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Distillery Waste Water Treatment using Photo-catalytic UV-TiO_2 System

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ABSTRACT

In this study, removal of chemical oxygen demand COD, total suspended solids TSS, total dissolved solids TDS and colour of distillery wastewater using photo-catalytic process with TiO_2 was carried out. Wastewater treatment from anaerobic sedimentation tank, COD: 4476 mg/L, TSS: 640 mg/L, total dissolved solids TDS: 720 mg/L was used for the photocatalytic process. The effectiveness of heterogeneous photocatalytic degradation on distillery wastewater using the UV-TiO_2 process was investigated in a laboratory scale. For the photocatalytic process, the effect of the catalyst was studied using various amounts of TiO_2 (0.1 to 0.5 g/L). Also, the effect of contact time (30 to 180 min) with the different UV power (10 to 30 W) was studied. For 0.1 g/L TiO_2 dosage, COD removal 94% with minimum contact time 110 min in 20 W UV power. For 0.2 g/L TiO_2 dosage, COD removal 94% with minimum contact time 110 min in 20 W UV power. For 0.3 g/L TiO_2 dosage, COD removal 95% with minimum contact time 100 min in 30 W UV power. For 0.4 g/L TiO_2 dosage, COD removal 95% with minimum contact time 80 min in 20 W UV power. For 0.5 g/L TiO_2 dosage, COD removal 95%L with minimum contact time 80 min in 30 W UV power. By the usage of TiO_2 dosage (0.1 to 0.5) g/L, the COD values of treated water effluents were reduced to standard emission guideline 250 mg/L. In the use of the energy usage, the condition with UV power 20 W with TiO_2 dosage at the contact time of 110 min was the optimum. In the use of processing time, the condition with UV power 30 W with the 0.4 g/L of TiO_2 dosage at the contact time of 80 min was the optimum.

Key Words: *Chemical Oxygen Demand, Distillery Waste Water, Photo-Catalytic Degradation, Titanium Dioxide (TiO_2), UV-TiO_2 Process.*

1. INTRODUCTION

Environmental pollution is the major cause for most of health illness. Water is the main source of contamination and pollution which effects health through bio magnification. Water gets polluted by harmful chemicals, dyes, oils etc. All the waste water that contains harmful chemicals is drained into nearby water bodies. This causes water pollution and will lead to various health problems to flora and fauna [1]. Alcohol distilleries are highly water intensive units generating large volumes of high strength waste water which pose a serious environmental concern. The production and the characteristics of the spent wash are highly variable and dependent on the raw material used and various aspects of the ethanol production process [2]. Distillery waste water is one of the most polluted waste products to dispose because of the low pH, high temperature, dark brown colour, high ash content and high percentage of dissolved organic and inorganic matter with high biological oxygen demand (BOD) and chemical oxygen demand (COD) values. Therefore, distillery waste water must be treated before discharge to the environment. Advanced oxidation process (AOP), which involved the generation of highly reactive hydroxyl radical ($OH^{\bullet}$), have emerged as a promising water and waste water treatment technology for the degradation or mineralization of a wide range of organic contaminants. The characteristics are depending on the feed stock and various aspects of ethanol production process. AOPs are chemical oxidation processes. Several methods are available for generating OH radicals. These include both non-photo chemical and photochemical methods [3]. There has been over decades of intense research into many different types of AOPs as well as wide adoption of some of these processes. Of the many AOPs tested ozonation, UV/ozone, UV/hydrogen peroxide, and UV/photo catalysis are most commonly studied and used for many applications [4]. Most of the commercially viable advanced oxidation processes use either

ozone or photochemical processes (ie. ultraviolet UV or visible light) to generate OH [5]. Advanced oxidation processes (AOPs) with UV irradiation and photo catalyst titanium dioxide (TiO_2) are gaining growing acceptance as an effective waste water treatment method. TiO_2 photo catalysis is effective for decomposition of various organic contaminants in water. Ultraviolet light is part of the light spectrum. The process usually involves the use of low-pressure UV lamps with a principal wavelength of 254 nm [6]. UV irradiation is often used in combination with O_3, H_2O_2, Fenton's reagent and TiO_2 catalyst to accelerate the radical formation, and thus cause an indirect photolysis [7].

UV light exposure time has an incremental effect on colour and COD removal [8]. When the TiO_2 is illuminated by UV, it generates a conduction band of electrons (ecb) and valence band holes (h+) (Eq.3). These band electrons interact with surface adsorbed oxygen to produce superoxide radical anions. The hydroxyl radicals are produced when the band holes interact with water.

$$TiO_2 + h\nu \rightarrow ecb + h^+ \quad (1)$$

$$ecb + O_2 \rightarrow O_2^{-}\bullet \quad (2)$$

$$h^+ + H_2O \rightarrow H+ + HO\bullet \quad (3)$$

It has been shown that many organic complexes can be degraded by oxidation in the presence of UV/TiO_2 [9-11]. As with all the other processes in AOP, the degradation of organic compounds takes place by reacting with the hydroxyl radicals. Furthermore, TiO_2 nanoparticles are deemed suitable for waste water treatment, because they are non-toxic, chemically and biologically inert, and inexpensive [12]. In addition, TiO_2 has a comparatively high oxidative power as compared to other oxidizing species [13]. Suspended TiO_2 particles were used in most studies that pertain to the photo catalytic oxidation of contaminants [14-16]. Therefore, the aim of this investigation is to treat distillery waste water discharged from anaerobic sedimentation tank by photo–catalytic UV- TiO_2 system.

2. MATERIALS AND METHODS

2.1. Sample Collection

The distillery waste water was obtained from Shwe Myin Pyan industry located in Mandalay Region. The waste water sample was collected from the outlet channel of anaerobic sedimentation tank from waste water treatment plant in distillery industry. Distillery waste water sample was stored in refrigerator (4˚C). The required TiO_2, nanoparticles was purchased from local market.

2.2. Process for Distillery Waste Water Treatment in UV- TiO_2 System

The flowchart for distillery waste water treatment in UV- TiO_2 process is shown in Figure1. Firstly, waste water (1L) from anaerobic sedimentation tank was passed UV reactor with various amount of TiO_2 catalyst (0.1, 0.2, 0.3, 0.4 and 0.5 g/L) for various contact time (30 to 80 min) and different UV light (10, 20, 30 W). COD values for treated water were determined.

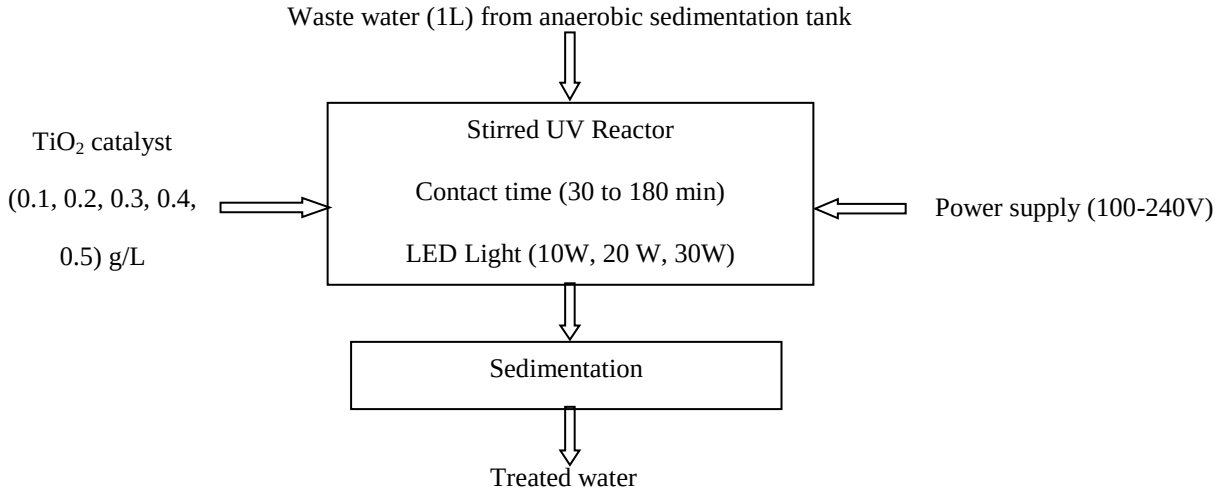

Figure1. Flowchart for Distillery Waste Water Treatment in UV-TiO_2 System

2.3. Mechanism for the Treatment of Distillery Waste Water Using UV-TiO_2 System

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The experimental set-up for photo-catalytic UV-TiO_2 reactor is shown in Figure2 rectangular reactor (1 x 1 x 1.5) cubic feet was constructed with mild steel. In the photo-catalytic reactor, LED flood light (10 W, 20 W and 30 W) was located at the top of the reactor for UV and the potable fan was assembled at one side of the reactor. The magnetic stirrer was applied to give for the speed of revolution per minute. The experiment was carried out by loading 1L of waste sample into the photo-catalytic reactor with a power supply with 100-240 volts AC power source. The reactor had one flood light of UV LED wavelength of 388 nm. This resulting reaction was the splitting of a water to generate a hydroxyl radical:

$$TiO_2\ (h^+) + H_2O\ (aq) \rightarrow TiO_2 + OH^{\bullet} + h^+$$

Photo-catalyst was combined with photons to form strong oxidizing hydroxyl radical. Finally water and CO_2 formed due to the bacteria pollutants were decomposed as intermediate oxygenated molecules as shown in equation (1).

$$\text{Organic Contaminants} + TiO_2/h\,v \rightarrow \text{Intermediate (s)} \rightarrow CO_2 + H_2O \qquad (1)$$

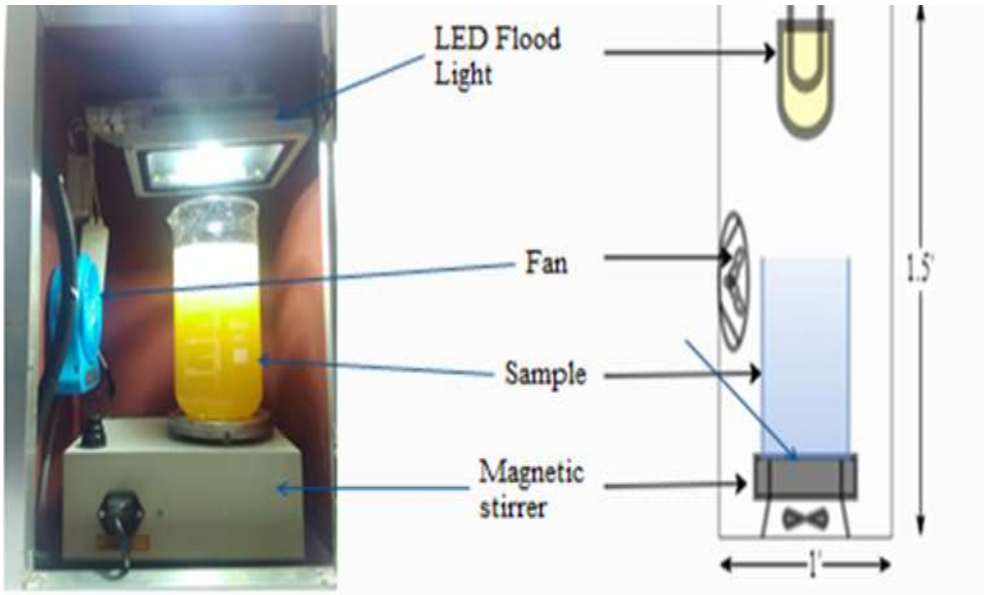

Figure2. Photo-catalytic UV-TiO_2 Reactor

2.4. Energy Phenomena for Photo-Catalytic UV Reactor

The band gap energy was determined based on the numerical derivative of the optical absorption coefficient. The fundamental absorption method refers to band transitions by using energy relation. The optical transmittance of the UV measurements indicates that direct band gap energy of the titanium dioxide TiO_2 nano particles is 3.196 eV.

Energy of photons can be calculated by the following equation (2):

$$(E) = (hc / \lambda) \qquad (2)$$

$$= 1.513 \times 10^{-19}\ \text{J (by inserting below data)}$$

Where, h is the planks constant = $6.636 \times 10^{(-34)}$ JS

λ is the wave length of the spectrum =388nm (for my research)

c is the speed of light in vacuum = 3×10^8 m/s

Number of photons can be calculated as follows:

Number of photons = (Total Energy)/(Energy of photon)

Example: Number of photon for 10 W = $(10W/1.513 \times 10^{-19}\ J) = 6.609 \times 10^{19}$ photons/s.

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3. RESULTS AND DISCUSSIONS

3.1. Characterization of Distillery Waste Water from Anaerobic Sedimentation Tank

Waste water from anaerobic sedimentation tank was characterized and the results were shown in Table1. It can be seen that the colour of waste was brown. BOD, COD, TSS and TDS values were higher than the standard emission guide line's values. Therefore, it needs to reduce pollutants from distillery waste water before discharge into the environment.

Table1. Characteristics of Anaerobic Sedimentation Tank Distillery Waste Water

Characteristics	Discharged from Anaerobic Sedimentation Tank Waste Water (Values)
COD (mg/L)	4476
BOD (mg/L)	1228
pH	7.8
Total Dissolved Solid (mg/L)	720
Total Suspended Solid (mg/L)	640

3.2. Characterization of TiO_2 Catalyst

The TiO_2 catalyst was characterized by Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX). The surface morphology of the sample TiO_2 was characterized by SEM. Figure3 shows typical scanning electron microscopic image of TiO_2 nanoparticle. From the figure, the most of the particles are almost spherical in shape with uniform size distribution. It is evident that the growth of particle is restrained by TiO_2. Closer examination of this figure reveals a well-defined particle like morphology, having abundance of spherical-shaped particles. According to the SEM image, the smaller size of TiO_2 could give higher surface area. The highest specific surface area will provide the high photo catalyst effect.

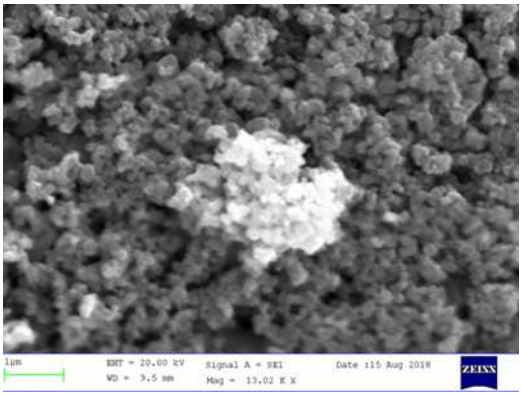

Figure3. Scanning Electron Microscope (SEM) Image of TiO_2 Catalyst

According to the Table2, 98.311% of TiO_2 is clearly demonstrated. The result suggests that this percentage of TiO_2 composition was achieved the effective amount of photo-catalytic emission for UV-reactor process. The amount of SiO_2, SO_3, NbO and CuO compositions were very small and these amounts can be neglected.

Table2. EDX Result of TiO_2 Catalyst

Measurement Condition									
Channel	kV		uA	Filter	Acq.	Collimator Analysis	10mm Time	Atmos. DT%	Vac.
Na-U		50	14-Auto	----	0 - 40	0.00-40.00	Live- 60	29	

Quantitative Result						
Analyte	Result		Std.Dev.	Calc.Proc	Line	Intensity
TiO2	98.311	%	[0.175]	Quan-FP	TiKa	3548.805
SiO2	0.989	%	[0.127]	Quan-FP	SiKa	1.4197
SO3	0.446	%	[0.037]	Quan-FP	S Ka	3.6253
NbO	0.226	%	[0.003]	Quan-FP	NbKa	59.3430
CuO	0.029	%	[0.003]	Quan-FP	CuKa	2.3670

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3.3. Effects of TiO_2 Dosage, Contact Time and UV Power in Photo-catalytic UV Reactor

Figure4 shows that 0.1 g/L TiO_2 dosage for 10W UV power was reduced COD to 233 mg/L at 180 min. And then, 0.1 g/L TiO_2 dosage for 20 W UV power reduced to COD 246 mg/L at 110 min. Moreover the same TiO_2 dosage for 30 W UV power reduced COD to 256 mg/L at 110 min. According to these results, COD was reduced to standard emission guideline (250 mg/L) for all experimental conditions. But, to save time and energy, UV power 20 W and contact time 110 min was selected as the optimum condition for 0.1 g/L of TiO_2 dosage.

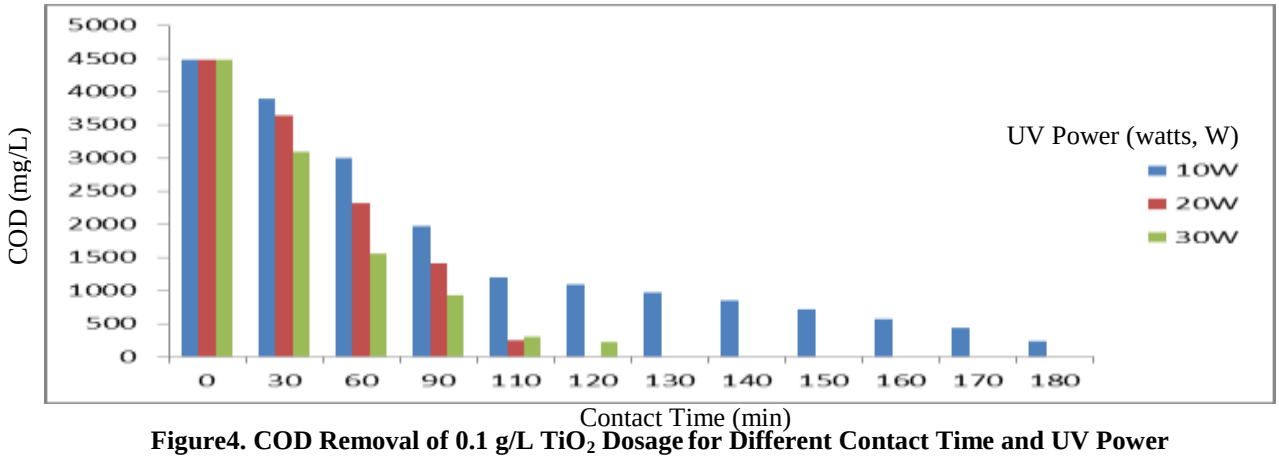

Figure4. COD Removal of 0.1 g/L TiO_2 Dosage for Different Contact Time and UV Power

Figure5 shows that 0.2 g/L TiO_2 dosage for 10W UV power was reduced COD to 243 mg/L at 150 min. And then, 0.2 g/L TiO_2 dosage for 20 W UV power reduced to COD 212 mg/L at 120 min. Moreover the same TiO_2 dosage for 30 W UV power reduced COD to 248 mg/L at 110 min. According to these results, COD was reduced to standard emission guideline (250 mg/L) for all experimental conditions. But, to save energy, UV power 20 W and contact time 120 min was selected as the optimum condition for 0.2 g/L of TiO_2 dosage. But, to save time, UV power 30 W and contact time 110 min was selected as the optimum condition for 0.2 g/L of TiO_2 dosage.

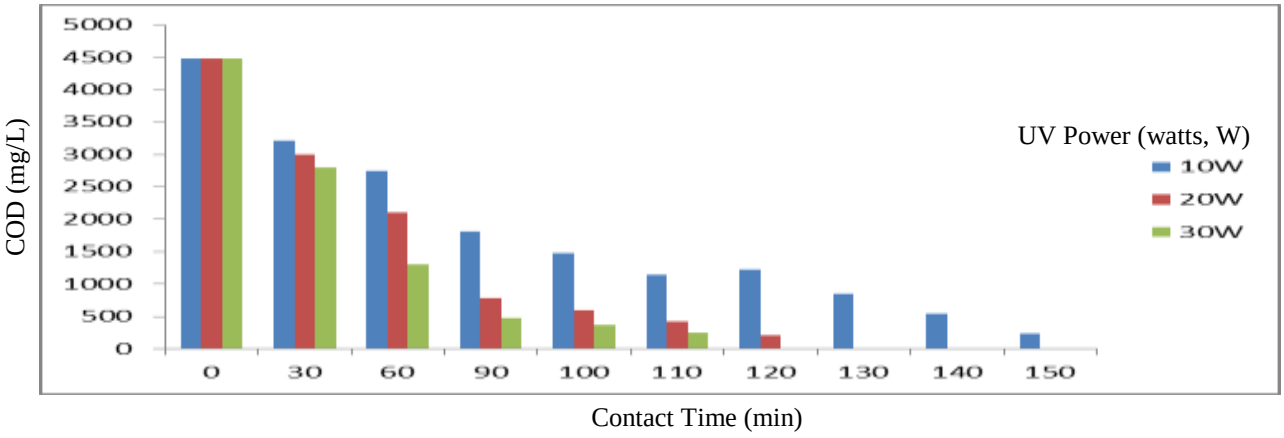

Figure5. COD Removal of 0.2 g/L TiO_2 Dosage for Different Contact Time and UV Power

Figure6 shows that 0.3 g/L TiO_2 dosage for 10W UV power was reduced COD to 256 mg/L at 140 min. And then, 0.3 g/L TiO_2 dosage for 20 W UV power reduced to COD 253 mg/L at 120 min. Moreover the same TiO_2 dosage for 30 W UV power reduced COD to 230 mg/L at 100 min. According to these results, COD was reduced to standard emission guideline (250 mg/L) for all experimental conditions. But, to save energy, UV power 20 W and contact time 120 min was selected as the optimum condition for 0.3 g/L of TiO_2 dosage. . But, to save time, UV power 30 W and contact time 100 min was selected as the optimum condition for 0.3 g/L of TiO_2 dosage.

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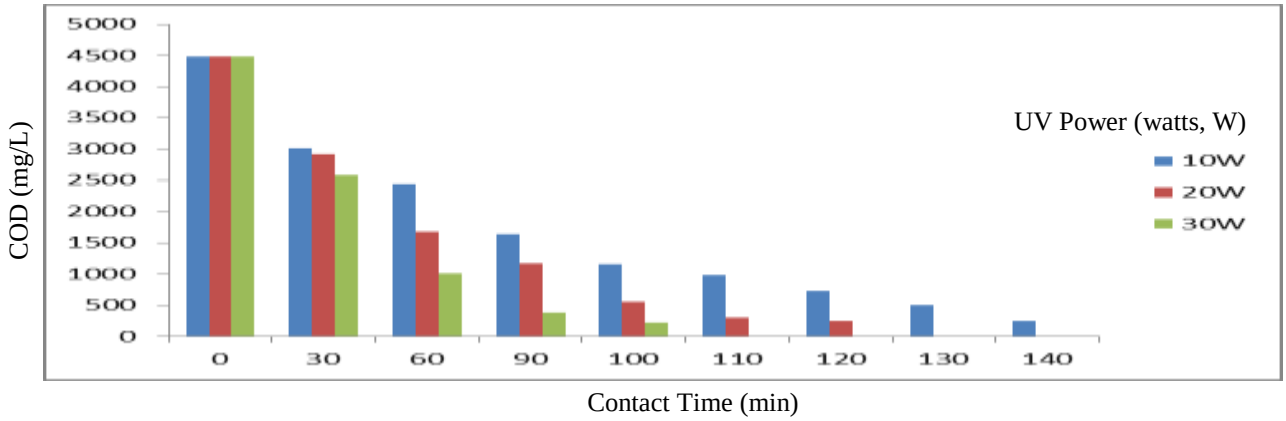

Figure6. COD Removal of 0.3 g/L TiO_2 Dosage for, Different Contact Time and UV Power

Figure7 shows that 0.4 g/L TiO_2 dosage for 10W UV power was reduced COD to 248 mg/L at 140 min. And then, 0.4 g/L TiO_2 dosage for 20 W UV power reduced to COD 257 mg/L at 90 min. Moreover the same TiO_2 dosage for 30 W UV power reduced COD to 246 mg/L at 80 min. According to these results, COD was reduced to standard emission guideline (250 mg/L) for all experimental conditions. But, to save energy, UV power 20 W and contact time 90 min was selected as the optimum condition for 0.4 g/L of TiO_2 dosage. . But, to save time, UV power 30 W and contact time 80 min was selected as the optimum condition for 0.4 g/L of TiO_2 dosage.

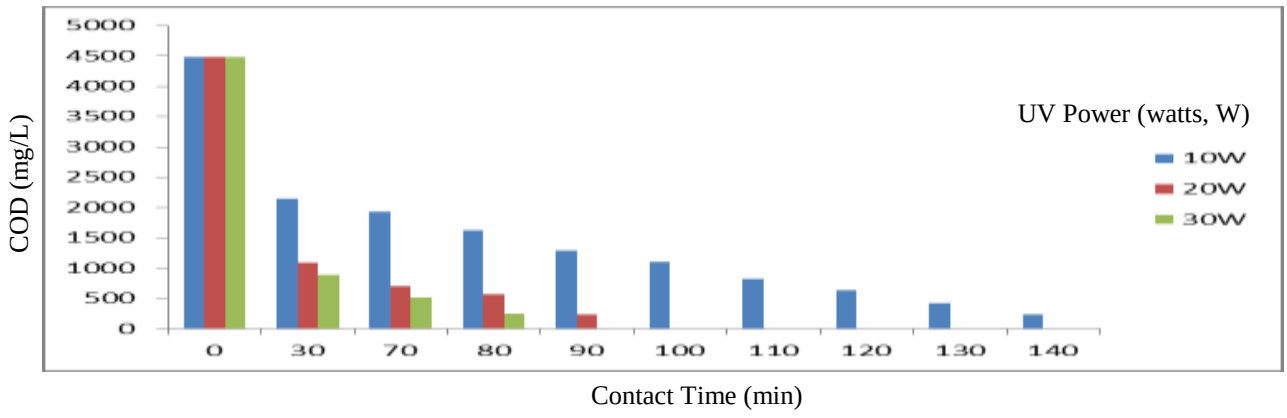

Figure7. COD Removal of 0.4 g/L TiO_2 Dosage, for Different Contact Time and UV Power

Figure8 shows that 0.5 g/L TiO_2 dosage for 10W UV power was reduced COD to 240 mg/L at 130 min. And then, 0.5 g/L TiO_2 dosage for 20 W UV power reduced to COD 243 mg/L at 100 min. Moreover the same TiO_2 dosage for 30 W UV power reduced COD to 216 mg/L at 80 min. According to these results, COD was reduced to standard emission guideline (250 mg/L) for all experimental conditions.

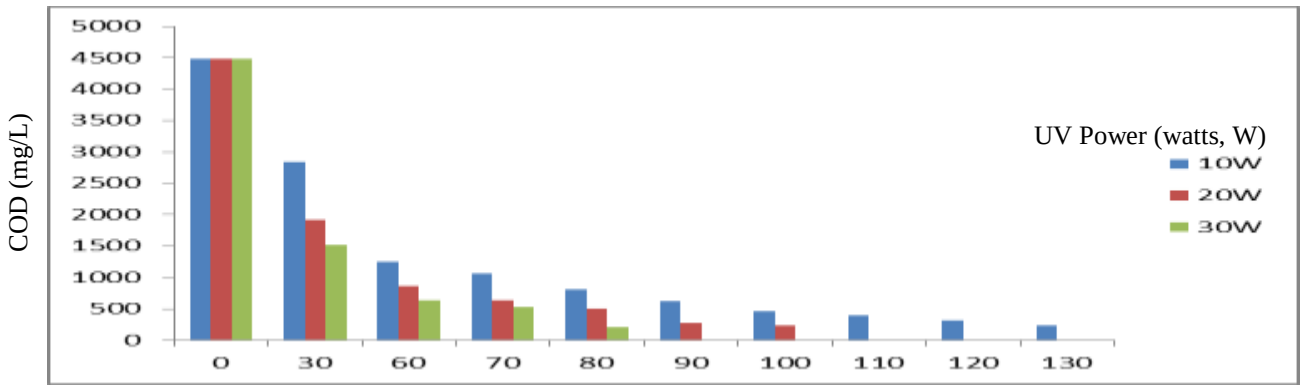

Figure8. COD Removal of 0.5 g/L TiO_2 Dosage for, Different Contact Time and UV Power

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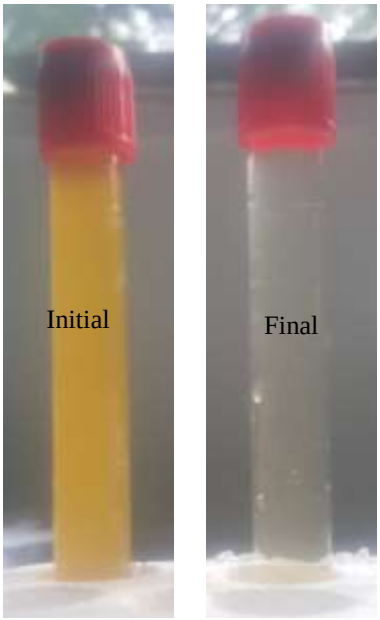

Figure9. Colour changes of Anaerobic Sedimentation Tank Waste Water at Optimum Contact Time 80 min with TiO_2 0.4 g/L and 30 W UV Power for Photo Catalytic UV Reactor

4. CONCLUSION

In summary, distillery waste water from anaerobic sedimentation tank treatment by photo-catalytic waste water treatment process with TiO_2 catalyst was investigated. And also photo-catalytic UV TiO_2 process was found to be effective in treating most micro pollutants. Photo-catalytic reactor design is very important where intense research is in progress. An efficient distillery waste water photo-catalytic UV reactor should be simple, cheap to build, energy efficient and able to operate large amount of waste water. In this study, the photo catalytic effect of TiO_2 on degradation of COD was studied. The studies showed that addition of catalyst makes faster the reaction and achieved the maximum percentage removal of compound concentration as well as COD reduction in short reaction time. The COD removal efficiency was strongly affected by many factors such as the dosage amount of TiO_2 catalyst, contact time and power of UV light. The influence of TiO_2 dosage and contact time on the rate of degradation was studied. After UV-TiO_2 photo-catalytic reactor process, total dissolved solid (TDS) and total suspended solid (TSS) values were reduced by 96% and 94% respectively. By the usage of TiO_2 dosage (0.1 to 0.5) g/L, the COD values of treated water effluents were reduced to standard emission guide line 250 mg/L. In the use of the energy usage, the condition with UV power 20 W with TiO_2 dosage at the contact time of 110 min was the optimum. In the use of processing time, the optimum condition, the COD removal achieved with 0.4 g/L of TiO_2 dose in heterogeneous process (initial 4476 mg/L to 246 mg/L) was the contact time of 80 min and UV power of 30 W.

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