On-site Treatment of Dyeing Wastewater by a Bio-photoreactor System

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ABSTRACT

Synthetic dyeing wastewater consisting of the three types of commercial dyes with different strengths of COD (about 900 and 3000 mg/L respectively) were initially treated by an Intermittent Decanted Extended Aeration reactor (IDEA) for BOD removal, and then continuously treated by a TiO_2 sensitised photoreactor for a further COD removal and decolorization. The catalysed photooxidation process can degrade those non-biodegradable organics in the effluent treated by a biological treatment process and also can decolorize colour in the effluent completely. It is also found that some non-biodegradable organics can be converted to biodegradable forms by the sensitized photo-oxidation reaction. A bio-photoreactor system was designed to combine this photocatalytic reactor with the IDEA reactor for the treatment of dyeing wastewater. The performance of this combined bio-photoreactor system with and without recycle water was investigated and compared. The system with recycle water has similar efficiency for decolorization and COD removal to that without recycle water, but has a high capacity to eliminate the effects caused by a peak loading, and also the system can treat dyeing wastewater with a higher organic concentration.

KEYWORDS

Dye wastewater; biological treatment; photocatalytic oxidation; titanium dioxide.

INTRODUCTION

In the textile industry, the main pollution source of wastewater comes from dyeing and finishing. Wastewater generated from dyeing and finishing factories in Hong Kong also created a significant proportion of water pollution.

Application of biological processes in the treatment of textile wastewater has been reported extensively. However there is a practical limit to the degree of organic removal and colour removal in addition to the inability of biological treatment processes in removing non-biodegradable substances. With different processes of activated sludge, following elimination rates could be achieved: about 90%BOD_5**,** 40 - 50% COD and 20 -30% colour. Nowadays, the dyeing wastewater cannot be effectively dealt with by a single method. The major problems of dyeing wastewater are colour and non-biodegradable substances. As a result, there has been an increasing awareness of alternative or supplementary processes.

At present, there are several methods such as adsorption, chemical flocculation, UV photo-oxidation and ozonation have been used as supplementary processes to improve the quality of textile effluent. However, some methods cannot be effectively used individually or high cost has limited the wide application of these techniques in practical situations. For example, the activated carbon absorbent effectively decolorizes soluble dyes ,but does not work well for insoluble dyes. Also the chemical flocculation is not suitable for soluble dyes. The oxidation process, such as ozonation effectively decolorizes almost all dyes, but does not remove COD well and has high treatment cost.

With the role of sunlight in modifying organic compounds in the environment has been now recognised, a newly developed photochemical technology, called photocatalytic oxidation reaction, is based upon the wavelength range of radiation closed to sunlight, using titanium dioxide as catalyst and molecular oxygen system. We have investigated the use of a photocatalytic process in the presence of TiO_2 to decolorize synthetic dyeing wastewater. The results show that most dyes can be degraded and the process can enhance the biodegradability of the dyeing wastewater. Therefore, a new process of treating dyeing wastewater with the combined system of biological and photocatalytic reactors (bio-photoreactor) has been examined in this paper. The system use a photocatalytic reactor after a biological reactor and the effluent is recycled between the bioreactor and photoreactor in. It is expected that the process could effectively and economically decolorize various dyeing wastewater, remove non-biodegradable substances of COD.

EXPERIMENTAL

Dye Wastewater: The wastewater used in this study was synthetic dye wastewater which contain three different types of dye solution. The three types of dye solution (reactive dye: Ciba cvron Red FB; disperse dye: Dispersal Yellow C-4R and direct dye: Solophenyl Orange T4RL) were prepared according to the real recipes of textile industry in Hong Kong. Other nutritions needed by microbe were also added to the wastewater and the COD:N:P ratio was adjusted to 100:5:1(mg/L).Two kinds of dye wastewater used in different experimental phase were prepared. The main characteristics of the wastewater are shown in Table 1.

Table 1. Characteristics of synthetic dye wastewater

The kind of wastewater	COD (mg/L)	BOD_5 (mg/L)	Reactive dye (mg/L)	Disperse dye (mg/L)	Direct dye (mg/L)	Colour*		pH
						Red	Yellow	
I	830~930	320~390	100	80	80	25	7	~7
II	2600~3000	700~900	200	150	150	40	20	~7

*****Colour unit: Lovibond unit with 1 inch optical glass cell channel.

Experimental procedure: In order to contrast the effluents quality treated by different processes, four experimental phases were conducted during this study. The first phase was wastewater (I) treated by biological reactor alone. The second phase was wastewater (I) treated by photocatalytic reactor alone. The third phase was wastewater (I) treated by photocatalytic reactor after biological reactor. The last phase was wastewater (I and II) treated by bio-photoreactor system. Fig. 1 is a schematic of bio-photoreactor system. There is no recycle water in phase 3 .

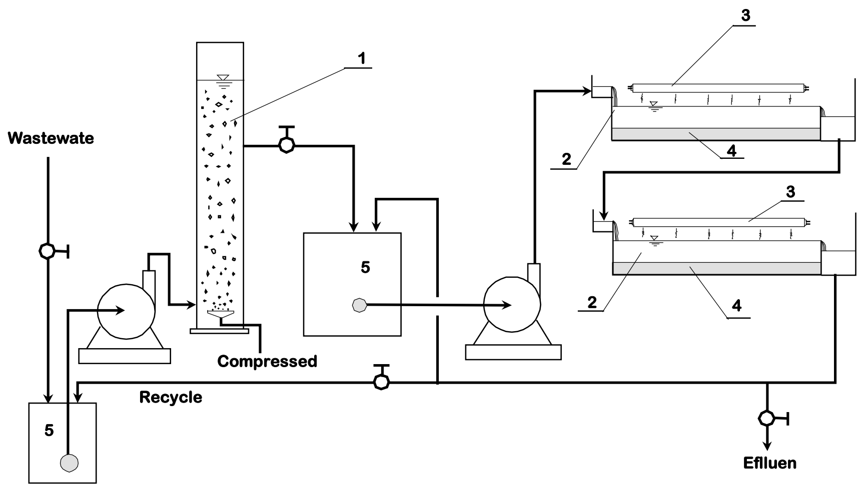


Fig.1. Schematic diagram of bio-photoreator

1: IDEA biological reactor 2: Photocatalytic reactor 3:UV light source (UV lamp or Sun)
4: TiO_2 coated zeolit 5: storage tank 6: pump

Apparatus: Three bio-photoreactor systems were used in this study simutaniously during the phase 4.

Biological reactors: Three intermittently decant extended aeration (IDEA) reactors were used in this study. The IDEA reactors were constructed of Perplex with a height of 100 cm and 10 cm ID. As shown in Fig. 1, influent was pumped into the reactor from the bottom and was supplied at a flow of 1 L/day/per reactor(HRT of 3 days) through the Masterflex Microcessor pump duriug all phases. Aeration and settling time was controlled by the timer and the ratio of which was controlled at 5:1 during the study. During the first phase, the sludge age (HRT) of IDEA reactor was different (10, 20 and 30 days respectively)for each reactor to evaluate optimum operating condition. At phase 3 and 4 ,the HRT of each reactor were 20 days. Before collecting the experimental data, each IDEA reactor was allowed an acclimation period of 2 months.

Photocatalytic reactor: Reciculating batch plate type photocatalytic reactors were used in this study. Each photocatalytic reactor was a pane 60 cm long by 8 cm wide with 3 cm wall height and constructed of Pyrex glass. While it was working, a Masterflex Microcessor pump was used for recirculation of the solutions in the range of flow rates from 100 to 130 L/min. The photocatalyst used throughout the course of this study was titanium dioxide (TiO_2) with coated natural zeolite (0.8 to 1.8 mm). Each photocatalytic reactor contain 150g zeolite coated with 4g TiO_2 except phase 3. A 365 nm NEC blacklight lamp (T10 20W) was installed at each photoreactor 1.5 cm above the water surface (except phase 3) as an UV light source, which provides 30W/m^2 light intensity on the water surface. During the third phase, 1.5g TiO_2 coated 150g zeolite was also used and the lamp was 3 cm above the water surface (20 W/m^2) to study various photocatalytic reaction conditions. As shown in Fig. 1, each bio-photoreactor system contain two photocatalytic reactors, that were connected in series.

Materials: Titanium dioxide (TiO_2) was purchased from BDH with GPR grade and used as a catalyst without any further purification. Zeolite was purchased from the Zeolite Australia Company and washed in the boiling water for 2 h to remove dirty and vegetable matter. The zeolite was coated with TiO_2 by preparing a suspension of 1.5 ~ 4g TiO_2 in 150 ml distilled water (with sonication for 10 minutes), adding 150g of zeolite to the sonicated suspension and evaporating to dryness in an oven at 105 ^{O}C. the coated zeolite was then heated at 550 ^{O}C for

0.5h. Other chemicals used in this study were purchased from Flukachemie AG of Switzerland. The dyes were commercial dyes used in Hong Kong textile industry.

Analyses: The colour of the wastewater was measured by a Tintometer (Model E AF 900) with 1 inch optical glass cell channel and expressed as red (R) and yellow (Y) read directly from the meter. COD, BOD, dissolved oxygen ,pH and MLVSS were measured by the standard methods. After acclimatising, samples for COD, BOD and MLVSS were collected twice per week from the bioreactors or bio-photoreactor system.

RESULTS AND DISCUSSION

The wastewater treated by biological reactor alone: After acclimatising, the performance of COD, BOD and colour of IDEA bioreactors is shown in Table 2.

Table 2. The performance of IDEA bioreactor *

Reactor No.		1	2	3
HRT	(day)	3	3	3
SRT	(day)	10	20	30
MLVSS	(g/L)	0.62~0.67	0.73~0.76	0.97~1.02
Effluent COD	(mg/L)	335~358	310~340	302~336
Removal of COD	(%)	58.9~59.9	61~62.5	61.8~63.6
Effluent BOD	(mg/L)	24 ~ 27	22.8~23.8	24~26.4
Removal of BOD_5	(%)	92.8~92.9	93.2~94	92.8~93
Effluent red colour **		25	25	25
Effluent yellow colour **		6.0	6.0	6.0
pH		7.32~7.38	7.21~7.35	7.35~7.42

***** The characteristic of influent see wastewater I of table 1.

****** The colour unit: Lovibond unit with 1 inch optical glass cell channel..

As shown in Table 2, under the extended aeration condition, high BOD removals above 92% were achieved in the reactors, while the highest rate of BOD removal was obtained in No. 2 reactor with a SRT of 20 day. At same time, the COD reductions were only achieved between 50 to 64% in the three reactors, while the highest COD removal of 63.8 % was found in No. 3 reactor with a SRT of 30 day. The results confirmed that conventional aerobic process could only achieve a limited COD reduction, due to the nonbiodegradability of those dye chemicals, and a longer SRT could enhance the biodegradability of the system. The results showed that yellow colour removals were about 14% and no red colour removal was achieved in all reactors As we all known, the reactive dye is nonbiodegradable, especially for the red reactive dye. So it is worth notice that biological oxidation in the IDEA shown no red colour decrease during the treatment since the source of red colour comes from reactive dye (Cibacron Red FB). According to the results described in Table 2, all IDEA reactors' SRT were 20 days during the flowing study.

The wastewater treated by photocatalytic reactor alone: Figure 2 illustrates the procedure of dye wastewater (wastewater I of Table 1) treated by photoreactor without any pre-treatment. Although photocatalytic oxidation can decolorize the dye wastewater effectively, a very long period is required for the procedure. It doesn't seem to be economical in the real factory.

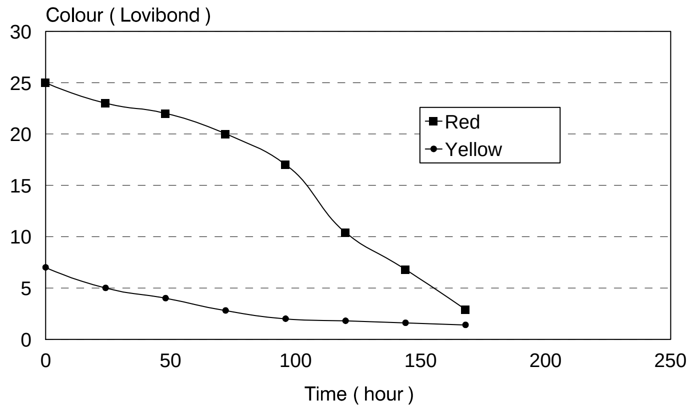


Fig. 2. Decolorization of dye wastewater by photoreactor
Illumination area =48 cm^2 ;wastewater volume = 1.2L; light =30 w/m^2;
recirculation flow rate = 200 ml/min; 1.5g TiO_2/ 150g zeolite,

__The wastewater treated by photocatalytic reactor after biological reactor:__ The dye wastewater treated by No. 2 IDEA biological reactor was used for experiment of various photocatalytic decolorization and removal nonbiodegradable matter condition. Figure 3 illustrates the effects of light intensity and the amount of TiO_2 photocatalyst on the rate of decolorization of wastewater. As other researchers pointed, photocatalytic oxidation in presence of TiO_2 has been demonstrated to be effective in totally decolorizing most dyes. From Figure 3, we can conclude that the decolorization rate of reactive dye is lower than other dyes and the rate of photocatalytic oxidation reaction is a first-order behaviour. As shown in figure 3, the rate of decolorization of 4 g TiO_2 coated 150 g zeolite under 30 W/m^2 light intensity is two times of 1.5 g TiO_2 coated 150 g zeolite under 20 W/m^2 light intensity. It demonstrated that the catalyst concentration and light intensity are also important factors of the reaction rate. In the contrast to Figure 2, the illumination time of the photoreactor treating dye wastewater after bioreactor can be shortened to 10% of that without biological treatment at the same operating conditions.

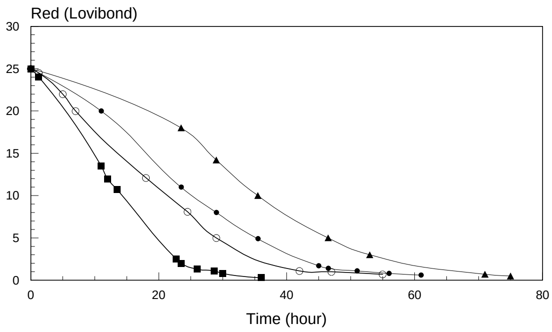
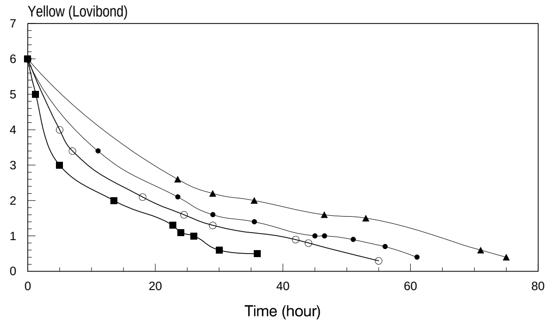


Fig. 3. Decolorization of dye wastewater by photocatalytic reactor after biological reactor
Illumination area =48 cm^2 ;wastewater volume = 1.2L; recirculation flow rate = 200 ml/min;
♦ 1.5g TiO_2/ 150g zeolite, light =20 w/m^2; ● 1.5g TiO_2/ 150g zeolite, light =30 w/m^2;
❍ 4g TiO_2/ 150g zeolite, light =20 w/m^2; ■ 4g TiO_2/ 150g zeolite, light =30 w/m^2.

Two series connected photocatalytic reactors (8g TiO_2 coated 300g zeolite; the light intensity 30 W/m^2) were used to investigate the variation of COD and BOD during the photocatalytic oxidation. The result of the test, as shown in Figure 4, indicate that BOD in the wastewater was increased while the COD was decreased during the reaction. It demonstrated that the reaction in the photoreactor can break down specific bonds or to rearrange molecular structures of some nonbiodegradable organic and convert them to biodegradable forms. There is a slight decrease of pH during the period from the 5th to 20th hour, while the decolorization and the removal of COD were at their higher rates. It may indicate that the medium products of reaction could be some organic acid or the result of accumulation of the final product (CO_2) of the reaction.



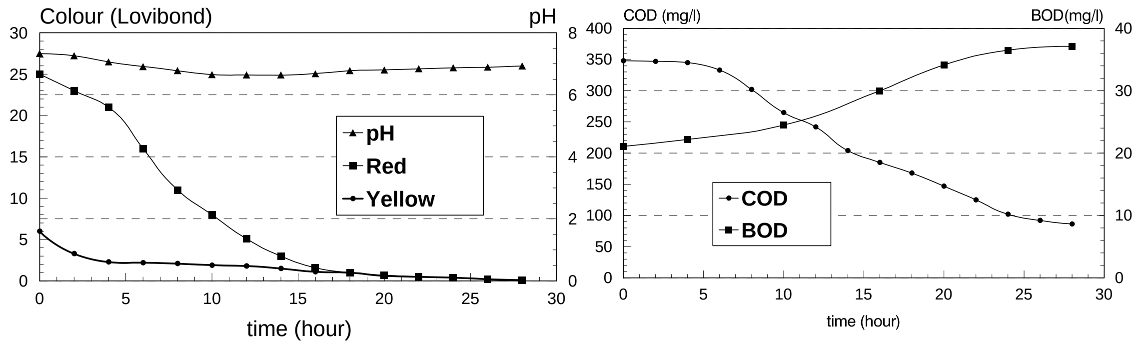


Fig. 4. Variation of COD and BOD during the photocatalytic decolorization
Illumination area = 96 cm^2; wastewater volume = 1.2 L; recirculation flow rate = 200 ml/min.

The wastewater treated by bio-photoreactor system: The results of the bio-photoreactor system treating different concentration synthetic dye wastewater (wastewater I of table 1) were presented in Table 3, Figure 5 and Table 4. As shown in Table 3, the BOD of effluent from the system with different recycle rate can be 5~10 mg/ L lower than that
of no recycle water system, when the COD of the system effluent was controled at about 80 mg/L lever, while the red and yellow colour were 0.2 (colourless under the nacked eye). It doesn’t seem to be economical as a longer illumination time is required

Table 3. The performance of bio-photoreactor system*

System No.	0#	1#	2#	3#
Recycle rate	0	0.5	1	1.5
Illumination time (h)	24	28	30	36
Photoreactor water volume (L)	1	1.5	2	2.5
Bioreactor effluent COD (mg/L)	310~340	250~286	217~234	161~171
Bioreactor effluent BOD (mg/L)	22.8~23.8	18.6~21.4	15.5~16.2	13.7~15
Bioreactor effluent colour**	R=25,Y=6	R=19,Y=3.5	R=16,Y=3.5	R=13,Y=3.5

System effluent COD (mg/L)	78~80	81~84	76~84	81~87
System effluent BOD (mg/L)	36~37	30.5~34.5	32.6~34.9	29.2~33.5
Remove of COD (%)	90.4~91	90.2~90.8	90.8~91.3	90.2~91.6
Remove of BOD_5 (%)	88.8~90.4	90.4~91.2	89.9~91.2	90.8~91.3
System effluent colour**	R=Y=0.2	R=Y=0.2	R=Y=0.2	R=Y=0.2

* The characteristic of influent see wastewater I of table 1.

** The colour unit: Lovibond unit with 1 inch optical glass cell channel..

by the system with recycle water. But the system has many advantages in dealing with the impact load and treating higher concentration dye wastewater (as shown in Figure 5 and Table 4).

Figure 5 shows the values of COD and BOD of influent and effluent from each system during the impact test. Although the COD and BOD of influent were changed to 3 times the normal conditions, there are only one day's COD changed from 1.5 to 1.9 times the normal conditions and no any effects on BOD for the system with different recycle rate.

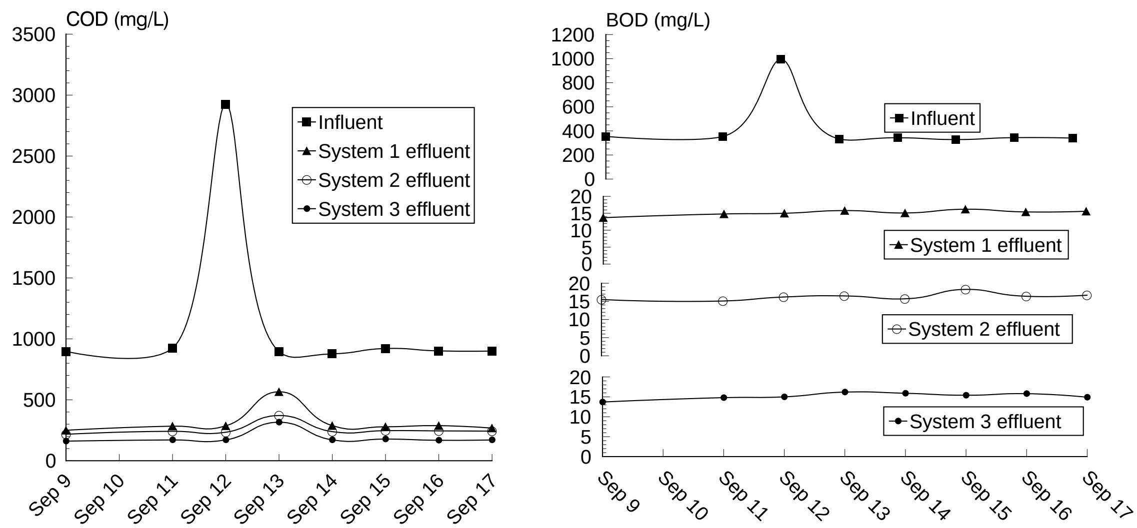


Fig 5. The results of impact test on bio-photoreactor system

Because the bio-photoreactor system with recycle water can dilute the concentration of toxic matter for biomass in the influent, it can be utilized to treat dye wastewater with higher concentration. Although the COD concentration of influent was raised to about 3000 mg/L, over 95% removal rates of COD and BOD can be obtained (see Table 4) for the bio-photoreactor system. The higher the recycle rate, the higher the BOD removal

Table 4. The performance of bio-photoreactor system treated high concentration dye wastewater*

System No.	1#	2#	3#
Recycle rate	0.5	1	1.5
Illumination time (h)	32	36	44
Photoreactor water volume (L)	1.5	2	2.5
Bioreactor effluent COD (mg/L)	334~374	253~308	233~294
Bioreactor effluent BOD (mg/L)	24.8~29.3	19.3~20.3	14.9~18.8
Bioreactor effluent colour**	R=24; Y=5.1	R=22; Y=4.1	R=21; Y=4.0
System effluent COD (mg/L)	79~83	78~84	80~88
System effluent BOD (mg/L)	34.7~39.4	30.4~40.3	29.4~35.3
Remove of COD (%)	96.9~97.1	96.9~97.2	97.0~97.1
Remove of BOD_5 (%)	95.5~95.8	95.6~95.8	96~96.5

System effluent colour**	R=Y=0.2	R=Y=0.2	R=Y=0.2

* The characteristic of influent see wastewater II of table 1.

** The colour unit: Lovibond unit with 1 inch optical glass cell channel..

rate of the system, when COD of the effluents were controlled at same level. On the contrary, the biological reactor of the system without recycle water didn't work well, as some of toxic matter in the wastewater is higher than the limits of the biological treatment.

On the other hands, the quality of effluent from the bio-photoreactor system may be good enough (colourless; SS < 10 mg/L and pH ≈ 7) to reuse in the textile factory.

CONCLUSION

The biological reactor and photocatalytic reactor were combined as a bio-photoreactor system. The two kinds of synthetic dye wastewater consisting three different commercial dyes were treated by bio-photoreactor system to study its removal efficiency of organic matter and decolorization. According to the experimental data, some conclusions can be drawn as follows:

- The photocatalytic oxidation can be effectively used as a supplementary process to improve the quality of the textile effluent treated by biological process. The process use in this experiment may be the most economical and effective one.
- The bio-photoreactor system is proved to be effective in totally decolorizing the dye wastewater (to colourless)and has higher COD removal rate (over 90%).
- The bio-photoreactor system with recycle water between the bioreactor and photoreactor has enough capacity to resist higher impact load.
- Because the bio-photoreactor system with recycle water can dilute the concentration of toxic matter for biomass in the influent, it can be utilized to treat dye wastewater with higher concentration (about 3000 mg/L). In this case, over 95% COD and BOD removal rate can be obtained.

REFERENCES

Barnes, D.; Coan, E. and Li, X. , (1987). Catalyzed Decomposition of Chlordane, *Proceedings of Australia Second National Hazardous Waste Management Conference. 1987, Nov. , Sydney*.

N. Z. Muradov, Detoxification of Nitroglycerine-contaminated Water Using Immobilized Titania, *Solar Energy, Vol.52, No. 3, pp.283--288.*

P. Reeves, R.Ohlhausen and D. Sloan, Photocatalytic destruction of organic dyes in aqueous TiO_2 suspensions using concentrated simulated and natural solar energy, *Solar Energy, Vol. 48, No. 6 (1992)pp 413--20*

R. W. Matthews, Potooxidative Degradation of Coloured Organic in Water Using Supported Catalysts TiO2 on Sand, *Water Research Vol. 25, No.10. pp 1169--1176*

R. J.Davis, J. L. Gainer and G. O'Neal, Photocatalytic Decolorization of WastewaterDyes, *Water Env, Res. Vol.66 No.1, pp50--53, 1994*.

C. P. Huang, C. D. Dong and Z. H. Tang, Advanced Chemical Oxidation: Its present Role and Potential Futuren in Hazardous Waste Treatment, *Waste Management, Vol. 13 (1993), pp. 361--77*