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Energy efficient operation of photocatalytic reactors based on UV LEDs for pollution remediation in water

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Abstract — Photocatalytic technology using TiO_2 is one of the emerging approaches for water treatment, especially as a final step to remove complex organics such as pesticides, hormones or humic acids. Titanium dioxide (TiO_2) is a semiconductor material with strong UV absorption band and exhibits strong photocatalytic activity. The photocatalytic activity of TiO_2 powders have been extensively studied, using UV light sources. However, the incident photons that initiate the process of photocatalytic oxidation using titanium dioxide are not efficiently used, this is responsible for the low photonic efficiency that characterise oxidation of aqueous pollutants hence its limitation in industrial applications. Periodic illumination has been investigated as a means of increasing the photonic efficiency in a photoreactor with acid orange as a model pollutant. Results indicate more than four-fold increase in photonic efficiency through periodic illumination compared to continuous illumination. This approach can improve the energy efficiency of the photocatalytic water treatment systems.

Keywords — Water treatment; Titanium dioxide; Azo dyes; photocatalysis; UV LEDs;

I. INTRODUCTION

Factories or oil refineries discharge effluent into rivers or water bodies which may contain one or more pollutants. Some factories directly discharge their effluents or partially treat before the discharge. Eventually, these pollutants will end up in the ocean affecting the biological life and causing severe environmental problem. The treatment of water contaminated with traces of toxic organic compounds is a common problem throughout the world. Conventional water treatment processes based on filtration, flocculation, adsorption and chemical methods are being widely used [1-3]. Most of these processes are for separating the toxic compounds from water rather than totally destroying them. This eventually needs further

remediation through some other method to totally destroy the compounds to avoid future toxicity. Photocatalysis is one of the emerging environmental friendly processes which can alleviate the toxicity through complete mineralisation of the compounds which has been reported [4,5]

Water treatment based on photocatalysis using titanium dioxide (TiO_2) is an emerging approach for organic pollutant elimination. TiO_2 is a photocatalyst which, in the presence of ultra-violet (UV) light, is capable of breaking down organic pollutants in water. This is of particular interest to the water treatment industry as a final step to remove complex organics like pesticides, hormones or humic acids. These contaminants are of emerging concern because they are commonly found in the marine environment and have possible negative environmental and biological implications, yet most have no current regulation for their uses.

Titanium dioxide (TiO_2) is a semiconductor material with relatively large band gap and has been widely used in application areas such as catalysis, photovoltaic cells, paints, paper, sensors, water splitting, self-cleaning and cosmetics. TiO_2 exists mainly in three forms rutile, anatase, and brookite and exhibit strong photocatalytic activity [6]. Some of these forms have been utilized for the process of photocatalytic oxidation to remediate the various organic compounds that pollute the environment. The mechanism and applications of photocatalytic activity of TiO_2 have been extensively studied by researcher [7-9]. However, incident photons that initiate the process of photocatalytic oxidation using TiO_2 are not efficiently used; this is responsible for the low photonic efficiencies or quantum yields that characterize oxidation of aqueous pollutants hence its limitation in industrial applications. Periodic illumination has been identified as a means of increasing the photonic efficiency and improving the

conversion of reactants or formation of products in TiO₂ photocatalysis [10, 11]. Szczechowski et al suggested that photons are not required for the rate-limiting step to occur and that illuminating the catalyst periodically, gives more time for the rate-limiting step to occur. During the dark times, reactant molecules concentrate at the surface of the catalyst and the introduction of photons during the light time leads to high instantaneous reaction rates [12].

The conventional UV lamps and UV light fluorescent tubes are suitable for continuous illumination. The new generation UV LEDs is more energy efficient, and therefore cheaper to run, than traditional UV light sources [10]. In addition, they generally have longer lifetimes and are suitable for periodic operation. Periodic illumination studies usually involve light and dark times of short duration, sometimes in the milliseconds time-scale. LEDs are generally small in size, can be arrayed in any form, they have high illumination efficiency.

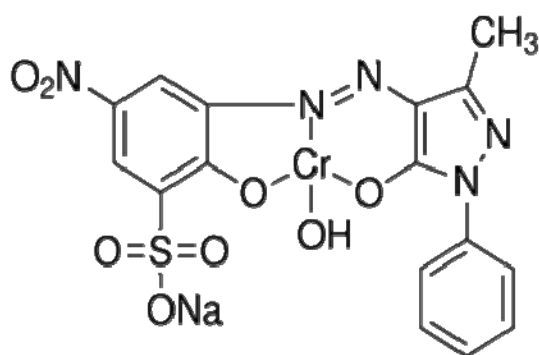


Fig. 1. Chemical structure of Acid Orange 74

The particular pollutant of interest in this investigation is Acid Orange (AO); a mono-azo dye commonly used in industry for dyeing, weaving and tanning. Azo dyes are aromatic compounds with one or more $-N=N-$ groups [13], as shown in Figure 1, and considered as electron deficient xenobiotic compounds because they possess electron withdrawing groups, generating electron deficiency in the molecule and making them resistant to degradation [14]. Azo dyes and their breakdown products are often harmful to living organisms and during the dyeing process, 15% of world dye production is lost and released into effluents [15-17]. Therefore it is vital that these harmful compounds are removed from wastewater and effluents before release into the environment. Hence this paper investigates the photonic efficiency enhancement in TiO₂ based photocatalytic degradation of acid orange 74 through periodic UV LED illumination.

II. EXPERIMENTAL

The industrial standard TiO₂ is Degussa P25 (approx. 75% anatase and 25% rutile) was supplied by Sigma-Aldrich and used as received. The UV-visible absorption spectrum of P25 is shown in Figure 2, with strong absorption below 380nm. Acid orange74 was also procured from Sigma-Aldrich. 25 μ M aqueous solutions in distilled water were used as the starting AO concentrations and 1% P25 loading for the experiments.

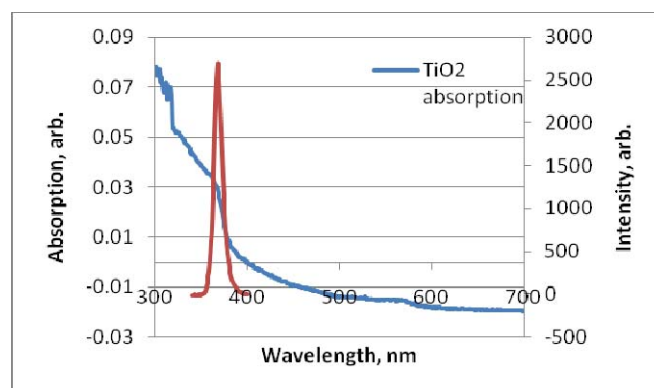


Fig. 2. Absorption spectra of TiO₂ powder and emission spectra of the UV LED

A schematic of the experimental setup is shown in Figure 3. The test photoreactor unit consists of an annular arrangement of an aluminium coated cylindrical PMMA tube and a glass vial. The vial containing 32 mL of aqueous solution was placed in the tube and sparged using an air pump for fluidisation. Nichia LED with peak wavelength around 368 nm was used as illumination source and the aluminium coating on the PMMA tube to prevent light escaping from the enclosure. The LED has a radiant power of 28 mW and powered by a DC power supply (Farnell TOP S/2). Figure 2 also shows the light emission spectrum from the LED with a peak at 368nm.

The experiments took place in a dark chamber and each experiment lasted for 80 minutes, with 20 minutes of dark adsorption and then exposure to UV light for 60 minutes. Samples were taken at regular ten minute intervals during the experiment. Sample aliquots of 1mL was taken in triplicate with a syringe (B-D plastiplate) and filtered with a Whatman 0.45 μ m filter. Further, these samples were centrifuged to separate the TiO₂ powder. Absorbance spectra of AO were studied using a Perkin Elmer Lambda950 UV-VIS spectrometer and the spectral peak was identified at 470 nm (Fig). The figure shows the absorption spectra for AO for various samples (S1-S6 every ten minutes) with reducing peak, indicating decrease in AO concentration through photocatalytic process. For subsequent samples, measurements were carried out using Novaspac II spectrometer at 470nm.

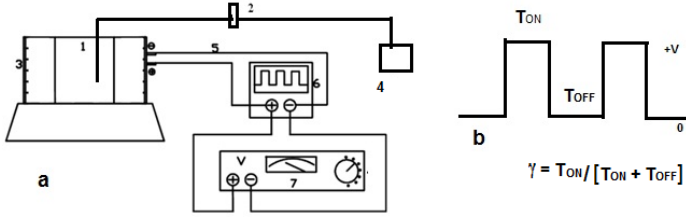


Fig. 3. (a) Schematic of the experimental setup, 1. Glass vial; 2. Rotameter; 3. Al-coated outer tube; 4. Air pump; 5. Electric wire connection; 6. Pulsing circuit; 7. Power supply (b) LED pulses showing T_{ON} & T_{OFF} periods

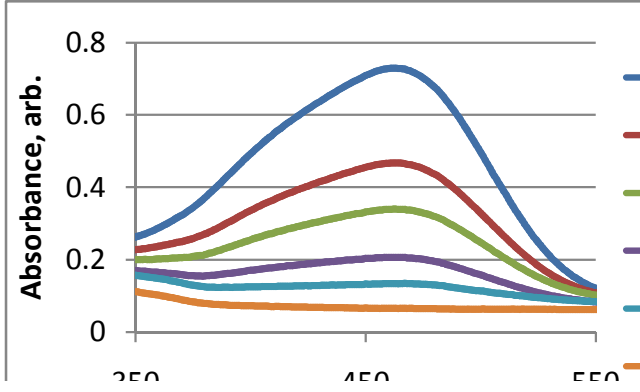


Fig. 4. Absorption spectra of acid orange for different samples indicating their concentration

The same experimental procedure was followed for different duty cycles of illumination and an electronic astable multivibrator was used to control the duty cycle of the LED light pulses with different illumination periods (T_{on}) and dark periods (T_{off}) while the frequency was kept constant. The incident photon rate was calculated to be 5×10^{-8} einsteins $L^{-1} s^{-1}$ and the reaction rate was given as $(C_1 - C_0)/\text{time}$, where C_1 & C_0 are the initial and final concentrations respectively. Photonic efficiency for the photocatalytic degradation of AO, was calculated in all cases as the reaction rate divided by the incident photon rate:

$$\zeta = \frac{\text{Reaction rate (mol L}^{-1} \text{s}^{-1})}{\text{Incident photon rate (einstein L}^{-1} \text{s}^{-1})} \quad (1)$$

III. RESULTS & DISCUSSIONS

Experiments were carried out to investigate the effect of light and dark times (T_{ON} and T_{OFF}) cycles on the photonic efficiency of the photocatalytic degradation of AO under UV light illumination. In the experiment, T_{ON} and T_{OFF} cycles were varied while the period remained constant at 964 ms, that is, given the primary steps of charge-carrier generation and recombination, which occur during the light time; and the slower steps of radical formation and interfacial charge transfer, which occur during the dark time (or light time) depending on the pulse duration.



These initiation steps for photooxidation process of TiO_2 have been well explained in our previous publication [18]. The mechanism of semiconductor photocatalysis has been detailed by Tokode et al., 2016 [19]. T_{ON} ranged from 72ms to 826ms. Figure 5 shows that the dye degradation with time for different duty cycles with continuous (CW, duty cycle = 1) illumination showing the fastest degradation. The degradation rate slowly reduced with reducing duty cycle (1 to 0.15). The percentage degradation of AO increased as the average intensity, I_{avg} increased, where ($I_{avg} = \gamma I_{max}$) and γ is the duty cycle [$\gamma = T_{ON}/(T_{ON}+T_{OFF})$].

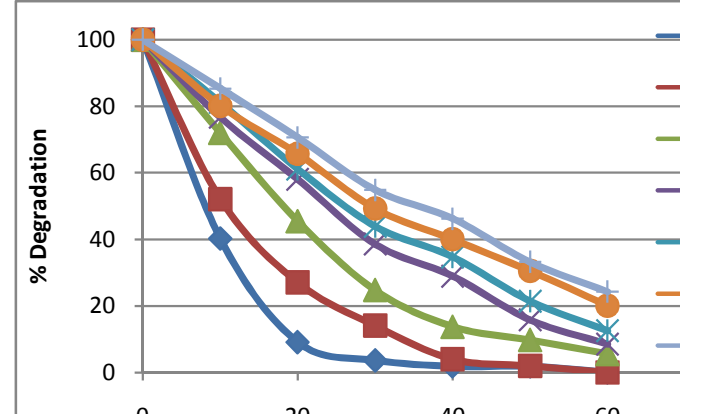


Fig. 5. AO degradation with time for different duty cycles

Photonic efficiency increases with T_{ON} reduction because of a corresponding increase in T_{OFF} . This implies a brief period of charge-carrier generation (2) and less time for charge-carrier recombination (3), influenced by rising levels of e_{cb}^- , which is the primary reason for low efficiency [20]. The corresponding increase in T_{OFF} also gives rise to the titration of holes by the high electron concentration (3), effectively stopping hole oxidation reactions while giving ample time for the interfacial charge transfer of electrons to adsorbed oxygen or adsorption of oxygen/substrate to the TiO_2 surface; two steps previously identified as rate-limiting in the photocatalytic process [21, 22].

Figure 6 shows dye degradation with duty cycle which varies nearly linear with duty cycle. This is due to the linear increase in light average intensity with duty cycle (T_{ON} increases while T_{OFF} reduces by keeping total cycle time constant at 964 msec). It also shows the variation of photonic efficiency with duty cycle which increases faster at lower duty cycles. Previous studies have shown that there is generally an improvement in photonic efficiency when reactors use low light intensity, this gradually increases until the reaction becomes photon limited [10].

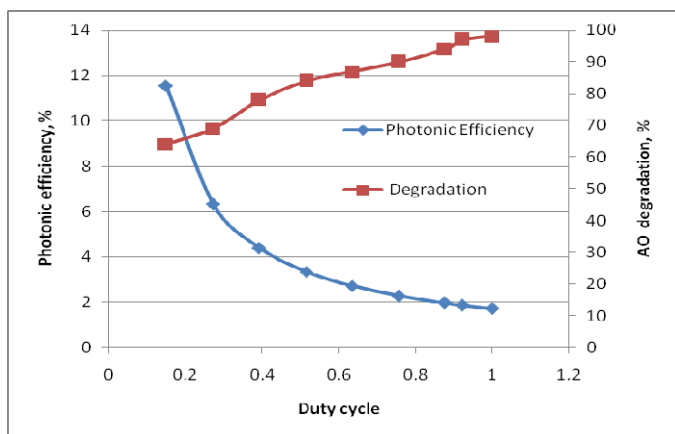


Fig. 6. Photonic efficiency and AO degradation variation with duty cycle



When T_{OFF} was maintained and T_{ON} varied; there was also an improvement in photonic efficiency. This improved photonic efficiency reached a minimum value of 6.5, at the maximum incident photon rate because of the prolonged occurrence of reactions as per (2) and (3) without a corresponding increase in time for reactions as per (4)–(6). This demonstrates the importance of both the light and dark times when TiO_2 is periodically illuminated.

The dark time influenced photonic efficiency as reported by Stewart and Fox who achieved a 1.8-fold improvement when the dark time was increased from 0.1 s to 1 s [23]. A similar improvement in photonic efficiency was observed in this study with an increase in the dark time. It is believed that this is a result of depleted oxygen being re-adsorbed onto the surface during the dark time, with some re-adsorption of methyl orange onto the TiO_2 surface as well. The oxygen subsequently reacts with the excess electrons, hence inhibiting recombination with holes. This improvement is, however, sensitive to the oxygen re-adsorption/reduction rate, which is a slow process and has previously been suggested to be the rate-limiting step in photocatalytic reactions [22].

These results reveal a general increase in photonic efficiency as the duty cycle or average intensity decreases irrespective of a decrease in T_{ON} or increase in T_{OFF} . The trend shows that the photonic efficiency depends on duty cycle rather than the individual variation of T_{ON} and T_{OFF} times. These results agree with the findings of Cornu et al. [24] that the reaction is not limited by mass diffusion or by adsorption/desorption from TiO_2 powder surface.

IV. CONCLUSIONS

This study has shown that the UV LED illuminated photocatalytic reactor was suitable for degrading acid orange 74 and the dye degradation was a function of duty cycle of the illumination. Further, the photonic efficiency for AO degradation increased with decreasing duty cycle. The photonic efficiency enhancement approach through periodic illumination can improve the overall energy efficiency of the photocatalytic water treatment systems and hence reducing their energy cost and carbon footprints.

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