

## Degradation of *C.I. Reactive Orange 4* and its simulated dyebath wastewater by heterogeneous photocatalysis

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### Abstract

The commercial azo dye *C.I. Reactive Orange 4* in its reactive and hydrolysed forms can be efficiently photodegraded, using commercial samples of  $\text{TiO}_2$  as a photocatalyst. With UV light, aqueous solutions containing only dye and no dyebath additives are decolourised slightly more rapidly with Riedel-de-Haën  $\text{TiO}_2$  than with Degussa P-25  $\text{TiO}_2$ . The rate of decolourisation increases markedly with increasing pH. Sunlight is also very effective as a light source. On the other hand, comparison experiments involving UV irradiation of hydrolysed and unhydrolysed *Reactive Orange 4* in a simulated spent dyebath showed Degussa P-25  $\text{TiO}_2$  to be significantly the more efficient catalyst, giving more than 90% decolourisation after 20 min.

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### 1. Introduction

The textile industry is the largest consumer of colourants, using them in conjunction with a wide range of auxiliary chemicals for various dyeing, printing and finishing processes. Several dye application classes are utilised for cotton colouration, and of these reactive dyes are probably the most important. Irrespective of dye or fibre class, mill effluents are invariably deeply coloured by unabsorbed dyes, the extent of which varies according to the dye–fibre system. The treatment of industrial wastewaters in order to reduce visual colour and dissolved organic contaminants to meet increasing environmental demands has continued to attract the interest of research groups.

Most textile dyes are photolytically stable and refractory towards chemical oxidation [1] and these

characteristics render them resistant towards decolourisation by conventional biochemical and physico-chemical methods. Alternative methods, such as activated carbon adsorption and dissolved air flotation, are not only costly, but result in phase transfer of pollutants. Hence there is considerable current interest in developing alternative and more cost-effective methods.

The combination of UV irradiation with photocatalysts such as  $\text{TiO}_2$  is one of such methods which has attracted considerable attention in recent years, due to its effectiveness in mineralisation (i.e. conversion to inorganic species) of organic compounds [2–4]. This has included removal of dye pollutants from residual textile treatment waters [5–8]. Interest in this photocatalytic process stems mainly from its low cost, combined with the non-toxicity, insolubility, stability, and high photoactivity of the catalyst ( $\text{TiO}_2$ ). A further important advantage is the fact that the process can be powered by natural sunlight [9–13], thus reducing significantly the electrical power requirements and operating costs. It should be noted that with visible light, the photodegradation

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processes proceed by different routes, involving for example electron transfer from the excited state of the dye molecules adsorbed on the TiO<sub>2</sub> surface into the conduction band of TiO<sub>2</sub>. Such processes are less efficient than those occurring with UV light.

On the other hand, when aqueous TiO<sub>2</sub> suspension is irradiated with light energy greater than the band gap energy of the semiconductor ( $h\nu > E_g = 3.2 \text{ eV}$ ;  $\lambda < 390 \text{ nm}$ ), conduction band electrons ( $e^-$ ) and valence band holes ( $h^+$ ) are formed. The photogenerated electrons react with adsorbed molecular O<sub>2</sub>, reducing it to superoxide radical anion O<sub>2</sub><sup>•-</sup>, and the photogenerated holes can oxidise either the organic molecules directly, or can oxidise OH<sup>-</sup> ions and water molecules adsorbed on the TiO<sub>2</sub> surface to OH<sup>•</sup> radicals [2]. These will act as strong oxidising agents that can easily attack any organic molecules adsorbed on, or located close to, the surface of the catalyst, thus leading to their complete degradation into small inorganic species (Eqs. (1)–(5)) (Fig. 1).

Our previous studies on photocatalytic decolourisation of dyes [14] have now been extended to include the important reactive dye *C.I. Reactive Orange 4* (Fig. 2). This is a monoazo dichlorotriazinyl reactive dye [ICI (Zeneca) *Procion MX* type] that can be considered representative of the class. As a dichlorotriazinyl dye, it has a high reactivity towards nucleophiles, and readily undergoes dyebath hydrolysis [15]. It is applied to cotton at about 30 °C in the presence of common salt, and base (final pH 10.5–11.0), and other auxiliary products are generally present to aid dyeing. Dye fixation onto the fibre occurs by nucleophilic displacement of the reactive triazinyl chlorine atoms by ionised glycosidic hydroxyl groups of the cellulose, resulting in covalent bonding of the dye to the fibre by ether bonds. However, hydroxide ions in the dyebath can compete with the cellulose, so causing hydrolysis of the dye without fixation [16,17]. With the *Procion MX* dyes, the hydrolysed unfixed dye can amount to as much as 15–40% of the total applied [18], and this poses a major problem with highly coloured dyebath effluent. The present paper examines the efficiency of photocatalysis as a means of decolourising *C.I. Orange 4*, both in water alone and in a simulated dyebath effluent, and for this

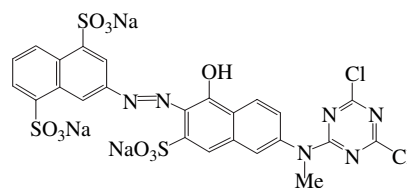


Fig. 2. Chemical structure of *C.I. Reactive Orange 4*.

purpose compares the relative efficacy of two commercially available photocatalysts, namely Degussa P-25 and Riedel-de-Häen TiO<sub>2</sub>.

## 2. Experimental

### 2.1. Materials

A commercial sample of *C.I. Reactive Orange 4* was used in this study, without further purification. The photocatalysts employed were technical grade TiO<sub>2</sub> Riedel-de-Häen and TiO<sub>2</sub> Degussa P-25. Additives for the preparation of the simulated dyebath effluent were from Bayer (Erkantol AS) and Sandoz (Sandopan CBH), and all other chemicals were of technical grade.

Adjustment of pH of the dye solutions prior to degradation was carried out with 6 M sodium hydroxide or 0.1 M perchloric acid.

Chemical oxygen demand (COD) measurements were carried out with a specific commercial reagent low range kit (HACH DR/2000).

### 2.2. Apparatus

UV–vis spectra were recorded on a Hitachi U-2000 spectrophotometer.

UV irradiation experiments were carried out using an immersion reactor fitted with a medium pressure 400 W Hg vapour lamp (Photochemical Reactors, Applied Photophysics, APQ 40). For sunlight exposure, a Pyrex flask of 22.5 cm internal diameter was used, and the light intensity was measured as 28,000–30,000 lux, using a Testo 545 lightmeter.

### 2.3. Irradiation and analysis of dye solutions

Three types of dye solution were investigated, all at a dye concentration of 38 mg/l: (a) the unhydrolysed dye in water alone; (b) the unhydrolysed dye in a simulated dyebath liquor; (c) hydrolysed dye in the same simulated dyebath liquor. The composition of the simulated effluent and the functions of the additives in the mixture are described in Table 1. A solution of unhydrolysed dye in this medium was prepared by mixing the components at room temperature and used as such. Conversion of the

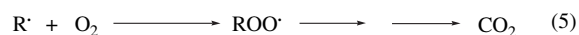
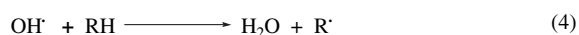
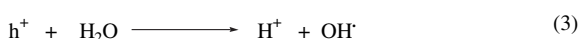
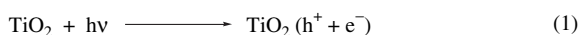


Fig. 1. Mechanism of the TiO<sub>2</sub>-catalysed UV oxidative degradation of organic species.

Table 1  
Composition of the simulated dyebath effluent

Component	Concentration (mg/l)	Function
Dye	38	—
NaCl	$1.2 \times 10^3$	Promotes exhaustion of the dye onto cotton
Na <sub>2</sub> CO <sub>3</sub>	5	Adjustment of the starting alkaline pH (8.8–9.3)
NaOH	5	Adjustment of the final dyeing pH (10.5–11.0) to cause further ionisation of the cellulose and dye–fibre reaction
Erkantol AS	10	Lubricant for fibre; minimises creases and rope marks
Sandopan CBH	20	Detergent for washing off
EDTA	10	Removes unwanted metal ions in the dyebath water
CH <sub>3</sub> CO <sub>2</sub> H	10	Reduces the alkalinity of the effluent

reactive dye into its hydrolysed form was ensured by heating the solution near the boiling point for 5 min and allowing it to cool overnight.

After addition of the required amount of photocatalyst, the dye solutions were magnetically stirred in the dark for 30 min to equilibrate. No adsorption of the dye on the catalyst (i.e. no change in the solution absorbance) was observed to occur during this period. Irradiation was then commenced and the dispersion was kept stirred throughout the duration of the experiment. Aliquots were removed at intervals and, after centrifugation and/or filtration through a 0.20  $\mu\text{m}$  syringe filter, the absorbance was read at 482 nm on a Hitachi UV-2000 spectrophotometer. Catalyst concentration was studied at 1 g/l and 360 mg/l. For the rate determinations, calibration curves for the dye in water were obtained at its  $\lambda_{\text{max}}$  (482 nm) at pH values of 10, 13 and 5.6 (pH of distilled water).

Blank experiments were also conducted (without TiO<sub>2</sub>) under sunlight and UV light irradiation.

#### 2.4. Kinetic analysis

In all the experiments the disappearance of the dye during the first 10 min of irradiation followed *pseudo* first order kinetics, as may be seen from the data of Table 2. Initial decolourisation rate constants were determined from the slope of  $\ln(C_0/C)$  vs  $t$  (min) plots, where  $C_0$  and  $C$  are the dye concentrations at zero time and time  $t$ , respectively. The value of  $C_0/C$  was taken as the ratio  $A_0/A$ , i.e. the absorbance value of the solution at  $\lambda_{\text{max}}$  at zero time divided by the absorbance at time  $t$ .

Table 2

Pseudo first order rate constants for the decolourisation of solutions of *Reactive Orange 4* (concentration 38 mg/l dye powder) (UV irradiation except where noted)

Solution <sup>a</sup>	[TiO <sub>2</sub> ] (type) <sup>b</sup> (g/l)	pH	$r^2$ <sup>c</sup>	$k$ (min <sup>-1</sup> ) <sup>d</sup>
Aqueous	0.36 (P25)	5.6	0.9993	0.0702
Aqueous	0.36 (P25)	10	0.9916	0.0909
Aqueous	0.36 (P25)	13	0.9363	0.3281
Aqueous	1.00 (P25)	10	0.9790	0.1306
Aqueous	1.00 (RH)	10	0.9985	0.0952
Aqueous <sup>e</sup>	1.00 (P25)	10	0.9958	0.0605
Dyebath hydrolysed	1.00 (P25)	10	0.9740	0.0765
Dyebath hydrolysed	1.00 (RH)	10	0.9980	0.0234
Dyebath unhydrolysed	1.00 (P25)	10	0.9052	0.0202
Dyebath unhydrolysed	1.00 (RH)	10	0.9952	0.0159

<sup>a</sup> “Aqueous” refers to a solution of the dye in water with no other additives.

<sup>b</sup> P25 = Degussa P-25; RH = Riedel-de-Häen.

<sup>c</sup> Correlation coefficient of the straight line.

<sup>d</sup> Pseudo first order rate constant determined for the first 10 min of irradiation.

<sup>e</sup> Sunlight irradiation.

### 3. Results and discussion

#### 3.1. Photocatalytic decolourisation of *Reactive Orange 6* alone in water

Experiments were first carried out using an aqueous solution of the unhydrolysed dye alone, without any dyebath additives, using a pH value of 10. As shown in Fig. 3, the Riedel-de-Häen catalyst was found to be marginally superior to the Degussa P-25 product for effecting decolourisation of the solutions. Also shown in Fig. 3 is the rate of decolourisation of a similar solution, using TiO<sub>2</sub> Degussa P-25 with sunlight irradiation. It can be seen that the process is only slightly slower than for the UV-irradiated solutions, with ca 45% loss of colour after only 10 min exposure, rising to 88% after a further 50 min. Relevant kinetic data are summarised in Table 2.

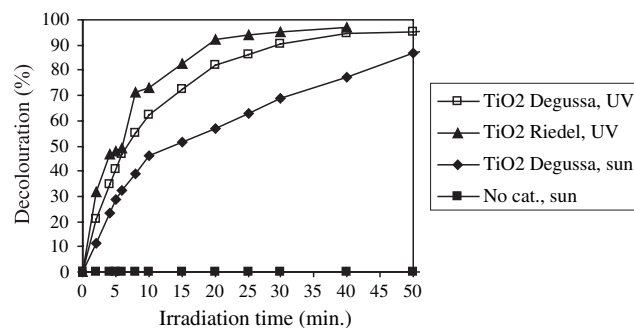


Fig. 3. Influence of catalyst and irradiation source on the rate of decolourisation of solutions of *Reactive Orange 4* in water alone (pH 10, TiO<sub>2</sub> 1 g/l).

Control experiments, using UV or solar irradiation in the absence of catalyst, showed no loss of colour after 60 min exposure, confirming the critical role played by the  $\text{TiO}_2$  catalyst in dye degradation.

The pH dependence of the rate of decolourisation for the dye-only solutions was next examined by carrying out UV-irradiated experiments with a lower concentration of the  $\text{TiO}_2$  Degussa P-25 catalyst (360 mg/l), at pH values of 5.6, 10, and 13. The kinetic results are summarised in Fig. 4, and show that even at this lower  $\text{TiO}_2$  concentration, decolourisation of the reactive dye is rapid, and the reaction rate increases with pH. The acceleration at high pH may be due to the presence of higher proportion of hydrolysed forms of the dye, and/or the higher concentration of hydroxide ions, leading to the photogeneration of more of the reactive hydroxyl radical species. When parallel experiments were carried out with the Riedel-de-Häen catalyst, a similar pH dependence was observed, and for example at pH 5.6 it required a irradiation time of 2.5 h to achieve 90% decolourisation, whereas at pH 13 it required only 1.5 h to achieve the same effect.

Relevant first order rate constants are indicated in Table 2.

In advanced oxidation processes, such as ozone treatment,  $\text{UV}/\text{H}_2\text{O}_2$  and irradiation in the presence of  $\text{TiO}_2$  hydroxyl radicals are formed. It may be assumed that intermediates involved in these three types of treatment may be similar. In this work there was no attempt to identify intermediates or final products. However, previous photocatalytic ( $\text{TiO}_2$ ) work on dyes containing triazinyl [19] units which was followed by GC-MS analyses concluded that nitrogen was eliminated, benzene and naphthalene rings were broken and fragments containing the triazine system were identified as intermediates. Colonna et al. [20] in studies with  $\text{UV}/\text{H}_2\text{O}_2$  on dyes containing anthraquinone and sulphonated naphthol rings suggest nitrogen is evolved at an earlier stage, from the azo group and the sulphonic groups were replaced by hydroxyl groups forming polyhydroxylated species. Continuing photooxidation may lead to quinone type compounds and later to

aromatic ring cleavage with formation of diacids. Studies by Zhang et al. [21] also on triazine containing dyes using ozonation gave as the main degradation products sulphate, nitrate, formate and oxalate. When the oxidation is complete organic compounds end up as  $\text{CO}_2$ . We may then write a general type equation, considering the complete oxidation of the dye:



### 3.2. Photodecolourisation of simulated dyebath effluent

In an attempt to relate our present study to the real situation arising with effluent from the commercial dyeing of cotton with reactive dyes, it was decided to formulate a simulated spent dyebath and to test its response to photocatalytic degradation.

The rinsing, soaping (98 °C, 15–30 min) and acidic neutralisation processes which follow the reactive dyeing of cotton result in a considerable dilution of the dyehouse effluent [1]. Two types of spent dyebath effluent were investigated. One of them contained the fully hydrolysed dye with relevant additives, while the other one contained essentially unhydrolysed dye with the same additives. In the latter case, solutions were made up in cold water and were used the same day to minimise hydrolysis. In the former case, the solutions were boiled and kept for several hours to ensure complete hydrolysis of the chlorotriazinyl groups. The simulated dyebath effluents containing either hydrolysed or unhydrolysed dye both gave a pH reading of ca 10. The results for the photocatalysed decolourisation reactions are presented in Fig. 5, and show that, for both the Degussa P-25 and Riedel-de-Häen catalyst types, at 1 g/l concentration, the solutions containing hydrolysed dye decolourised faster than those containing unhydrolysed dye. In addition, the Degussa P-25 catalyst was the more efficient of the two, showing more than 90% decolourisation after 20 min irradiation.

Relevant kinetic parameters are summarised in Table 2.

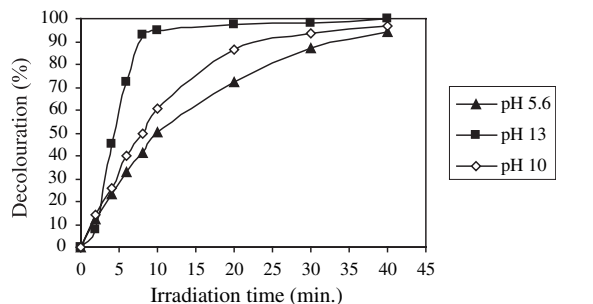


Fig. 4. Influence of pH on UV-induced decolourisation of dye-only solution in the presence of Degussa P-25  $\text{TiO}_2$  (360 mg/l).

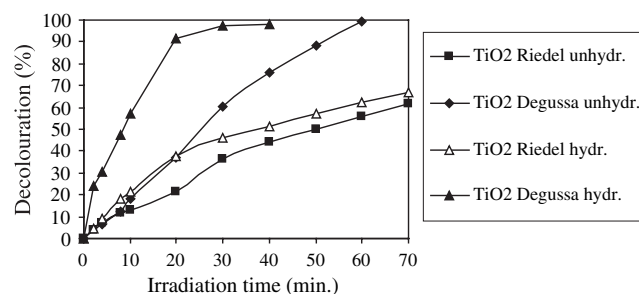


Fig. 5. Influence of catalyst type on decolourisation of simulated dyebath effluent ( $\text{TiO}_2$  1 g/l).

### 3.3. COD decrease

COD decreases of 80 and 94% were observed after 1 h of UV or solar irradiation, respectively, for experiments with solutions of the dye only and TiO<sub>2</sub> Degussa P-25 (1 g/l), at pH 10. Under similar UV irradiation conditions, at pH 5.6, 2 h were needed to obtain a 70% decrease. This is consistent with the observed enhancement of photodecolourisation with increasing pH.

### 4. Conclusions

We have shown that photocatalysis using UV light or sunlight in conjunction with TiO<sub>2</sub> is a promising method for degrading *C.I. Reactive Orange 4* either alone in water, or in its hydrolysed and unhydrolysed forms in spent dyebath liquor. The rate of decolourisation is higher for hydrolysed dye than for unhydrolysed dye in a simulated dyebath effluent. At the same pH, the simulated dyebath effluent is decolourised at a somewhat slower rate than solutions of the dye in water alone, presumably due to competition from the organic additives in the dyebath. For the dye-only solutions, the Degussa P-25 catalyst was more efficient at decolourisation than the Riedel-de-Häen catalyst when using sunlight as the light source. These results are very promising, and further investigations are warranted to examine the commercial potential of the technique as an economic means of treating dyehouse effluent.

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