DECOLORIZATION AND BIODEGRADABILITY OF DYEING WASTEWATER TREATED BY A TIO_2-SENSITIZED PHOTOOXIDATION PROCESS

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ABSTRACT

Colour substances in dyeing effluents normally cause certain difficulties in traditional biological treatment processes due to their nonbiodegradable nature. It is necessary to remove colour from dyeing effluents with the help of some physical or chemical treatment processes. This study aims to investigate the colour removal from dyeing wastewater by a TiO_2-sensitized photooxidation process and the biodegradability of the products formed in the wastewater. Synthetic dyeing wastewater samples were exposed to a near UV radiation at a wavelength of 350 nm with the present of TiO_2 and aeration. The results show that the most dyes used in the experiment can be degraded by the sensitized photooxidation successfully. Colour removal from the wastewater was above 95% after 4 - 6 hours treatment. It was found that the relationship between the COD, TOC and BOD was interacted. While COD and TOC in the wastewater were decreased during the reaction, BOD was found to be increased, which implies that the TiO_2 -sensitized photo-oxidation can enhance the biodegradability of the dyeing wastewater. As a process, it might be an effective method to remove colour and to further remove COD after dyeing effluent treated by a conventional biological treatment process.

KEYWORDS

Sensitized photooxidation; sensitizer; photooxidation; titanium dioxide; colour; color; dye; wastewater; dyeing effluent; treatment;

INTRODUCTION

For the textile industry in Hong Kong, the main pollution source of wastewater comes from the dyeing and finishing processes. Major pollutants include high suspended solids (SS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), heat, colour, acidity, basicity and other soluble substances. The colour of wastewater has difficulties to be effectively removed through the most biological treatment processes due to the limited biodegradability of dying chemicals.

Since the role of sunlight in modifying organic compounds in the environment has been recognized, a newly developed photochemical technology called the sensitized photo-oxidation reaction is based upon the wavelength range of radiation close to sunlight, using a sensitizer and molecular oxygen system.

(Matthews, 1990; Ollis, *et al*., 1990). In the semiconductor-sensitized photo-oxidation process, metal chalocogenide semiconductors (TiO_2, ZnO, C_dS, WO_3, and SnO_2) have been widely utilized in photocatalytic processes destined for energy production (formation of chemical fuels) and degradation of environmental contaminants via light-induced redox reactions at the semiconductor/solution interface. These are light-induced redox reactions involving the generation of conduction band electrons and valence band holes by near UV illumination of the semiconductor material with suitable bandgap light energy. Many studies on semiconductor sensitized photodegradation have been carried out since the mid 70's, in which titanium dioxide powder was used as the most popular sensitizer either in slurry suspension or coated on the surface of solid media. This method has been fully investigated for the degradation of many refractory organics such as halogenated organics in synthetic aqueous solution and natural water systems (Matthews, 1986; Pruden and Ollis, 1983). The research presented in this paper is designed to investigate the relationship between decolorization of dyeing wastewater and biodegradability of the products formed in the sensitized photooxidation.

METHODOLOGY

Material and equipment

Five series of commercial dyes were used to prepare simulated dyeing wastewater in the laboratory. They were reactive dye, disperse dye, sulphur dye, direct dye and vat dyes, which are intensively used in dyeing and finishing industry today. Titanium dioxide (TiO_2) was purchased from BDH with GPR grade and used as a sensitizer without any further purification. Slurries of TiO_2 were prepared by mixing the powder with the synthetic dyeing solutions and then ultrasonicated for 15 minutes before use. The experiments consist of two stages. The purpose of the first stage is to preliminarily determine an optimum pH condition for colour and COD reduction. A batch reactor system was used as shown in Figure 1. In the system, 100 ml beakers were used as reactors and a NEC blacklight lamp (T10 20W) was used as an UV light source. The tests were performed at ambient temperature between 20 - 25 °C. The light intensity was 15.2 W/m^2. Compressed air was supplied to each reactor to saturate dissolved oxygen in the wastewater samples. Each test lasted for one hour with variation of initial pH around 3, 7 and 10.

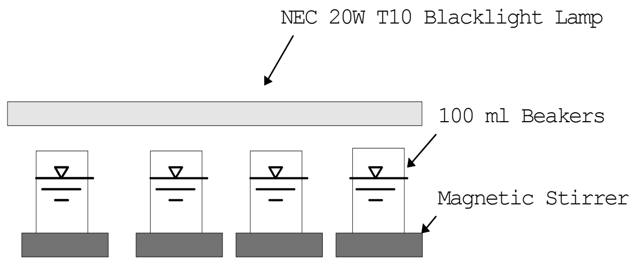


Figure 1 Batch Photoreactor System

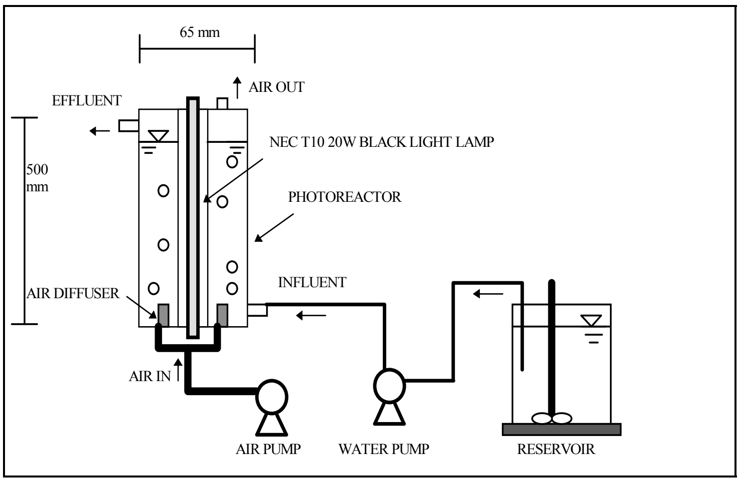


Figure 2. Continuous flow photoreactor system

The purpose of the second stage is to further investigate the reduction of colour interacted with COD, BOD, and TOC. All tests were performed in a continuous flow photo-reactor system as shown in Figure 2, which is a cylindrical borosilicon glass reactor with an effective volume of 1.1 litre. The NEC blacklight lamp (T10 20W) used in the preliminary study is placed at the centre of the reactor as an artificial light source to provide near UV radiation. The wastewater slurry as influent was pumped into the reactor from an inlet at bottom and effluent was collected from an outlet at top. Hydraulic retention time was up to 6 hours for a complete decolorization of the wastewater samples.

Analyses

COD, BOD, dissolved oxygen (DO), pH and temperature were measured by the standard methods. Total organic carbon (TOC) was measured by a TOC analyzer (Astro 2001 System 2) and colour was measured by a Tintometer (Model E AF900) with results expressed in Lovibond unit, which is a colour measurement method for industrial wastewater recommended by Hongkong Environmental Protection Department.

RESULTS AND DISCUSSION

Preliminary study

To determine the optimum pH for the colour and COD removal in the TiO_2 sensitized photo-oxidation, 8 different dye chemicals (Caledon Green 4G, Caledon Orange 2RTD, Caledon Red FB, Dispersal Scarlet B-RN, Dispersal Yellow C-4R, Solophenyl Orange T4RL, and Hydrosol Yellow 3RT) were used as substrates in the wastewater samples and tested in the batch reactors. Reaction conditions include concentration of dyes = 100 mg/L, concentration of TiO_2 = 1000 mg/L, light intensity = 15.2 W/m^2 and reaction period = 1 hour. For each dye chemical, three tests were performed with the captioned conditions except for different initial pH at 3, 7 and 10. According to the results shown in Table 1, an optimum pH range for each dye chemical was determined based on the reduction of COD and colour after 1 hour photoreaction treatment, which indicate that acid condition can enhance the photo-degradation rates for most dye chemicals. A range of pH between 3 - 7 may be suitable for wastewater containing mixed dying chemicals such as real effluents from dyeing process.

Table 1. Preliminary results

Dye	Initial Data		Final Data						pH*
			pH = 3		pH = 7		pH = 10		
	COD (mg/L)	colour (*)	COD (mg/L)	colour (*)	COD (mg/L)	colour (*)	COD (mg/L)	colour (*)	
Dispersal Yellow C-4R	171.1	23.5	85.5	15.9	83.6	17.3	97.2	39.5	7
Dispersal Scarlet B-RN	147.4	12.2	81.6	13.1	95.3	13.6	112.8	14.9	3
SolophenylOrange T4RL	62.9	40.9	41.6	26.0	34.9	33.1	55.2	33.1	7
Solophenyl Brown 8RL	134.8	39.0	88.1	61.0	103.6	48.0	103.6	52.0	3
Hydrosol Yellow 3RT	32.8	10.5	16.4	0	3.1	0	58.4	58.4	7
Caledon Green 4G	482.3	-	263.2	-	414.4	-	457.0	-	3
Caledon Orange 2RTD	298.3	43.0	240.7	34.0	283.6	35	282.5	40.0	3
Cibacron Red FB	256.1	44.0	213.0	42.0	229.4	49	228.4	66.0	3

* Colour is expressed as Lovibond unit; pH* = Optimum pH

Some results show that the colour of the wastewater samples can be even darker after 1 hour treatment due to some intermediate products with new colour groups on the compounds, which will be discussed with the results from the experiment in Stage 2. Colour measurement using the Tintometer is based on Lovibond units at three different colour channels of red, yellow and blue. A colour shifting between different colours during the photo-oxidation reaction was also observed. An overall colour result can then be evaluated for the determination of treatment efficiency.

Decolorization

To investigate colour removal by the sensitized photo-oxidation, 8 dyeing chemicals were used in wastewater samples and tested within the optimum pH range determined in the preliminary study, which were Caledon Green 4G, Caledon Orange 2RTD, Caledon Red FB, Dispersal Scarlet B-RN, Dispersal Yellow C-4R, Solophenyl Orange T4RL, Solophenyl Brown 8RL, and Hydrosol Yellow 3RT. Exposure time at each test lasted for up to 6 hours when the complement of colour removal occurred. The results of colour reduction are shown in Figure 3. It was found that the colour in the synthetic wastewater mostly has a lag stage during the first hour photoreaction for all used dyeing chemicals and even an increase of colour during first hour was found for some dyeing chemicals such as Cibacron Red FB and Solophenyl Orange T4RL. An abrupt reduction of colour was found between 2 and 3 hours of exposure time as a critical period for a rapid disappearance of colour in wastewater samples. For most dyes used in the tests except for solophenyl Brown 8RL, a complete decolorization can be achieved by exposing the wastewater to TiO_2 sensitized photooxidation for 5 - 6 hours.

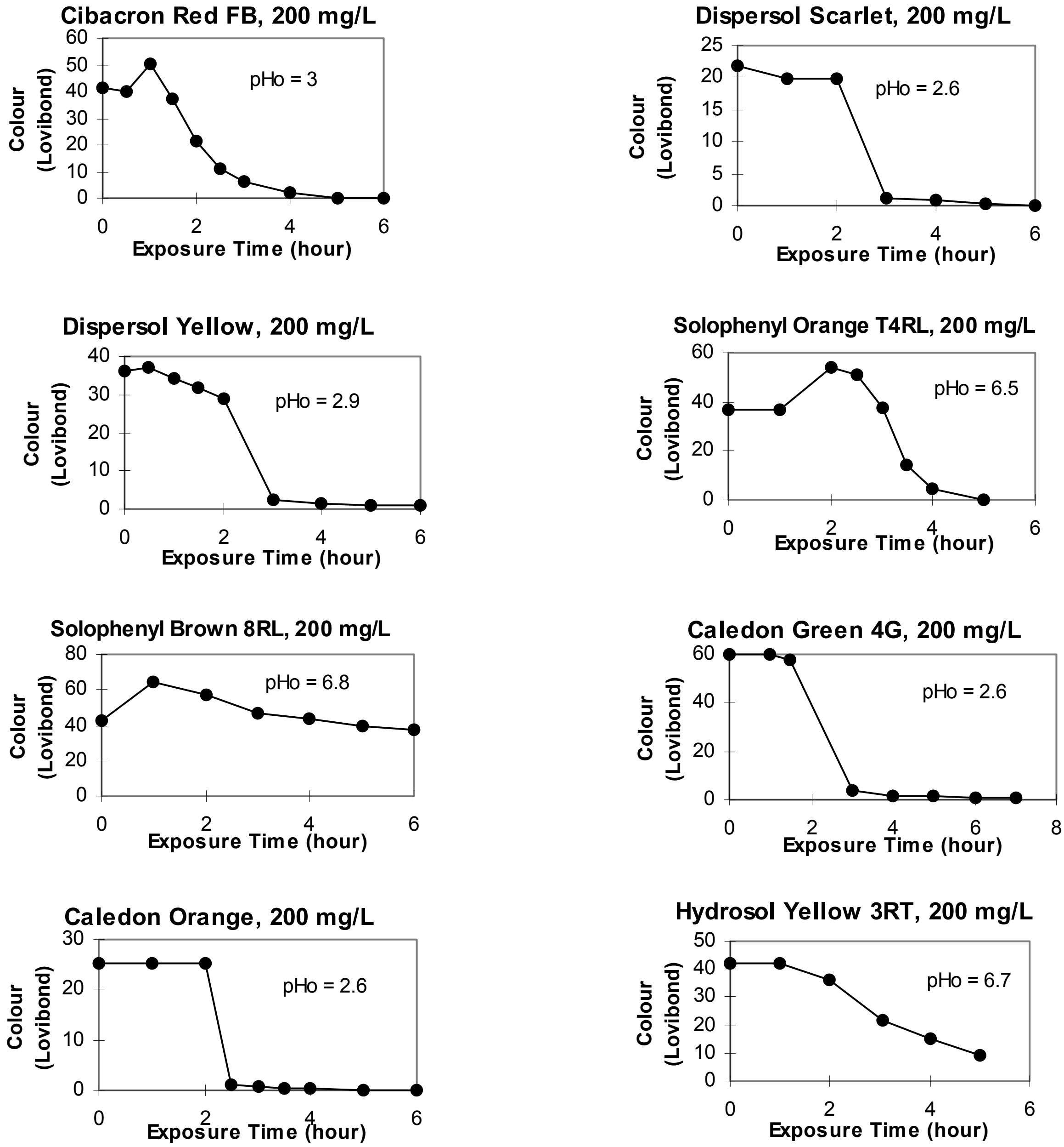


Figure 3. Decolorization of different dyeing wastewater samples

Biodegradability

To investigate the degradation of dyeing chemicals by photo-oxidation, 4 dyeing chemicals, Caledon Red FB, Dispersal Scarlet, Dispersal Yellow and Solophenyl Orange T4RL, were used in synthetic wastewater samples. Each wastewater sample was exposed to light irradiation for 6 hours and analytical samples were collected at t = 0, 3 and 6 hours for COD and BOD determination.

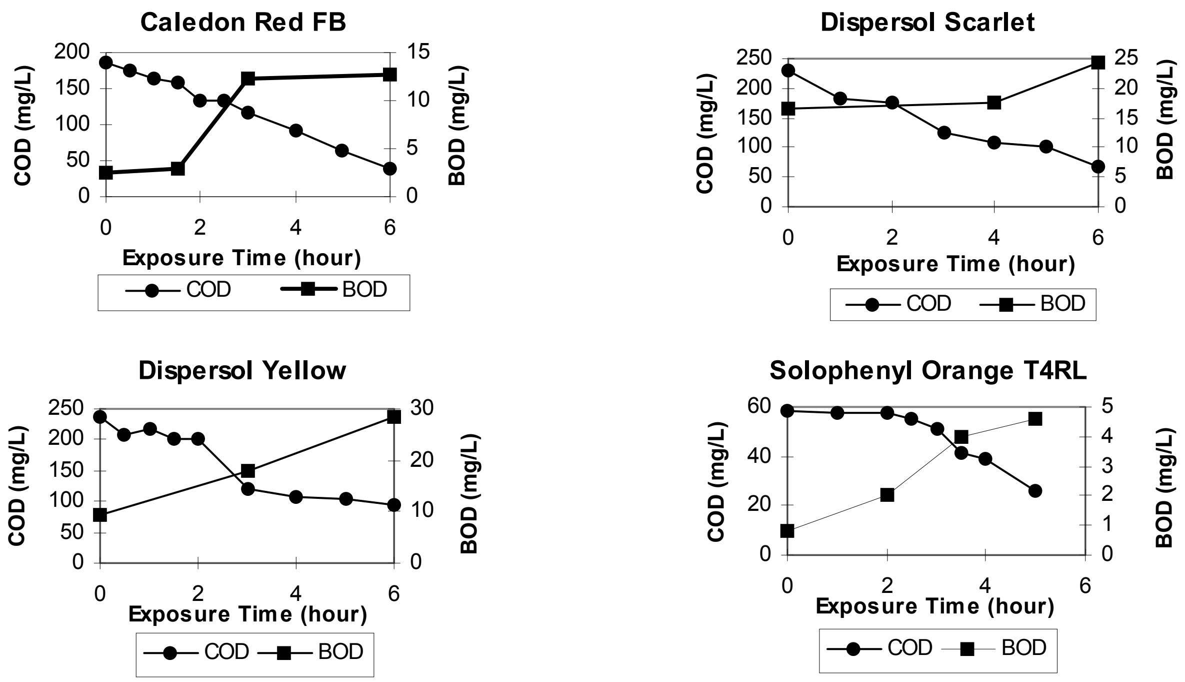


Figure 4. Variation of COD and BOD during the photo-oxidation

The results of tests as shown in Figure 4 indicate that BOD in the wastewater samples were increased after treatment for all cases of different dyeing chemicals, while the COD was decreased during the reaction. An decrease of pH in wastewater was also found after photo-oxidation. Specially the pH in those wastewater samples with initial neutral condition was significantly decreased from 6.5 to 3.2 as shown in Table 2.

Table 2. Decreases of pH in wastewater with different dyeing chemicals

Solophenyl Orange T4RL 200 mg/L		Solophenyl Brown 8RL 100 mg/L		Hydrosol Yellow 3RT 200 mg/L		Cibacron Red FB 200 mg/L	
t	pH	t	pH	t	pH	t	pH
0	6.48	0	6.76	0	6.71	0	2.95
1	5.67	1	6.21	1	6.30	1	2.52
2	5.14	2	5.86	2	5.51	2	2.43
2.5	4.42	3	5.73	3	3.79	3	2.39
3	3.98	4	5.71	4	3.19	4	2.38
3.5	3.61	5	5.70	5	3.09	5	2.37
4	3.35	6	5.94			6	2.37
5	3.20						

The increase of BOD may imply that biodegradability of the wastewater can be increased by the sensitized photo-oxidation reaction due to converting nonbiodegradable organics such as dyeing chemicals used to biodegradable forms. The decrease of pH may indicate that the biodegradable forms as the products of the reaction could be some organic acids.

A ratio of BOD/COD in wastewater is normally used to express the biodegradability of the wastewater. In these synthetic wastewater, the ratio of BOD/COD were initially low and significantly increased after treatment. The ratio of BOD/COD was changed from 0.05 to 0.35 depending on the nature of dyeing chemicals, which is shown in Figure 5.

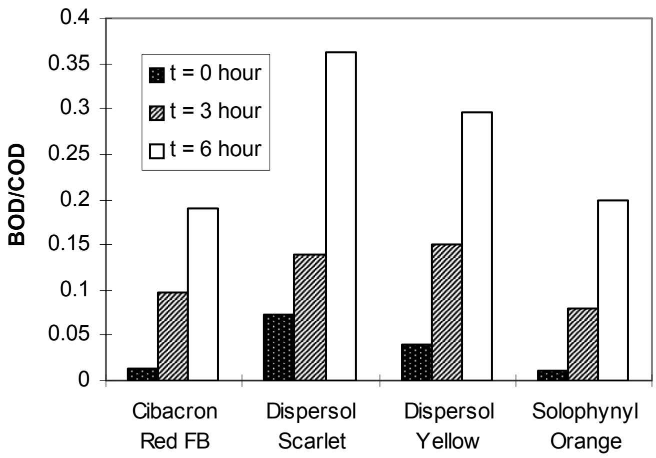
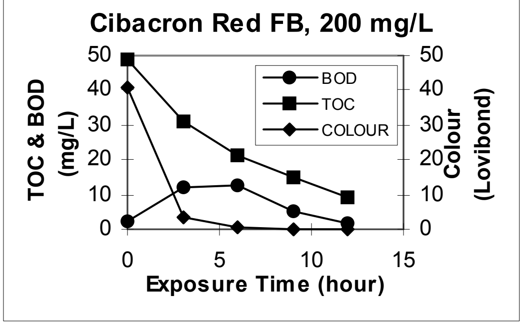


Figure 5. Increase of BOD/COD in wastewater with different dyeing chemicals

<u>Exposure time</u>

To determine the optimum exposure time of the reaction, two wastewater samples containing reactive dye and disperse dye were treated for a longer period of up to 12 hours and analytical samples were taken at retention time of 0, 3, 6, 9 and 12 hours for colour, TOC and BOD determination. Results show that the TOC in the wastewater were exponentially reduced against exposure time and the TOC reduction can be achieved up to 80% after 12 hours treatment. However, the BOD in the wastewater was initially increased and then decreased. A maximum BOD value occurred between 5 - 6 hours. The interactive relationship between decolorization and biodegradability as shown in Figure 6, indicates that a 5 - 6 hours retention time may be a critical period for this system to achieve a complete decolorization and also to improve the biodegradability of the dyeing wastewater, where minerallization is not a target for the dyeing wastewater treatment.



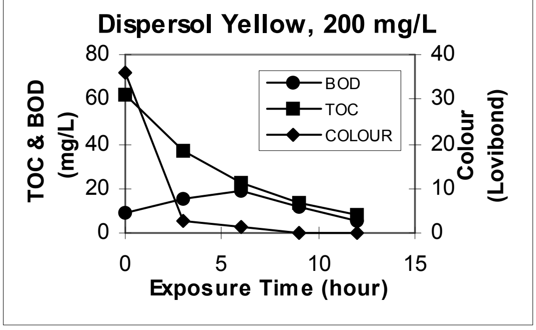


Figure 6. Interaction of decolorization and biodegradability

CONCLUSIONS

The synthetic wastewater containing 8 different dyeing chemicals were successfully decolorized by the TiO_2-sensitized photooxidation process. Above 95% of colour removal from the wastewater were achieved after 4 - 6 hours treatment for most used dyeing chemicals except solophenyl Brown 8RL. During the decolorization, COD and TOC in the wastewater were also reduced from 30 to 70 %, depending on the dyeing chemicals. It was found that BOD in the wastewater was increased after photo-oxidation. This implies that the biodegradability of the wastewater can be enhanced by the photo-oxidation. The sensitized photo-oxidation process could be one of the alternatives for decolorization and further COD removal of dyeing wastewater after a conventional biological treatment.

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