

## Photocatalytic Degradation of Acid Orange II Dye on Selected Commercial Titanium Dioxide Catalysts

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### Abstract:

Photocatalytic degradation of acid orange II dye in the presence of UV light was investigated using selected commercial TiO<sub>2</sub> as photocatalysts. The objective of this study was to determine the rate of photodegradation of the model dye using selected commercial TiO<sub>2</sub>. The types of TiO<sub>2</sub> used as photocatalysts in this study were P25 (Degussa), AV01 (Precheza) and S7001 (Euro support). The oxides were immobilized on microscopic glass slides measuring 75mm x 25mm to form a uniform layer of area 8.75 cm<sup>2</sup>. A four-hole position photoreactor and a UV panel reactor were used in batch mode during photocatalytic degradation. Source of UV light were fluorescent tubes that emitted light at 320-400 nm with a maximum wavelength being at 355 nm. A UV/Vis spectrophotometer (model Cecil 2020) was used to monitor the changes in dye concentrations. Changes in concentration during irradiation was used to determine the rate of photocatalytic degradation of the dye. The efficiency of the three dioxides in photodegradation of the acid orange II dye was compared and the study revealed that AV01 was the most efficient commercial TiO<sub>2</sub> as a photocatalyst followed by P25 and S7001 was the least.

**Keywords:** photocatalyst, photocatalytic degradation, acid orange II dye

### 1. Introduction

Fifteen percent of world production of dyes is lost during the dyeing process and the wastewater is released as textile wastewater [1]. The discharge of these untreated effluent into the environment is a great source of pollution and causes disturbances in the delicate aquatic ecosystems [2, 3]. International environmental standards have become more stringent on the effluent release in to the environment [4].

To treat the wastewater, Advanced Oxidation Processes (AOPs), have been developed to remedy wastewater loaded with organic pollutants including textile wastewater [5, 6]. Photocatalytic oxidation is an alternative method for the complete degradation of dyes. When energy in the form of a photon from UV light from artificial UV lamps falls on the surface of a suitable photocatalyst e.g.  $\text{TiO}_2$ , electrons are excited from the valence band to the conduction band. The holes left behind in the conduction band have strong oxidation potentials (2.8 vs SHE), convert water to ( $\cdot\text{OH}$ ) that oxidise organic pollutants to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  [7, 8].

Titanium dioxide also known as titania is a naturally occurring oxide of titanium with a chemical formula,  $\text{TiO}_2$ . It is a semi-conductor that has been used successfully as a photocatalyst for oxidative degradation of organic compounds including dyes [9].  $\text{TiO}_2$  exists in a number of crystalline forms of which the most important forms are anatase and rutile.  $\text{TiO}_2$  in the form of anatase is the most practical form that can be applied in photocatalytic environments such as in water purification, wastewater treatment and water disinfections. It is biologically inert and chemically stable with respect to photocorrosion and chemical corrosion and is inexpensive [10, 11]. Titanium dioxide has remarkable optical properties, with a very high refractive index close to that of diamond. It is also a very stable compound that can be heated to over 2000 Kelvin before melting. Its disadvantage however, is too high band gap energy about 3.2 eV that enables  $\text{TiO}_2$  to absorb only UV light with wavelength lower than 388 nm thus reducing the solar harvesting efficiency down to 5 % [12]. Commercial forms of  $\text{TiO}_2$  include: P25 (Degussa), AV01 (Precheza) and S7001 (Euro support). Studies have shown that P25 contains 70% anatase with a small amount of rutile in amorphous phase [13]. This study was conducted to determine the photocatalytic degradation of Acid Orange II (AO 7) dye

using selected commercial titanium dioxide photocatalysts. The structure of the acid orange II dye used in this study is shown in Figure 1.

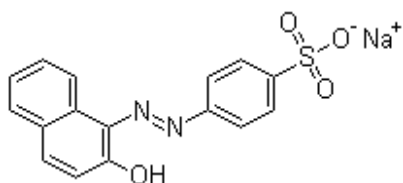


Figure 1. Structure of Acid Orange II dye

## 2. Materials and Methods

### 2.1 Preparation of $TiO_2$ particulate layers

Commercial titanium dioxide powders were provided by Precheza (AV01), Eurosupport (S7001) and Degussa (P25) and were used without any further purification.

Suspensions of concentration of 10g/l were prepared from the powders using distilled water in 100 ml volumetric flasks. The suspensions were homogenised using ultrasound equipment (Model- UP2005 ultrasonic homogenizer). Using a syringe, a volume of 3.75ml of the  $TiO_2$  suspensions were immobilised onto a degreased microscopic glass slides of dimensions 75 mm x 25 mm placed on ceramic tile and allowed to dry at room temperature for 30 minutes followed by drying at 50 °C in an oven for 2 hours to form a uniform layer. The catalyst loading on the glass slide was 0.5mg/cm<sup>2</sup>. The prepared particulate films were annealed in a furnace at 300°C (Figure 2) for 2 hrs. The final area covered by the photocatalyst was reduced to 8.75 cm<sup>2</sup> (Figure 3). The procedure described above was used to prepare particulate layers for each of the three commercial  $TiO_2$  catalysts. All the chemicals and the reagents used in this study were of analytical grade.



Figure 2. The calcination furnace (Model:classic Clare 4.0)

The TiO<sub>2</sub> particulate layers prepared as explained in 2.1 above are shown in Figure 3 below.

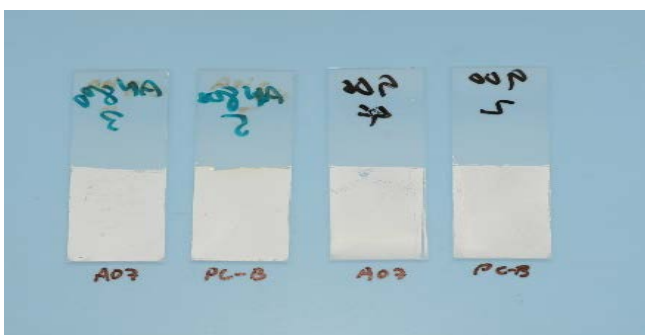


Figure 3. TiO<sub>2</sub> particulate layers on microglass slide

## 2.2 Photocatalytic degradation of Acid Orange II dye

The acid orange II dye in powder form was purchased from ACROS, London and was used without any purification. Photodegradation reaction was carried out in a four hole photoreactor and in a UV panel.

### 2.2.1 Four hole photoreactor

Three cuvettes of 30 ml equipped with magnetic stirers were each filled with 25 ml of AO II dye of concentration  $1 \times 10^{-4}$  M and a particulate layer from each of the three commercial TiO<sub>2</sub> photocatalysts were suspended as shown in Figure 3. Two UV lamps of

18 W (Sylvania LX ) were used as a source of irradiation. The experiment was done for 2 hours and sampling was done every 30 minutes. A UV/Vis spectrophotometer (Model Cecil 2020) was used to monitor the photodegradation progress in terms of concentration change. The change in concentration was calculated using Beer-Lambert's law. From literature the value of the extinction coefficient is  $2.1 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$  [14].

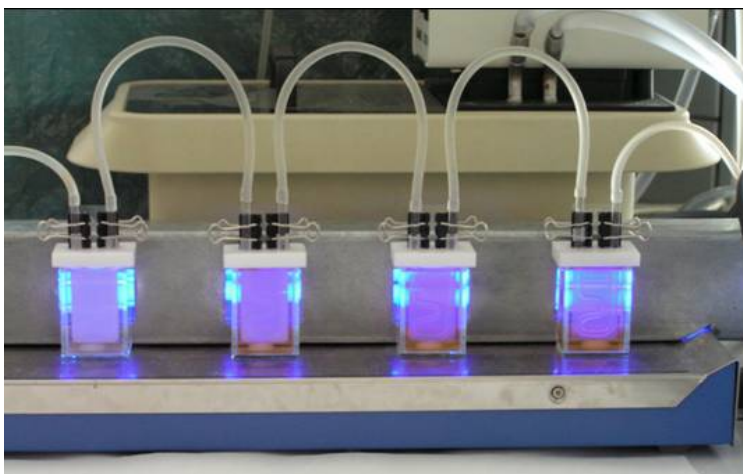


Figure 3. Four-hole Photocatalytic reactor

### *2.2.2 Photodegradation reactions in the UV panel*

The second set of experiments were done in a UV panel, consisting of a rectangular frame, covered with a suitable cloth to shield natural light from the frame and a magnetic shaker upon which three petri dishes were mounted. The magnetic shaker, ensured that the dye solutions were well mixed during the photodegradation reaction. As a source of irradiation, 2 UV lamps (sylvania) as in section 2.2.1 above was used. A volume of 50 ml AO II was placed into the 3 petri-dishes and into each petri-dish, a particulate layer from the 3 commercial  $\text{TiO}_2$  catalysts were placed into the solution making direct contact with the AO II solution.

Irradiation with the UV lamps was done for a duration of 2 hours while sampling was done after 30 minutes. Changes in dye concentration were monitored by a Cecil 2020 UV /Vis spectrophotometer as in section 2.2.1 above. The change in concentration was calculated using Beer-Lambert's law.

### *2.3 Spectral analysis of treated dye solutions*

Spectral analysis of the treated dye solution was performed only for the four hole photoreactor

#### *2.3.1 Spectral analysis for the Four hole photoreactor*

Samples from the experiments conducted in the four-hole photoreactor using commercial catalysts P25, AV01 and S7001 were analysed by a spectrophotometer to determine their concentrations. Sampling was done at 0 mins, 30 mins, 60 mins, 90 mins and 120 mins. Spectral analysis was performed between wavelengths 200-700nm, across both UV and Visible range. The results obtained are shown in Figures 6,7 and 8.

## **3. Results and Discussion**

### *3.1 Photocatalytic degradation of Acid Orange II dye on a four-hole photoreactor*

Photocatalytic degradation of AO II dye by the three commercial TiO<sub>2</sub> was compared (Figure 4 and Table 1). In the photocatalytic degradation of the dye on a UV panel, it was observed that AV01(Precheza catalyst)  $7.81 \times 10^{-6} \text{ mol.m}^{-2}\text{h}^{-1}$  was the most photoactive catalyst compared to S7001(Eurosupport)  $2.75 \times 10^{-6} \text{ mol.m}^{-2}\text{h}^{-1}$  which was the least photoactive. P25 ( degusssa)  $4.41 \times 10^{-6} \text{ mol.m}^{-2}\text{h}^{-1}$  photocatalyst was intermediate.

The variations in the photoactivity of the three commercial TiO<sub>2</sub> (Figure 4 and Table 1) could be attributed to the differences in their morphology i.e. the internal surface area, crystal sizes and particle sizes.

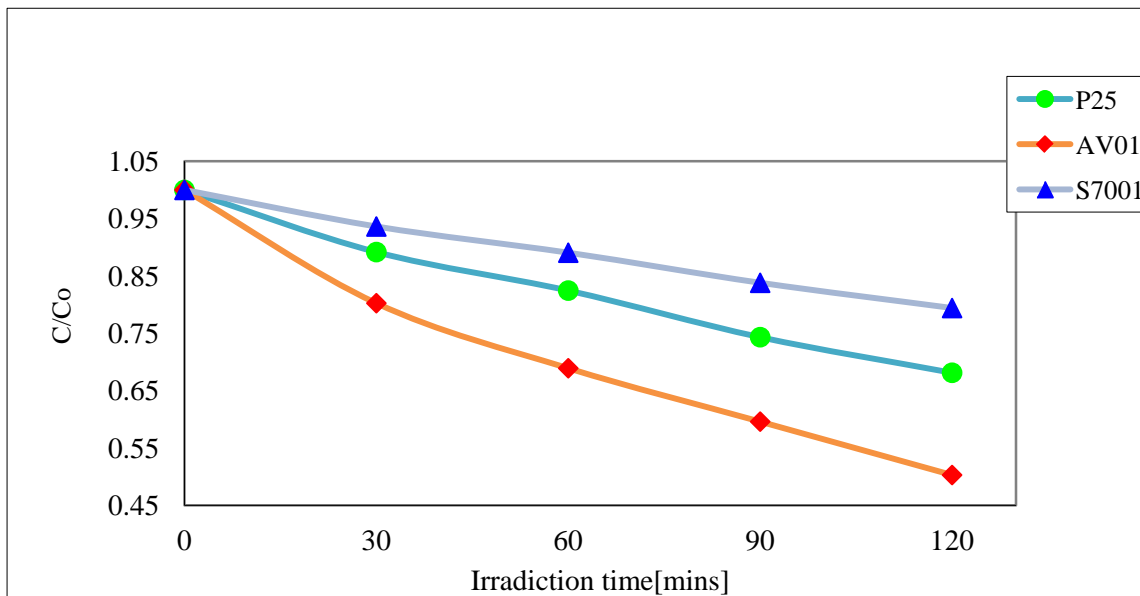


Figure 4. Photocatalytic degradation of Acid Orange II dye (Concentration =  $1 \times 10^{-4} \text{M}$ ) using commercial TiO<sub>2</sub> catalysts P25, AV01 and S7001 on a four-hole photoreactor

Table 1: Rate of the photocatalytic degradation of Acid Orange II dye after 1 hour in the four hole apparatus.

Commercial TiO <sub>2</sub>	Rate of photocatalytic degradation $\text{mol.m}^{-2}\text{h}^{-1}$
P25	$4.41 \times 10^{-6}$
AV01	$7.81 \times 10^{-6}$
S7001	$2.75 \times 10^{-6}$

### 3.2 Photodegradation of Acid Orange II dye on the UV panel

In the photocatalytic degradation of the dye on a UV panel, it was observed (Figure 5 and Table 2) that AV01 (Precheza catalyst)  $5.93 \times 10^{-6} \text{mol.m}^{-2}\text{h}^{-1}$  was the most photoactive

catalyst compared to S7001(Eurosupport)  $2.14 \times 10^{-6} \text{ mol.m}^{-2}\text{h}^{-1}$  which was the least photoactive. P25 (degussa)  $3.05 \times 10^{-6} \text{ mol.m}^{-2}\text{h}^{-1}$  photocatalyst was intermediate. The variation in photocatalytic activity of the three commercial  $\text{TiO}_2$  could be attributed to the differences in morphology i.e. the internal surface area, crystal sizes and particle sizes. .

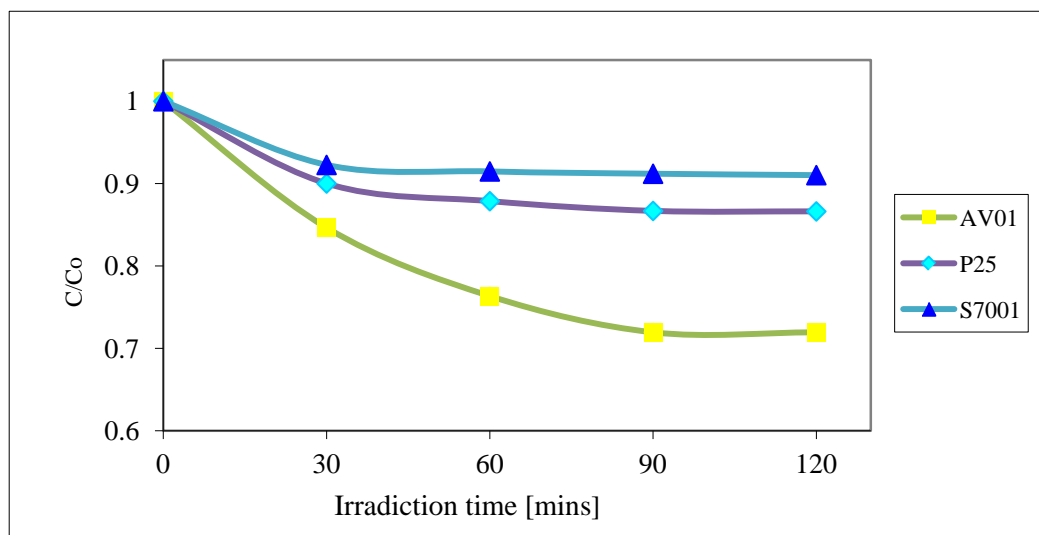


Figure 5 : Photocatalytic degradation of Acid Orange II Dye ( $1 \times 10^{-4} \text{ M}$ ) on the UV panel photoreactor

Table 2. Rate of the photocatalytic degradation for Acid Orange II dye after one hour in the UV panel.

Commercial $\text{TiO}_2$	Rate of photocatalytic degradation $\text{mol.m}^{-2}\text{h}^{-1}$
P25	$3.05 \times 10^{-6}$
AV01	$5.93 \times 10^{-6}$
S7001	$2.14 \times 10^{-6}$



### 3.3 spectral analysis of dye solution degraded by P25 catalyst

Figure 6. shows a spectral analysis of the dye solutions treated with commercial catalyst P25 in the presence artificial UV light irradiation under pre-detrmined time intervals. The maximum absorption wavelenth for the dye was  $\lambda= 485$  nm. It was observed that at irradiation time 0 mins, the concentration fo the dye solution was highest however at irradiation time 120 mins, the dye concentration was lowest.

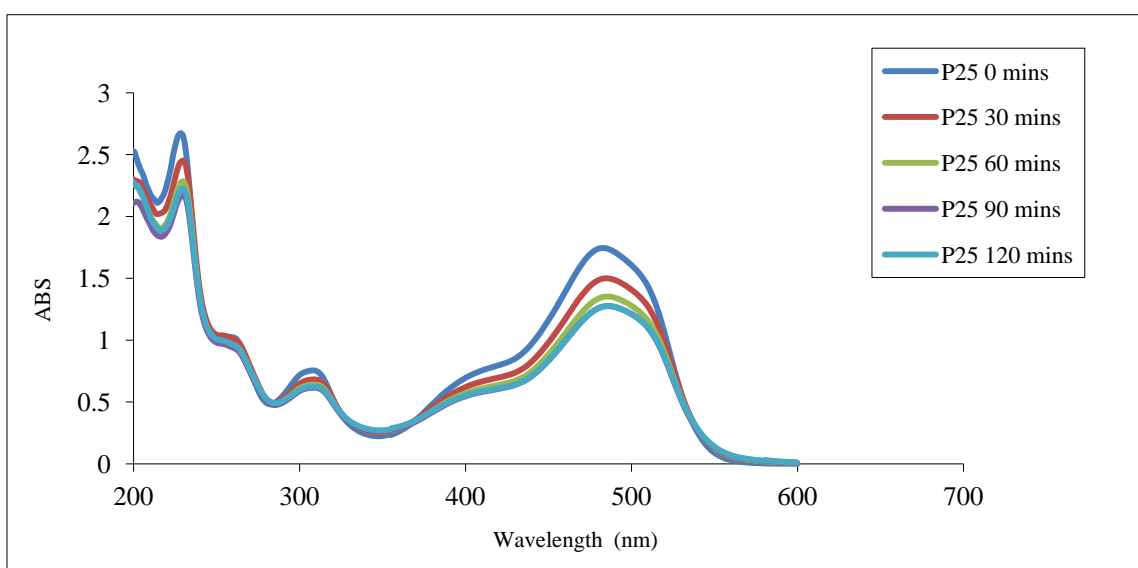


Figure 6: UV/Vis spectra for Acid Orange II dye solutions after 0,30,60,90 and 120 mins of irradiation in the four hole photoreactor with TiO<sub>2</sub> P25 Degussa

### 3.4 spectral analysis of dye solution degraded by AV01 catalyst

Figure 7 shows a spectral analysis of the dye solutions treated with commercial catalyst AV01 (Precheza) in the presence of artificial UV light irradiation under pre-detrmined time intervals. The maximum absorption wavelenth for the dye was  $\lambda= 485$  nm. It was observed that at irradiation time 0 mins, the concentration fo the dye solution was highest while at irradiation time 120 mins, the dye concentration was lowest

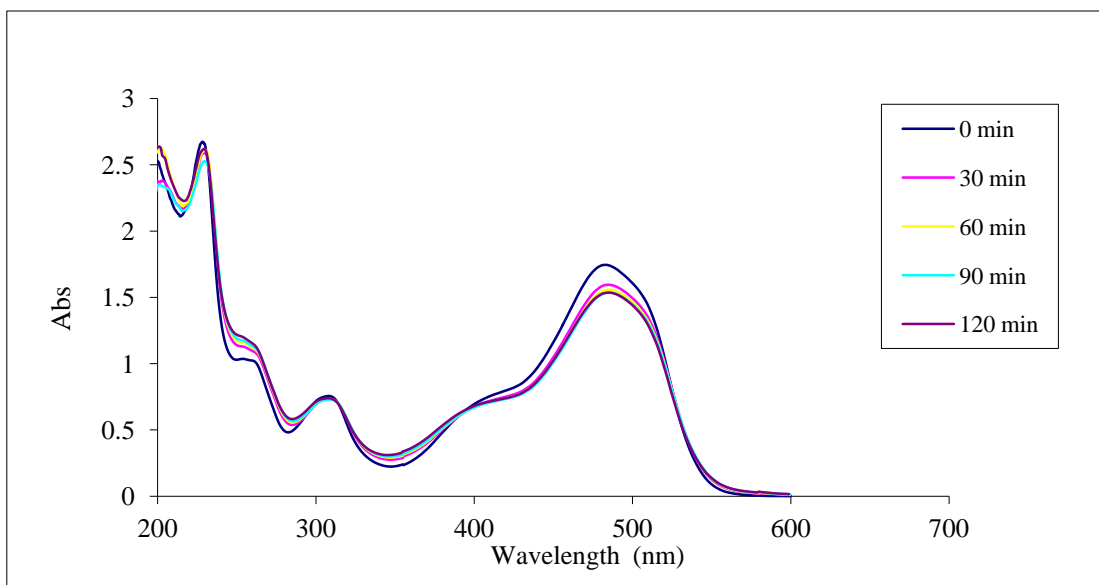


Figure 7. UV/Vis spectra for Acid Orange II dye solutions after 0,30,60,90 and 120 minutes of irradiation in the four- hole photoreactor spectra for TiO<sub>2</sub> (AV01) photocatalyst.

### 3.5 Spectral analysis of dye solution degraded by S7001 (Eurosupport) catalyst

Figure 8 shows a spectral analysis of the dye solutions treated with commercial catalyst S7001 (Eurosupport) in the presence of artificial UV light irradiation at pre-determined time intervals. The maximum absorption wavelength for the dye was  $\lambda = 485$  nm. It was observed that at irradiation time 0 mins, the concentration for the dye solution was highest while at irradiation time 120 mins, the dye concentration was lowest.

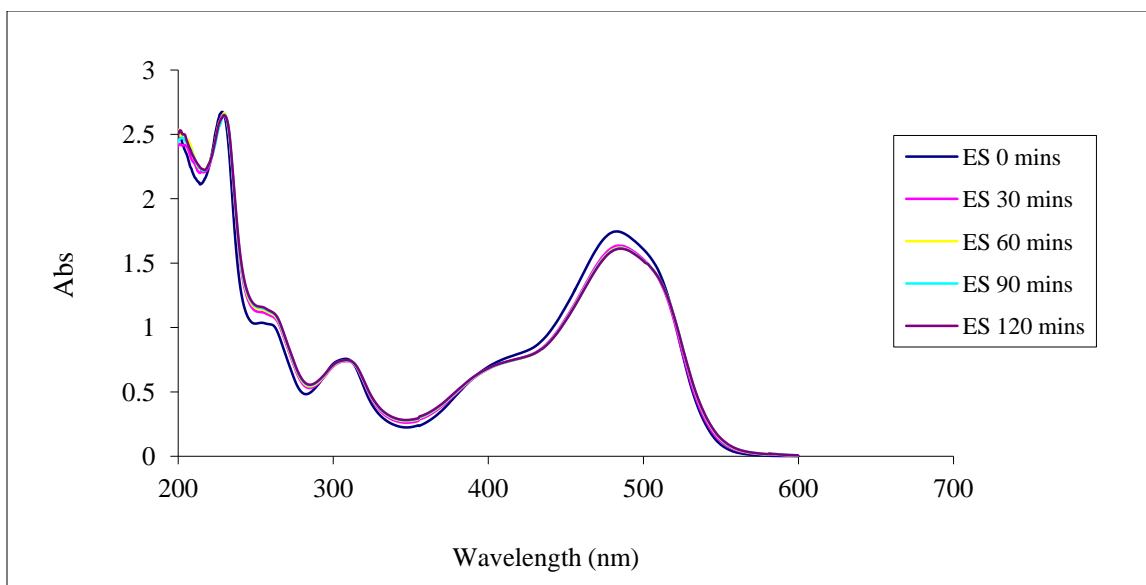


Figure 8. Spectra for S7001 (Eurosupport)TiO<sub>2</sub> photocatalyst after 0,30,60,90 and 120 mins

#### 4. Conclusions

The four-hole photoreactor experiments revealed that that the rate of dye photodegradation was highest for AV01(Precheza), P25(Degussa) and least for S7001(Eurosupport) catalysts. The UV panel photoreactor showed that the photocatalyst AV01(Precheza) is the most photoactive in degrading Acid Orange II dye. The least photoactive catalyst was S7001(Eurosupport). The study showed that after 90 minutes, the rates of photodegradation in the UV panel slowed down which could be attributed to sintering of the catalyst particles and fixation of the catalyst powder.

The rate of photocatalytic degradation using AV01(Precheza) was almost twice as fast as the photocatalytic reactions in the four-hole photoreactor compared to the UV panel. This could be due to the fact that in the four-hole photoreactor, photocatalytic degradation reactions were initiated by both the UV component in sunlight and the UV light from the lamps. The study on the spectral analysis confirmed the observations witnessed in the

four-hole photoreactor and further showed that the ideal wavelength for calculating the concentrations of the acid orange II dye is 485.2nm.

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