREST

The authors report no conflict of interest.

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