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# Photocatalytic degradation of commercial dye, CI Reactive Red 35 in aqueous suspension: Degradation pathway and identification of intermediates by LC/MS

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ABSTRACT

The photodegradation of Reactive Red 35 dye by artificial UV light was investigated in the presence of titania P-25. Six reaction intermediates were identified and separated by LC/MS, giving insight into mechanistic details and degradation pathways. The degradation process takes place through competitive reactions such as removal of chromophoric group, hydroxylation of the aromatic ring, substitution on aromatic ring, devinylsulphonation, C—N bond cleavage, decarboxylation and further ring opening to give aliphatic compounds. The probable degradation pathways were proposed and discussed.

## 1. Introduction

On a global scale, over 0.7 million tons of organic synthetic dyes are manufactured each year mainly for use in textile, leather goods, industrial painting, food, plastics, cosmetics and consumer electronics sector [1]. Unfortunately, exact data on the quantity of dyes discharged in the environment are not available. It is assumed that a loss of 1–2% in production and 1–10% loss in use are a fair estimate [2]. Due to large-scale production and extensive application and their direct discharge into aquatic streams, synthetic dyes can cause considerable environmental damage and related health problems. Reactive dyes constitute approximately 12% of the worldwide production of the commercialized synthetic dyes and are extensively used in the textile industry [3]. Reactive dyes contain a reactive anchor (e.g. vinylsulphone, chlorotriazine) that bonds covalently with the fiber during the dyeing process [4]. Some hydrolyzed reactive dyes, which undergo side-reactions of nucleophilic addition with water, have little affinity for the fabric in the dyeing process [5]. The level of unexhausted reactive dyes typically remain at $0.06\,\mathrm{g\,L^{-1}}$, but possibly even as high as $0.6–0.8\,\mathrm{g\,L^{-1}}$, in dyehouse effluents [6] can lead to severe organic and colour pollution in the water environment. Strict environmental regulations, water scarcity and sustainable approach have forced the industrial sector to adopt the practice of recycling and reuse of treated wastewater. The common method for the treatment of wastewater in the textile finishing industry is physicochemical flocculation in combination with the biological treatment [7]. The incapability of conventional treatment to effectively remove many bio-recalcitrant coloured pollutants leads to explore the new efficient treatment systems which are effective for complete degradation and mineralization of these compounds. In recent years, semiconductor-assisted photocatalysis has been extensively investigated, mainly due to its capacity to degrade a high number of recalcitrant chemicals in gaseous or aqueous systems, through relatively inexpensive procedures. Titanium dioxide ($TiO_2$) is found to be more efficient catalyst for photocatalytic degradation of pollutants due to faster electron transfer to molecular oxygen [8–10].

Reactive dyes consist of a chromophoric system (e.g. azo, anthraquinone, phthalocyanin), the anchor groups and the group which increase the water solubility (mostly $—SO_3^-$). The decolourization of reactive dyes results in destroying the chromophoric system; however, the formation of toxic/nontoxic intermediates or byproducts may take place. The requirements for recycling the decolourized water are: (i) it should have lower toxicity than untreated waste water and (ii) no intermediate/byproduct formed during degradation process should be present that negatively affect the dyeing process. Therefore, keeping these facts in consideration, the study of reactive intermediate formed during degradation process seems to be imperative. Until now, however, there have been only a few investigations on the identification of intermediates formed during the degradation process of reactive dyes. Degradation mechanism involving biological treatment of reactive Black was revealed by using LC–MS/MS [11]. McCallum et al. [12] analyzed only four early degradation products of reactive blue 19

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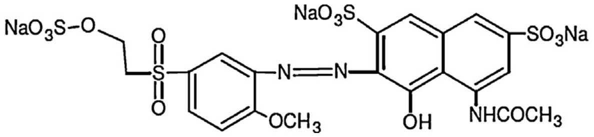

**Fig. 1.** Structure of Reactive Red 35.

by using NMR, LC/MS and Raman spectroscopy. The formation of highly oxidized products formed during ozonation of Reactive yellow 84 such as salts ($NO_3^-$, $SO_4^{2-}$, $Cl^-$) and short chained carboxylic acids (oxalic acid, formic acid, etc.) was observed using HPIC [13]. With the help of LC–mass spectrometry polar components in surface water were reported on the basis of accurate masses [14]. Degradation products of CI Reactive Orange 16 were identified by GC/MS [15]. In our earlier work [16,17] identification of intermediates of CI acid orange 7 by LC/MS and CI reactive blue 160 by GC/MS for establishing the mechanism of photocatalytic degradation was carried out.

CI Reactive Red 35 (RR35) is a monoazo commercial dye, commonly used for dyeing cotton, viscose, flex and jute but not suitable for silk, wool and polyester. These dyes suitable for white and colour resistant printing and tinting of white ground in printing and Reactive Red 35 is reasonably photostable to sunlight. However, only a few studies on their degradation have been reported in the literature [18] and no study on $TiO_2$-assisted photocatalytic degradation pathway of the RR35 dye under UV-irradiation has been reported. Keeping in view, widespread use in industries and thereby its possibility of release in the wastewater RR35 has been selected for present work. In continuation of our previous work on establishing the reaction pathway for photocatalytic degradation of synthetic dyes [16,17], the present research focuses on identification of the reaction intermediates formed during photodegradation of RR35 dye in the UV/$TiO_2$ process by using liquid chromatography–mass spectrometry (LC/MS) and ion chromatography (IC) for proposing the probable mechanistic pathway of the dye.

## 2. Experimental

### 2.1. Materials

Titania P-25 (surface area 50 $m^2/g$) was obtained from Degussa. Commercially available Reactive Red 35 (RR35) was obtained from Nahar Fabrics, Lalru, India and was used without further purification. Structure of the dye is shown in Fig. 1. Double distilled water was used for preparation of various solutions. pH of the solutions was adjusted with 1 M HCl or 1 M NaOH.

### 2.2. Instruments

Photochemical degradation experiments were carried out in specially designed reaction vessels (diameter 0.08 m, volume 500 ml) in the photoreactor equipped with 4 UV tubes each of 30 W (Philips). The intensity of UV light was $2.4 \times 10^{-6}$ einstein/min measured by chemical method, i.e. potassium ferrioxalate actinometry [19]. The experimental set-up was reported earlier [20]. Constant stirring of solution was ensured by using magnetic stirrers and aeration was done with the help of aquarium aerator. The spectra were taken with UV–VIS Spectrophotometer (Shimadzu 1650); pH meter (Thermo Orion 920A) was used to adjust the pH of the solution. COD analysis was carried with Thermo Orion Aqua Fast II AQ 2040 COD meter.

### 2.3. Procedure

The degradation experiments were carried out by adding 100 mg of photocatalyst ($TiO_2$ Degussa) to 100 ml of dye solution and suspension was subjected to irradiation under UV light. The aqueous suspension was magnetically stirred and aerated throughout the experiment. At different time intervals aliquot was taken out with the help of syringe and then filtered through Millipore syringe filter of 0.45 μm. The absorption spectra were recorded at $\lambda_{max}$ 536 nm. The rate of degradation was studied in terms of changes in absorption spectra. The decolourization efficiency (%) has been calculated as:

$$\text{Efficiency}\,(\%) = \frac{C_0 - C}{C_0} \times 100$$

where $C_0$ is the initial concentration of dye and $C$ is the concentration of dye after photo-irradiation. Similar experiments were carried out by varying the pH of the solution, concentration of dye and dose of photocatalysts.

To evaluate formation and degradation of the reaction intermediates and to assess the mineralization, the photocatalytic experiments were carried out up to 8 h under optimized conditions.

For COD analysis 2 ml of test solution was pipette into the standard amount of potassium dichromate oxidizing mixture and digested at 150 °C for 2 h. Then COD was measured using COD meter.

### 2.4. LC/MS analysis

For the identification of degradation products, the samples were analyzed by LC/MS (Water Alliance 2795 LC). A capillary column Terra C-18 (5 μm × 100 mm length) was used for separation of product intermediates. The mobile phase was a mixture of acetonitrile–water (70/30 (v/v)) filtered through Millipore syringe filter of 0.22 μm. The flow rate of elute was 0.08 mL $min^{-1}$ and the injection volume was 20 μL. The eluent from the chromatographic column successively enter the UV–vis diode array detector, the ESI interface and the quadruple ion trap mass analyzer. MS analysis in the positive ions mode was performed on a mass spectrometer equipped with an ESI ion source. The ESI probe tip and capillary potentials were set at 2.5 kV and 25 V, respectively. The mass range was 50–400 m/z. The heated capillary was set to 200 °C.

### 2.5. Ion chromatography

The concentration of $NO_3^-$, $SO_4^{2-}$ ions and low molecular weight aliphatic acids (formic, acetic and oxalic acid) in solution was determined by ion chromatography on a model 761 Compact IC (Metrohm) using a MetrosepASupp5-250 column and carbonate as standard eluent.

## 3. Results and discussion

### 3.1. UV–vis spectra

Time-dependent UV–vis spectrum of RR35 dye during photoirradiation with $TiO_2$ is shown in Fig. 2. The spectra of RR35 show peaks at 379, 310 and 234 nm in UV region and a main band with a maximum at 536 nm in visible region. The rate of decolourization was recorded with respect to the change in the intensity of absorption peak in visible region. The prominent peak was observed at $\lambda_{max}$, i.e. 536 nm which decreased gradually and finally disappeared indicating that the dye had been decolourized.