Journal of Molecular Catalysis A: Chemical 374–375 (2013) 66–72

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

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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ARTICLE INFO

Article history:
Received 22 October 2012
Received in revised form 16 March 2013
Accepted 18 March 2013
Available online 26 March 2013

Keywords:
Reactive dye
Photocatalysis
CI Reactive Red 35
Azo dye
LC/MS

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 g L^{-1}, but possibly even as high as 0.6–0.8 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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1381-1169/$ – see front matter
http://dx.doi.org/10.1016/j.molcata.2013.03.018

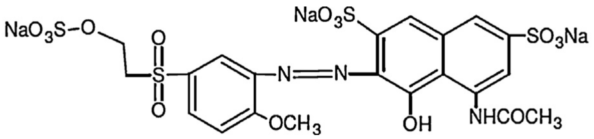


Fig. 1. Structure of Reactive Red 35.

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 2.4×10^{-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 λ_{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 λ_{max}, i.e. 536 nm which decreased gradually and finally disappeared indicating that the dye had been decolourized.

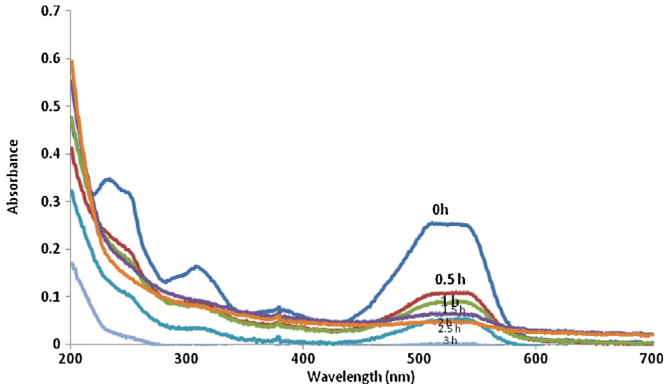


Fig. 2. Time-dependent UV–vis absorption spectra for decolourization of RR35 using TiO_2.

3.2. Photolysis/photocatalysis of Reactive Red 35

Decolourization of RR35 was investigated under different experimental conditions, viz. UV light alone, UV/TiO_2, and Dark/TiO_2. Fig. 3 depicts the photocatalytic decolourization of RR35 under these experimental conditions. The decolourization rate was recorded in terms of change in intensity of characteristic peak at 536 nm. Initially blank experiments were performed under UV irradiation without addition of any catalyst (UV alone) and only 4.55% decolourization was observed. The adsorption of the dye was also observed with TiO_2 catalyst, i.e. dark/TiO_2. Only 7% adsorption of the dye was seen with TiO_2 under dark conditions. After that photocatalytic experiments were carried out using catalyst at fixed dye concentration (25 mg/L), pH 7 and catalyst loading of 1 g/L (UV/TiO_2). The complete decolourization of dye was achieved after 3 h with TiO_2 as a photocatalyst (UV/TiO_2) under these experimental conditions.

3.3. Effect of process parameters on degradation of RR35

In order to optimize the process parameters, i.e. pH and dose of catalyst, the experiments were performed by varying catalyst concentration from 0.5 g/L to 2.0 g/L and pH of the dye (2–10). The graph plotted (Fig. 4) between amount of catalyst used and percentage degradation reveals that with an increase in catalyst dose degradation efficiency increases up to 1.5 g/L. Thus with the increase of catalyst dosage, total active surface area increases, hence the availability of more active sites on catalyst surface [21]. It has also been reported that the catalyst amount has both positive and negative impacts on the photodecomposition rate [22]. Moreover, TiO_2 powders (commercial photocatalysts) have scattering albedo (ω) higher than 0.5 [23], which increases the radiation scattering results in reducing the number of photons absorbed; hence further increase in catalyst dose decreases the decolourization efficiency. Therefore, the catalyst dose 1.5 g/L was fixed for degradation of RR35.

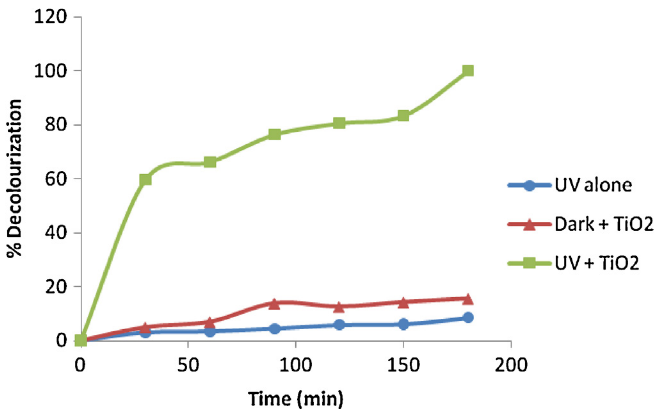


Fig. 3. Photocatalytic decolourization of RR35 dye (dye initial concentration – 25 mg/L, pH – 7, catalyst dose – 1 g/L).

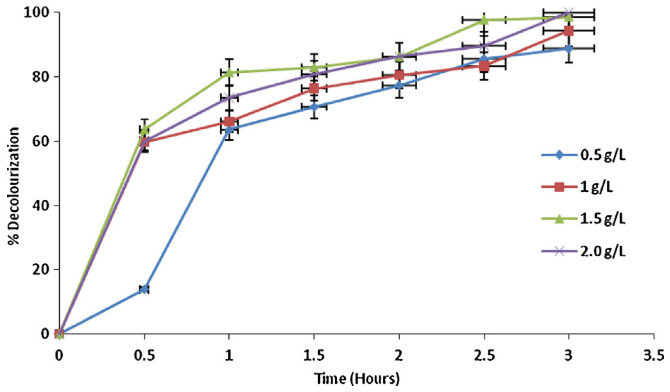


Fig. 4. Effect of catalyst dose on decolourization rate of RR 35 dye (dye initial concentration – 25 mg/L, pH – 7).

Fig. 5 shows the colour removal efficiency of photocatalysts as a function of pH. The results reveal that the lesser degradation of dye occurs in basic solution and higher in acidic region with TiO_2. The interpretation of pH factor on the efficiency of photocatalytic degradation process can be explained on the basis of acid–base property of metal oxide surface and the ionization state of ionizable organic molecule. The point zero charge (pzc) for TiO_2 (Degussa P25) is 6.8 [23]. TiO_2 surface is positively charged in acidic media ($pH < 6.8$) whereas it is negatively charged under alkaline condition ($pH > 6.8$). RR35 is an anionic dye in aqueous solution. For TiO_2, rate of photodecolourization increased with decrease in pH, exhibiting maximum efficiency (100%) at pH 4. Findings of others [24,25] also show that degradation of anionic dyes is more in acidic medium because at pH higher than pzc of titania, its surface becomes negatively charged, so adsorption will be less.

After optimizing the experimental conditions, the photocatalytic discolouration of RR35 was carried out by varying the initial concentration of the dye from 10 to 100 ppm. As the concentration of the dye is increased, the rate of photodegradation decreases indicating either to increase the catalyst dose or time span has to be increased for the complete removal. Fig. 6 clearly shows that with increase in initial concentration of dye percentage decolourization of RR35 decreases with TiO_2.

Fig. 7 shows the kinetics of disappearance of RR35 for an initial concentration of 25 mg/L under optimized conditions with TiO_2. The results show that the photocatalytic decolourization of the dye can be described by the first order kinetic model, $\ln(C_0/C) = kt$,

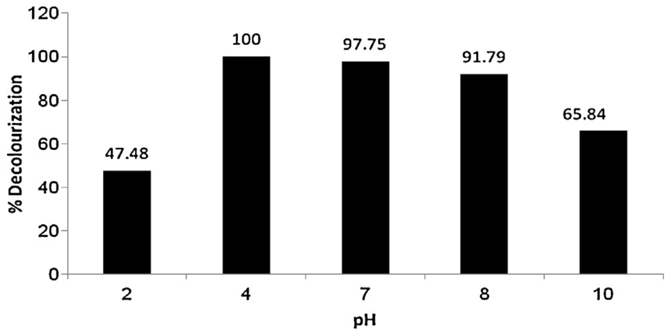


Fig. 5. Effect of pH on decolourization rate of RR35 dye (dye initial concentration – 25 mg/L, catalyst dose – 1.5 g/L, time – 3 h).

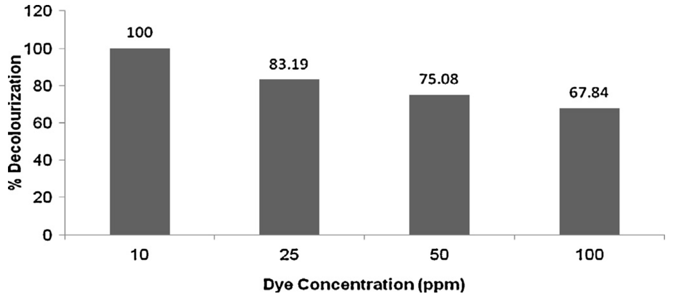


Fig. 6. Effect of initial concentration of RR35 dye on percentage decolourization under optimized conditions (catalyst dose – 1.5 g/L, pH – 4).

where C_0 is the initial concentration and C is the concentration at any time, t. The semilogarithmic plots of the concentration data gave a straight line. The correlation constant for the fitted line was calculated to be $R^2 = 0.909$ for TiO_2. The rate constant for degradation of RR35 using TiO_2 was calculated to be $0.029\,\text{min}^{-1}$. This constant is a function of many operational conditions and will vary with reactor configuration unless the effect of the photon absorption is included in the rate equation [26].

3.4. Mineralization of Reactive Red 35

As the reduction of chemical oxygen demand (COD) reflects the extent of degradation or mineralization of an organic species, the percentage change in COD was studied for dye sample (initial concentration 25 mg/L) under optimized conditions (catalyst dose 1.5 g/L, pH 4, time 3 h). The COD reduction is lesser (74.52%) in 3 h than percentage decolourization (100%) which may be due to the formation of smaller uncoloured products. Therefore, it seems that to achieve complete mineralization of dyes, longer irradiation time is required.

3.5. Analysis of intermediates formed after photocatalytic degradation of RR354

3.5.1. Spectrophotometric analysis

The spectra of RR35 show peaks at 379, 310 and 234 nm in UV region and a main band with maximum at 586 nm in visible region. The absorbance peak at 234 and 310 nm is due to the benzene and naphthalene rings [27], and the absorbance peak at 536 nm may be due to the azo linkage of RR35. To study the fate of colourless intermediates formed photocatalytic reaction was carried up to 8 h. The change in absorbance value of CI Reactive Red at 234, 310 and 536 nm as a function of irradiation time in aqueous solutions is shown in Fig. 8. It is observed that absorption at 536 and 310 nm decreases with time and disappears after 3 h and 6 h, respectively, resulting in complete decolourization of the solution and degradation of intermediates containing naphthalene ring. The absorbance at 234 nm first increases and then decreases up to 2 h, after that no regular trend is observed and even after 8 h it does not disappear; these changes can be attributed to the formation of intermediates resulting from the photodegradation of the azo dye and intermediate containing benzene ring.

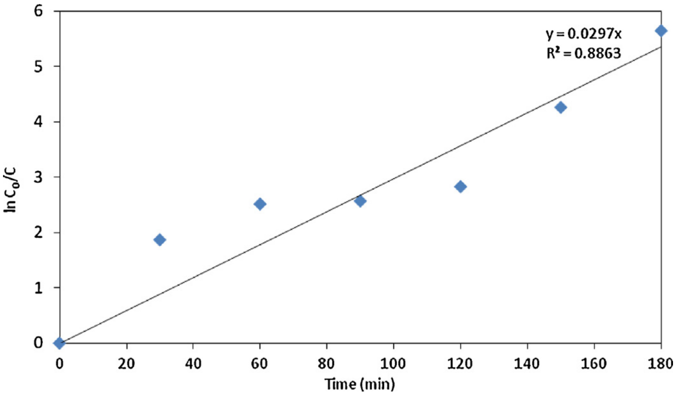


Fig. 7. Kinetics analysis for RR35 dye under optimized conditions.

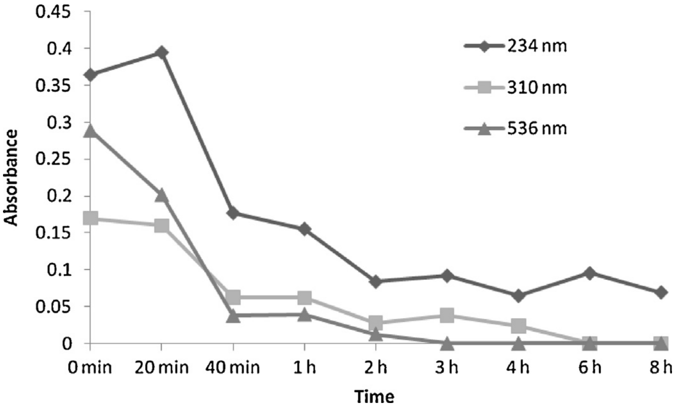


Fig. 8. Absorbance changes of spectral peaks (234, 310 and 536 nm) of RR35 at as function of irradiation time in aqueous solution.

3.5.2. LC/MS analysis

The retention time in the liquid chromatograms of various intermediates formed during photocatalytic degradation of RR35 at different time interval (40 min to 8 h) is shown in Table 1. The components eluted having different retention time were subjected to mass spectrometry and identified by interpretation of their fragment ions in the mass spectra. The chromatographs suggest that the entire components except E disappear after 8 h of photocatalytic treatment. The mass spectra of intermediates are shown in Fig. 9.

Six main compounds detected in the solution are presented in Table 2. The six intermediates of CI Reactive Red 35 appeared during 8 h of irradiation are: sodium 4-amino-5-hydroxy-6-(phenylediazenyl)naphthalene-2-sulphonate (intermediate A), sodium 3-((1-hydroxynaphthalen-2-yl)diazenyl)-4-methoxyphenolate (intermediate B), N-(7-diazenyl-3,8-dihydroxynaphthalen-1-yl)acetamide (intermediate C), 3-diazenyl-4-hydroxybenzenesulphonic acid (intermediate D), phthalic acid (intermediate E) and N-(m-tolyl)acetamide (intermediate F). Phthalic acid has already been reported during degradation of various dyes [15,27–30].

3.5.3. IC analysis

The formation of NO_3^-, SO_4^{2-} ($t_R = 17.4$ min and 25.5 min, respectively) and smaller aliphatic acids (acetate, formate, oxalate ions having $t_R = 6.2$ min, 7.1 min, 30 min, respectively) was

Table 1
Retention time of intermediates obtained formed photocatalytic degradation of RR35 identified by LC/MS.

Product	t_R (min)
A	19.45
B	12.30
C	5.13
D	7.42
E	5.05
F	4.98

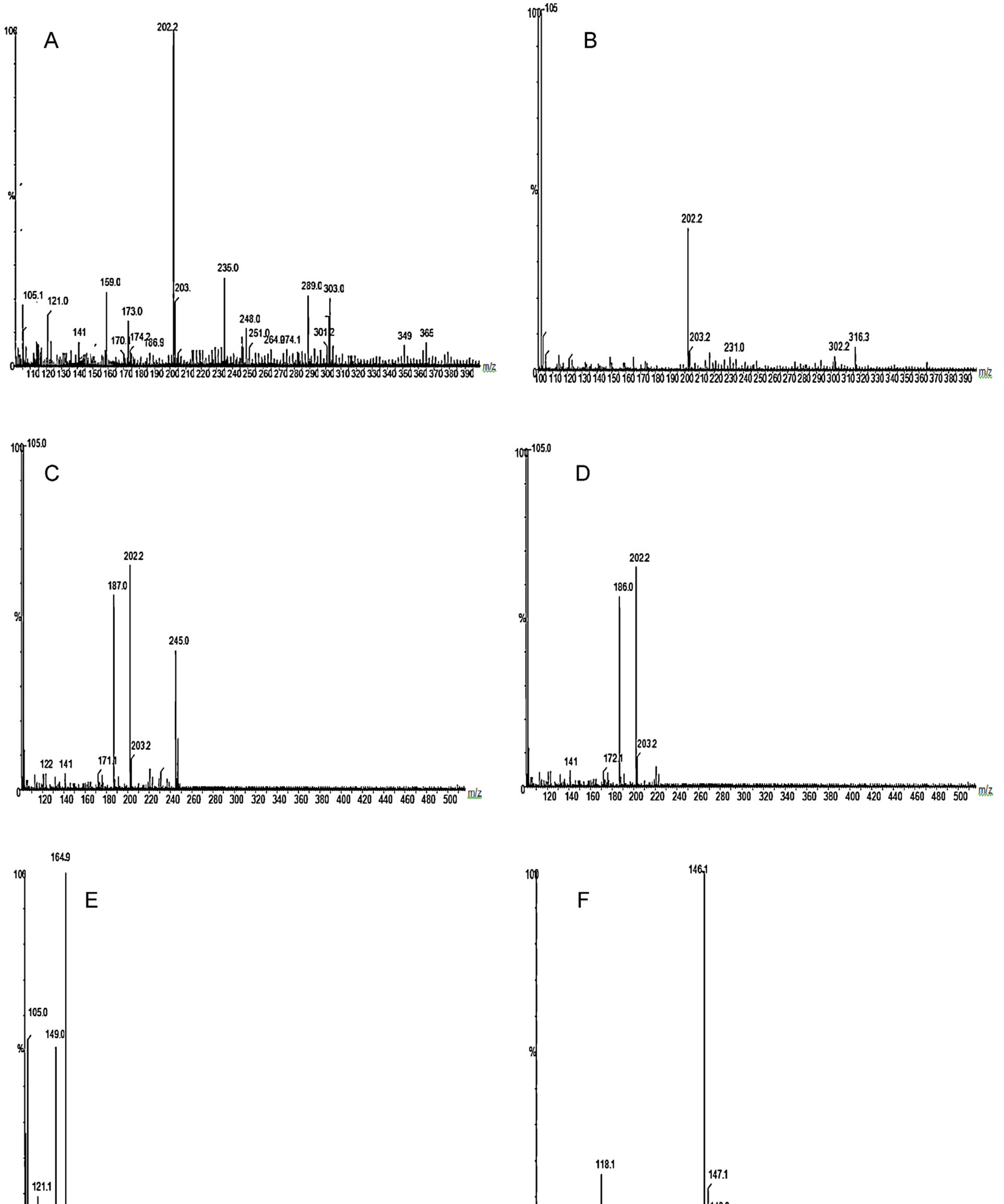


Fig. 9. Mass spectra of intermediates A–F.

confirmed by the ion chromatography (IC) by their retention time (t_R) and also during fragmentation pattern.

3.6. Probable mechanistic photocatalytic degradation pathway of Reactive Red 35 under UV light

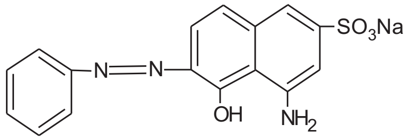
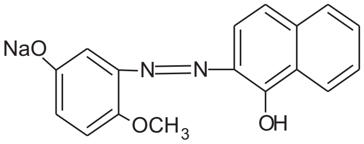
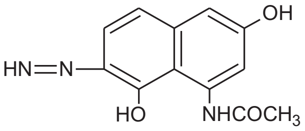
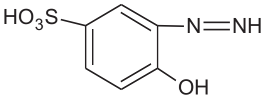
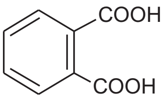
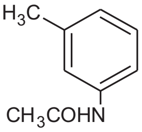
On the basis of the experimentally identified intermediate species a proposed degradation pathway of RR 35 (Fig. 10) is as follows.

3.6.1. Generation of $^{\bullet}$OH radical

When the catalyst is exposed to UV radiation with light energy greater than its band gap energy (E_g 3.14 eV) electrons are promoted from the valence band to conduction band and resulted in formation of an electron–hole pair [31].

$$TiO_2 + h\nu(UV) \rightarrow TiO_2(e_{CB}{}^- + h_{VB}{}^+)$$

Table 2
Chemical structures of intermediates of RR35 identified by LC/MS analysis.

	Name of compound	Chemical structure	M. Wt.
Fig. 9(A)	Sodium 4-amino-5-hydroxy-6-(phenylediazenyl) naphthalene-2-sulphonate		365.2
Fig. 9(B)	Sodium 3-((1-hydroxynaphthalen-2-yl)diazenyl)-4-methoxyphenolate		316.2
Fig. 9(C)	N-(7-diazenyl-3,8-dihydroxynaphthalen-1-yl)acetamide		245.2
Fig. 9(D)	3-Diazenyl-4-hydroxybenzenesulphonic acid		202.2
Fig. 9(E)	Phthalic acid		166
Fig. 9(F)	N-(m-tolyl)acetamide		149

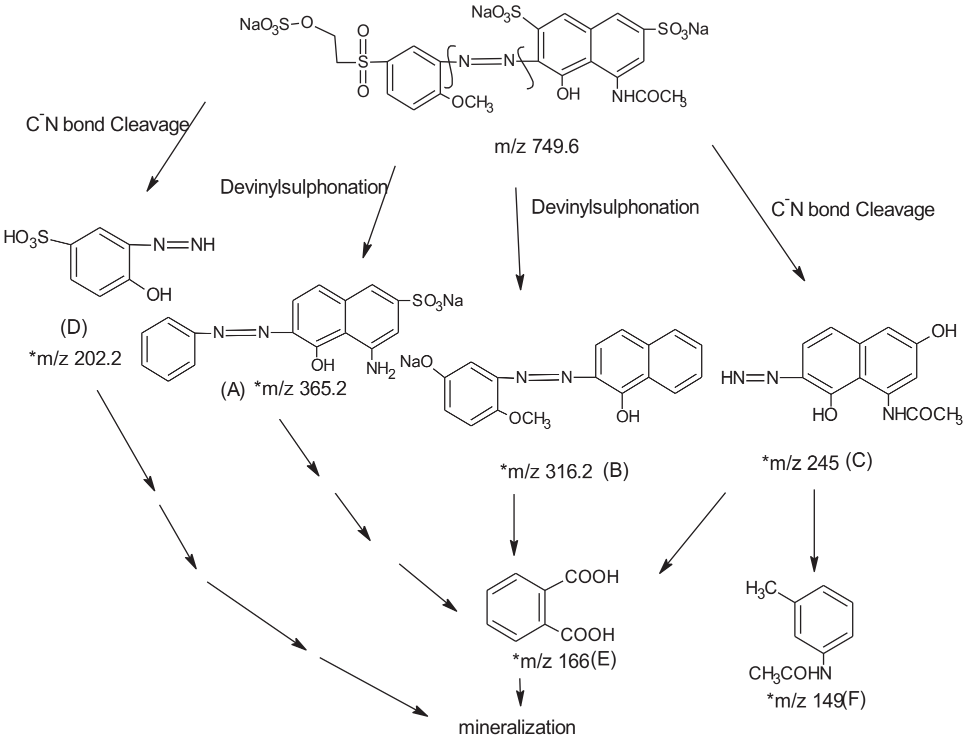


Fig. 10. Proposed degradation pathway of RR35 dye with TiO_2 under optimized conditions.

where e_{CB}^- and h_{VB}^+ are the electrons in the conduction band and holes in the valance band respectively. Further both these entities can migrate to the catalyst surface, where they can undergo redox reaction via the formation of $^\bullet$OH radical [32,33].

Redox potential of $^\bullet$OH radical is very high (E^0 +2.8 V); thus, it is a powerful oxidizing agent and attacks dye present at or near the surface of TiO_2 to oxidize it. The hydroxylated dye may degrade via devinylsulphonation and cleavage of C—N bond.

3.6.2. Devinylsulphonation

The first pathway involves the removal of vinylsulphone group leading to the formation of compounds A and B in which both benzene and naphthalene rings remain intact. Compound B undergoes oxidation to form compound E.

3.6.3. Cleavage of C—N bond

The second pathway involves the cleavage of C—N bond between naphthalene ring and azo bond or between benzene ring and azo bond resulting in formation of intermediates C and D. Compound C on further oxidation form compounds E and F via the opening of naphthalene ring. Lu et al. [34] reported 3-methylbenzensulphonic acid as degradation product of azo dye via the formation of 4-diazenyl-3-methylbenzenesulphonic acid. However, in our study hydroxylated isomeric intermediate was obtained (Compound D).

The intermediates formed A–E further degraded to smaller aliphatic and aromatic acids, which is in accordance with the earlier reports on degradation of dyes [27,29].

4. Conclusion

RR35 could be successfully decolourized and degraded by titania based photocatalysis. Sulphonated and polar intermediates are identified using LC/MS technique as polar components cannot be extracted efficiently in the solvents usually used in GC–MS analysis. Smaller aliphatic acids and inorganic ions ($SO_4^{2-}$and NO_3^-) were detected using IC technique. A detailed reaction mechanism has been established from the initial step of generation of $^\bullet$OH free radical to the final products. The formation of hydroxylated products, C-N bond cleavage, devinylsulphonation, opening of naphthalene ring and their subsequent degradation products were formed in agreement with general rules as proposed for the degradation of other complex molecules in water. Phthalic acid still remains after 8 h of degradation in very less quantity. LC/MS technique has been successfully employed for the detection of intermediate which cannot be detected by other techniques but form integral part of degradation of the dye. In addition, MS spectra collected during this work may be used as a spectral data bank for further studies as LC–ESI-TOF method, leading to additional information regarding the elemental composition which can be calculated based on determined accurate mass.

Acknowledgement

Support from NIPER, Mohali is gratefully acknowledged.

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