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ON-SITE TREATMENT OF DYEING WASTEWATER BY A BIO-PHOTOREACTOR SYSTEM

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ABSTRACT

Synthetic dyeing wastewater consisting of the three different commercial dyes with different strengths of COD (about 900 and 3000 mg/l respectively) was initially treated by an aerobic biological process, Intermittently 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 photo-oxidation process can degrade those non-biodegradable organic substances in the effluent treated by the IDEA process and also decolorize the effluent completely. It is also found that some nonbiodegradable organic substances 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 recirculation was investigated and compared. The system with recycled water has similar efficiency for decolorization and COD removal to that without recirculation, but has a high capacity to eliminate the effects caused by a shock loading, and also the system can treat dyeing wastewater with a higher organic concentration. © 1997 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Dyeing wastewater; biological treatment; photocatalytic oxidation; titanium dioxide; decolorization; sensitized photo-oxidation.

INTRODUCTION

The main pollution sources of the textile wastewater in Hong Kong come from dyeing and finishing processes, which create a significant proportion of water pollution. Application of conventional biological processes in the treatment of textile wastewater has been extensively reported (Reeves *et al.*, 1992; Li and Zhang, 1996; Muradov, 1994; Ollis *et al.*, 1991). However, there is a practical limit to the degree of COD removal and colour removal due to the inability of biological treatment processes in degrading dye chemicals. With different types of activated sludge processes, the following limited removals are normally achieved: about 90% of BOD_5, 40-50% of COD and 10-30% of colour (Li *et al.*, 1992, 1996; Keddie and Giannelis, 1991). As a result, there has been an increasing awareness of alternative or supplementary treatment processes (Ahmed and Ollis, 1984; Matthews, 1986; Davis *et al.*, 1994; Huang *et al.*, 1993; Matthews, 1991; Mayanair *et al.*, 1993; Muradov, 1994).

This study was designed to investigate the use of a TiO_2 photocatalytic process for the decolorization of synthetic dyeing wastewater, in which TiO_2 was coated on the surface of natural zeolite in a heterogeneous reactor. This sensitized photo-oxidation process was also combined with a biological treatment process to consist of an enhanced treatment system, a bio-photoreactor, for a complete decolorization and high degree of COD removal from dyeing wastewater as an on-site treatment system.

MATERIAL AND METHODS

Dyeing wastewater

Synthetic wastewater samples used in this study were prepared by using three different types of dye chemicals, which are reactive dye (Cibacron Red FB), disperse dye (Dispersal Yellow C-4R) and direct dye, (Solophenyl Orange T4RL), based on the recipes of a textile industry in Hong Kong. Other nutrition required by microbes was also added to the wastewater with a BOD:N:P ratio of 100:5:1. Two different strengths of the synthetic dyeing wastewater were used in this experiment and characterised as shown in Table 1.

Table 1. Characteristics of synthetic dyeing wastewater

Wastewater	COD	BOD_5	Reactive	Disperse	Direct	Colour (Lovibond)		pH
Sample	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	Red	Yellow	
I	830~930	320~390	100	80	80	25	7	~7
II	2600~3000	700~900	200	150	150	40	20	~7

Catalyst

Iitanium dioxide (TiO_2) was purchased from BDH with Gpr grade and used as a catalyst without any further purification. Zeolite was purchased from Zeolite Australia Company and washed in boiling water for 2 hours to remove dirty and vegetable matters. The zeolite was coated with TiO_2 by preparing a suspension of 1.5 ~ 4 g of TiO_2 in 150 ml distilled water (with sonication for 10 minutes), adding 150 g of zeolite to the sonicated suspension and finally evaporating to dryness in an oven at 105°C. The coated zeolite was then heated at 550°C for 0.5 hour. Other chemicals used in this study were purchased from Flukachemie AG of Switzerland. The dyes were commercially available, and are used in Hong Kong textile industry.

Experimental procedure

In order to compare the effluent quality treated by different processes, four experimental phases were conducted during this study. In the first phase, wastewater (I) was treated by a biological reactor alone. In the second phase, wastewater (I) was treated by a photocatalytic reactor alone. In the third phase, wastewater (I) was treated by the bio-photoreactor system without recirculation. In the last phase, wastewater (I and II) was treated by the bio-photoreactor system with recirculation.

Equipment

A schematic diagram of the bio-photoreactor system is shown in Fig. 1, which consisted of two types of reactors.

Biological reactors: An Intermittently Decanted Extended Aeration (IDEA) reactor was used as an aerobic process, which was constructed of perspex with a height of 1 m and ID of 100 mm. As shown in Fig. 1, influent was pumped into the reactor from the bottom by a Masterflex Microcessor pump at a flow rate of 1 l per day and retained for 3 days (HRT = 3 days). Aeration and settling periods were controlled by a timer with a ratio of 5:1 during the experiment. In the first phase study, the sludge ages (SRT) of 10, 20 and 30 days were used in three IDEA reactors respectively, to evaluate an optimum operating condition. In phase 3 and 4 studies, a HRT of 20 days was used in each reactor. After a period of 2 months acclimation, the system reached a stabilised condition.

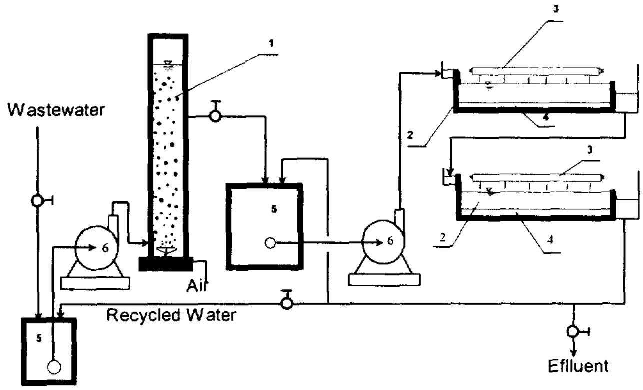

Figure 1. Schematic diagram of bio-photoreactor system. 1: IDEA biological reactor; 2: photocatalytic reactor; 3: UV source (UV lamp); 4: TiO_2 coated zeolite; 5: storage tanks; 6: pumps.

Photocatalytic reactor. Recirculating 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 perspex. 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. Titanium dioxide (TiO_2) was coated on the natural zeolite (0.8 to 1.8 mm). Each photocatalytic reactor contained 150 g zeolite coated with 4 g 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 30 W/m^2 light intensity on the water surface. During the phase 3 test, 150 g zeolite coated with 1.5 g TiO_2 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 contained two photocatalytic reactors, which were connected in series.

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) Lovibond unit. COD, BOD, dissolved oxygen (DO), pH and mixed liquor volatile suspended solids (MLVSS) were measured by the standard methods. After acclimatising, samples for COD, BOD and MLVSS determination were collected twice per week from the bioreactors or bio-photoreactor system. UV light intensity was measured by a Black-ray Ultraviolet Intensity Meter (Longwave meter, J-221, peak sensitivity approximately 365 nm).

RESULTS AND DISCUSSION

Characteristics of dyeing wastewater treated by biological process alone

The dyeing wastewater sample I was biologically treated in the IDEA reactors, all of which were operated with same HRT (20 days) and different SRT (10, 20 and 30 days) during the study. After an acclimation period, the removals of COD, BOD and colour in the IDEA bioreactors were stabilised and experimental data are shown in Table 2. It is indicated that, under the extended aeration condition, the highest COD removal rate was obtained in No. 3 reactor (SRT = 30 day), but the highest BOD removal was obtained in No. 2 reactor (SRT = 20 day). A reduction of yellow colour around 10-15% was achieved in all reactors, while there was no significant reduction of red colour in this biological treatment due to the non-biodegradability of the red reactive dye (Cibacron Red FB).

Table 2. 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
F/M	0.415~0.438	0.355~0.383	0.274~0.279
Effluent COD (mg/L)	335~358	310~340	302~336
Removal COD (%)	58.9~59.9	61~62.5	61.8~63.6
Effluent BOD_5 (mg/L)	24 ~ 27	22.8~23.8	24~26.4
Removal 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

*Colour unit: Lovibond unit

Raw dyeing wastewater treated by photocatalytic reactor alone

The dyeing wastewater sample I with high strength organic and colour was also treated by the TiO_2 photoreactor without any pre-treatment. Figure 2 illustrates the decolorization and the variation of COD and BOD in the dyeing wastewater during this sole photocatalytic oxidation which was carried out under a light intensity of 30 W/m^2 with a main wavelength of 365 nm. It was found that the wastewater samples were purified to colourless and a high COD reduction (over 90%) was also achieved. However, a very long period of 200 to 250 hours was required for this heterogeneous reaction to achieve the complete decolorization and the high COD reduction due to the high strength of organic substances in the dyeing wastewater without any pre-treatment.

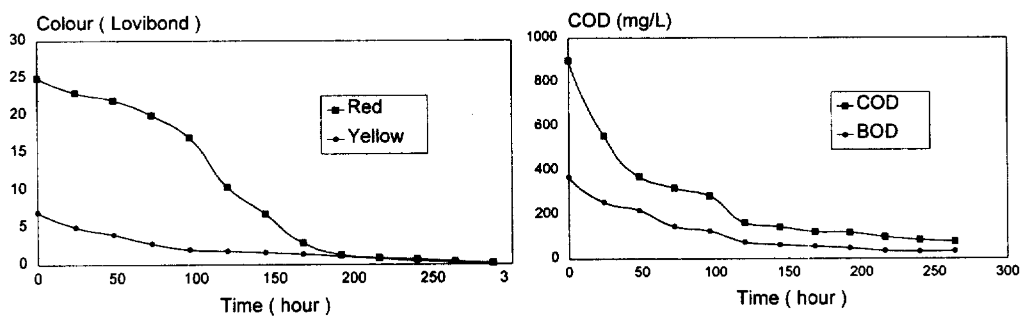

Figure 2. Decolorization of raw dyeing wastewater by photoreactor illumination area = 48 cm^2; Wastewater volume = 1.2 l; Light =30 W/m^2; Recirculation flow rate = 200 ml/min; 1.5 g TiO_2/150 g zeolite.

Wastewater treated by bio-photoreactor system without recirculation

A combined bio-photoreactor system was composed of an IDEA bioreactor and either one TiO_2 photoreactor (illumination area = 48 cm^2) or two (illumination area = 96 cm^2) in series as shown in Fig 1 but without recycle. The dyeing wastewater samples was primarily treated by the IDEA reactor (operational conditions as same as No. 2 reactor in Table 2) to mainly remove most biodegradable organic substances and then further treated by the TiO2 photoreactor to oxidise remaining dyes and other non-biodegradable substances in the dyeing wastewater. Figures 3 and 4 illustrate the effects of the light intensity and the amount of coated TiO2on the rates of the decolorization in one photoreactor system and the variation of COD and BOD in the two photoreactor system.

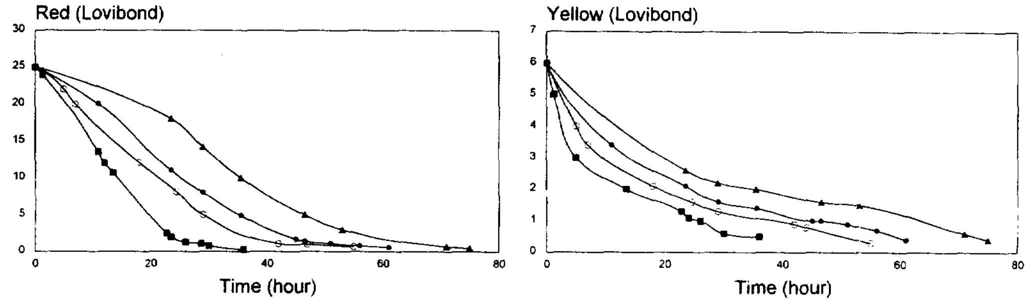

Figure 3. Decolorization of dyeing wastewater in the bio-photoreactor system without recycle illumination area = 48 cm^2; wastewater volume = 1.2l; Recirculation flow rate = 200 ml/min; (▲ 1.5 g TiO_2/ 150 g zeolite, Light = 20 W/m^2; (● 1.5 g TiO_2/ 150 g zeolite, Light = 30 W/m^2; (O 4 g TiO_2/ 150 g zeolite, Light = 20 W/m^2; (■ 4 g TiO_2/ 150 g zeolite, Light = 30 W/m^2.

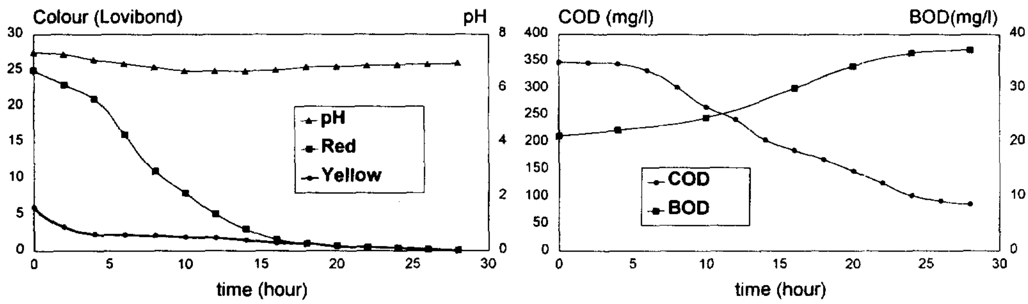

Figure 4. Variation of COD and BOD during the photocatalytic reaction Illumination area = 96 cm^2; Wastewater volume = 1.2 l; Recirculation flow rate = 200 ml/min.

The experimental results demonstrated that this photocatalytic oxidation in the presence of TiO_2 can be effective to completely decolorize the dyeing wastewater. The rate of decolorization was significantly affected by two factors which were the amount of TiO_2 coated on the zeolite (per gram) and light intensity. Figure 3 shows that the decolorization rate by using 150 g zeolite coated with 4 g TiO_2 under the irradiation of 30 W/m^2 light intensity is two times faster than that of coated with 1.5 g TiO_2 under irradiation of 20 W/m^2 light intensity. For a complete decolorization, the illumination time of the photoreactor treating this dyeing wastewater following the biological treatment can be shortened to only 20% (about 40-50 hours) of that without biological treatment in the same photo-oxidation conditions.

To investigate the variation of COD and BOD during the photocatalytic oxidation, two photocatalytic reactors (300 g zeolite coated with 8 g TiO_2 and light intensity = 30 W/m^2) were connected in series to treat the biologically treated dyeing wastewater. Figure 4 shows that the BOD in the wastewater increased while the COD decreased during the decolorization reaction. It indicated that the reaction in the photoreactor may break down specific molecular bonds or rearrange molecular structures of some organic complexes to simpler compounds, in which some nonbiodegradable organics were converted to biodegradable forms. A miniature decrease of pH during the reaction time of 5 to 15 hours was also observed, while decolorization and COD removal were achieving a high rate, that may be caused by the intermediates of some organic acids and the final product of CO_2 produced during the reaction.

Wastewater treated by bio-photoreactor system with recirculation

In this experiment, wastewater after photo-oxidation treatment was recycled to the IDEA reactor with different recycle ratios from 0 to 150%. The experimental results are presented in Tables 3 and 4 and Figure 5.

Table 3. Performance of bio-photoreactor system*

System No.	0#	1#	2#	3#
Recycle rate (R)	0	0.5	1	1.5
Illumination time (h)	24	28	30	36
Photoreactor volume (L)	1	1.5	2	2.5
Bioreactor eff. COD (mg/L)	310~340	250~286	217~234	161~171
Bioreactor eff. BOD (mg/L)	22.8~23.8	18.6~21.4	15.5~16.2	13.7~15
Bioreactor eff. colour**	R=25,Y=6	R=19,Y=3.5	R=16,Y=3.5	R=13,Y=3.5
System eff. COD (mg/L)	78~80	81~84	76~84	81~87
System eff. BOD (mg/L)	36~37	30.5~34.5	32.6~34.9	29.2~33.5
COD Removal (%)	90.4~91	90.2~90.8	90.8~91.3	90.2~91.6
BOD_5 Removal (%)	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

* Characteristic of influent see wastewater I in table 1.

** Colour unit: Lovibond unit

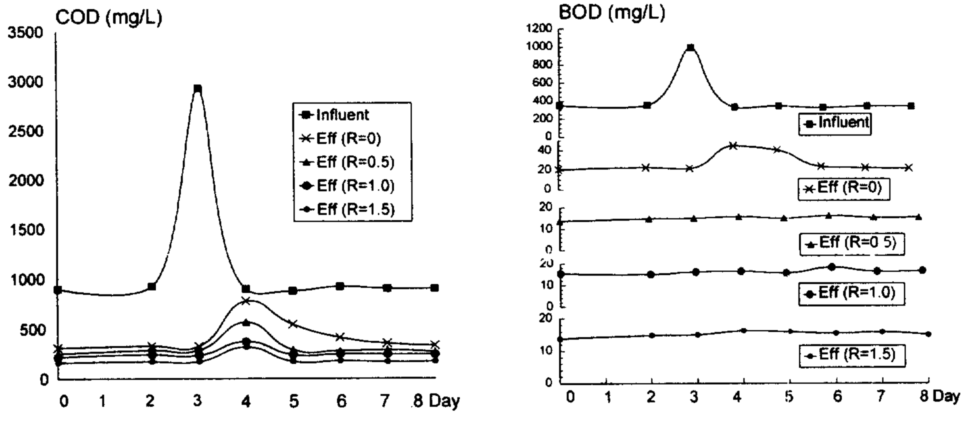

Figure 5. Results of shock loading test in bio-photoreactor system.

The results show that the BOD of effluent from the system with different recycle ratios can be reduced to 5~10 mg/l, which was lower than that of the system without recirculation. In shock loading test, while the COD of influent was suddenly increased about 3 times higher by a shock loading injection, the COD of effluent was only increased about 1.5 to 1.9 times higher for a recycle ratio from 150% to 50% and no significant increase of the BOD concentration of effluent was found in the system with recirculation.

The bio-photoreactor system with recycled water can dilute the concentration of toxic matters, which would be an advantage for treating high strength dyeing wastewater. To test the tolerant ability of the system with recirculation to a higher organic strength, the COD concentration of influent raised up to about 3000 mg/L and an over 95% removal of COD was still achieved (as shown in Table 4).

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

Table 4. Performance of bio-photoreactor system to treat high concentration dyeing wastewater*

System No.	1#	2#	3#
Recycle rate (R)	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
COD Removal (%)	96.9~97.1	96.9~97.2	97.0~97.1
BOD_5 Removal (%)	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 sees wastewater II in table 1.

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

CONCLUSIONS

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

Photocatalytic oxidation can be effectively used as a supplementary process to improve the quality of the textile effluent treated by a biological process. The process used in this experiment is a very economical and effective method.

Bio-photoreactor system is proved to be effective in totally decolorizing the dyeing wastewater (colourless) and has a high COD removal rate (over 90%).

Bio-photoreactor system with recirculation between the bioreactor and photoreactor has enough capacity to abate a shock loading effect.

Bio-photoreactor system with recirculation can dilute the concentration of toxic matter, which would be suitable for treating dyeing wastewater with high organic strength.

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