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Identification of photooxidation degradation products of C.I. Reactive Orange 16 dye by gas chromatography–mass spectrometry

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Abstract

The photodegradation of aqueous solutions of C.I. Reactive Orange 16 was investigated under UV irradiation. The degradation was studied by monitoring the change in absorption and relative intensity employing UV-spectroscopic and GC/MS analysis as functions of irradiation time. The rate of degradation of the dye was evaluated. The solution was completely decolorized after 100 min of photooxidation. The generated degradation products were detected by GC/MS. 6-Acetylamino-3-amino-naphthalene-2-sulfonic acid, *N*-(3,4-bis-hydroxymethyl-phenyl)-acetamide and phthalic acid were found during the degradation of C.I. Reactive Orange 16. The probable pathways for the formation of the degradation products were proposed. GC/MS analysis and degradation pathways demonstrated that naphthalene and benzene rings were observed during photooxidation.

Keywords: C.I. Reactive Orange 16; Photooxidation; Degradation products; GC/MS; UV irradiation; Wastewater

1. Introduction

Dyes are classified by their chemical and dyeing properties such as azo (monoazo, diazo, triazo, polyazo), anthraquinone, phthalocyanine and triarylmethane which are quantitatively the most important groups. Other groups are diarylmethane, indigoid, azine, oxazine, thiazine, xanthene, nitro, nitroso, methine, thiazole, indamine, indophenol, lactone, aminoketone and hydroxyketone dyes. Azo dyes, aromatic moieties linked together by azo (–N=N–) chromophores, represent the largest class of dyes used in textile-processing and other industries [1–3]. The release of these compounds into the environment can be undesirable, not only because of their color, but also because some azo dyes and their breakdown products are toxic and/or mutagenic to life [4–8]. To remove azo dyes from wastewater, a biological treatment strategy based on anaerobic reduction of the azo dyes, followed by aerobic transformation of the formed aromatic amines, holds promise. However, the first stage of the process, anaerobic azo dye reduction, proceeds relatively slowly [9,10].

Azo dyes have been widely used in a variety of products such as textiles, foodstuffs and leather [11,12]. About one-half of the dyes used in textile industry include azo dyes, and as a consequence toxicity problems have arisen due to the release of some of these products into the environment [13,14]. Because of the complex structures of these dyes biological, physical and chemical treatment of dye effluents are inefficient

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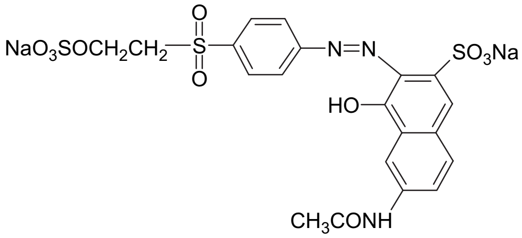
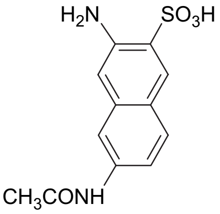
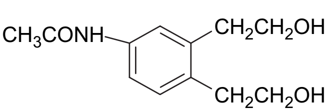
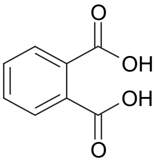
Name	Chemical Structure	Molecular Weight
Reactive Orange 16 (A)		617
6-Acetylamino-3-amino-naphthalene-2-sulfonic acid (B)		281
N-(3,4-Bis-hydroxymethyl-phenyl)-acetamide (C)		223
Phthalic acid (D)		166

Fig. 1. The chemical structures of C.I. Reactive Orange 16 and its degradation products.

[15–17]. Removal of azo dyes by photooxidation is more efficient due to the complete degradation until CO_2 and H_2O depending on the period of photooxidation. The method is inexpensive and non-toxic for treatment of wastewater. Although some of the azo dyes may produce toxic products, there is no literature in our knowledge about C.I. Reactive Orange 16 that may result in the formation of mutagenic and carcinogenic products.

Identification of degradation products of azo dyes can be performed by powerful chromatographic techniques such as gas chromatography–mass spectrometry (GC/MS). Sulfonated azo dyes are non-volatile and cannot be analyzed by GC/MS [18–20]. Therefore, liquid chromatographic techniques have been recommended [21]. However, although the sulfonated azo dyes are non-volatile, the degradation products coming from photooxidation process can be detected by GC/MS [22].

The aim of this study is to identify the degradation products of C.I. Reactive Orange 16 by GC/MS during UV photooxidation. It is possible to propose a degradation mechanism of the dye molecule after photooxidation. The kinetics study demonstrated some highlights about the photooxidation mechanism.

2. Experimental

2.1. Material

C.I. Reactive Orange 16 was obtained from Setaş Company, Turkey and used without any purification. Its chemical structure is shown in Fig. 1. The dye solution was prepared in double distilled MilliQwater (Millipore distillation unit). Other reagents, sodium chloride, sodium hydroxide, methyl-*tert*-butyl-ether, and methanol were purchased from Merck (Darmstadt, Germany). The pH of the solutions was adjusted using NaOH.

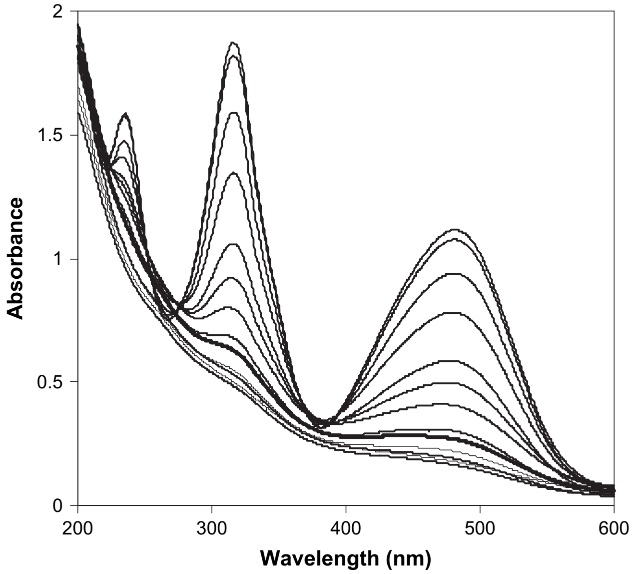


Fig. 2. UV/VIS spectral changes of C.I. Reactive Orange 16 in aqueous solutions with the increasing irradiation time at 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120 min.

2.2. Photoreactor

The Grantzel (Karlsruhe-Germany) photoreactor model was used for photooxidation. The photoreactor consisted of reaction vessel, immersion well and UV lamp. The lamp was placed in an immersion tube, which was immersed in the sample contained in the reactor vessel to be irradiated with UV radiation. The Hg lamp was emitted at 185–524 nm. The reactor was equipped with power supply (0–100 W). Photooxidation studies were conducted in a photoreactor of 500 ml capacity.

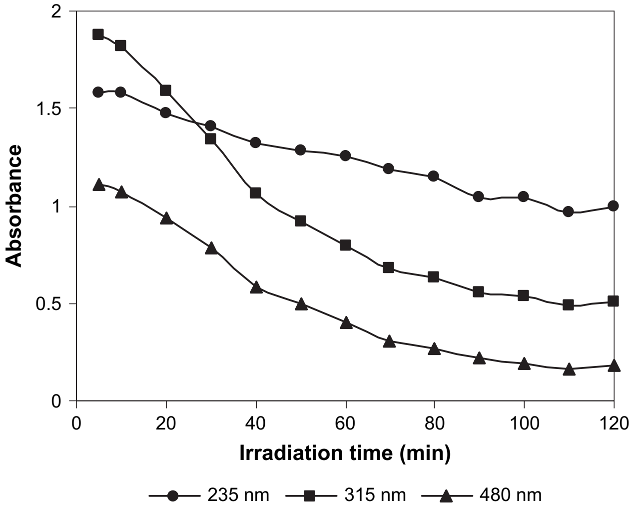


Fig. 3. Absorbance changes of C.I. Reactive Orange 16 at 235, 315 and 480 nm as function of irradiation time in aqueous solutions.

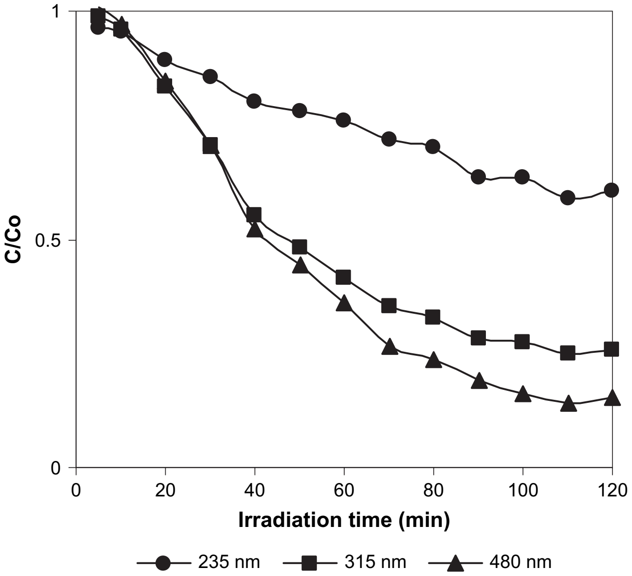


Fig. 4. C/C_0 changes of C.I. Reactive Orange 16 (RO16) as a function of irradiation time conditions as in Fig. 2; 20.8 °C; pH = 6.23; $[\mathrm{RO16}]_0 = 50\ \mathrm{mg\ L^{-1}}$.

2.3. Procedure

C.I. Reactive Orange 16 (50 mg $\mathrm{L^{-1}}$) was dissolved in distilled water and irradiated with UV lamp (80 mA) in the photoreactor. Samples were taken from photoreactor at 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110 and 120 min. UV/VIS spectra of each sample were recorded between 200 and 600 nm. The sample was first adjusted to pH 10 with NaOH. NaCl was added to each sample until saturation. The saturated sample (8 ml) was extracted with 3 ml of methyl-*tert*-butyl-ether. The ether fractions were evaporated to dryness. Finally, the residue was dissolved in 2 ml of methanol for GC/MS analysis.

2.4. UV/VIS spectroscopy

UV/VIS spectra were recorded between 200 and 600 nm, employing a double bundled UV/VIS spectrometer (Shimadzu, model UV-1601) equipped with 10 mm quartz cuvettes. The degradation of C.I. Reactive Orange 16 solution was followed by determining absorbance changes at 235, 315 and 480 nm by UV/VIS spectrometer.

Table 1
Kinetic constants of C.I. Reactive Orange 16 at 235, 315 and 480 nm

Wavelength (nm)	$k \times 1000$ ($\mathrm{min^{-1}}$)
235	4.60
315	13.00
480	17.20

Temperature = 20.8 °C; pH = 6.23; $[\mathrm{RO16}]_0 = 50\ \mathrm{mg\ L^{-1}}$.

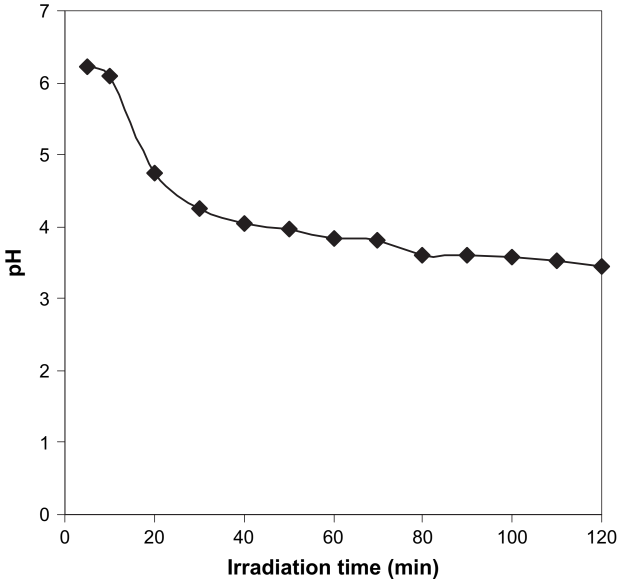


Fig. 5. pH changes of the solution during photooxidation of C.I. Reactive Orange 16 with irradiation time.

2.5. GC/MS conditions

The identification of degradation products of each sample was performed by GC/MS running in SCAN mode. The GC/MS (Shimadzu QP 5000) is equipped with a capillary column DB-1 (30 m × 0.25 mm × 0.25 μm film thickness). The GC column was operated in a temperature programmed mode with an initial temperature of 60 °C held for 5 min, ramp at 280 °C with a 10 °C min^{-1} rate, and held at this temperature for 5 min.

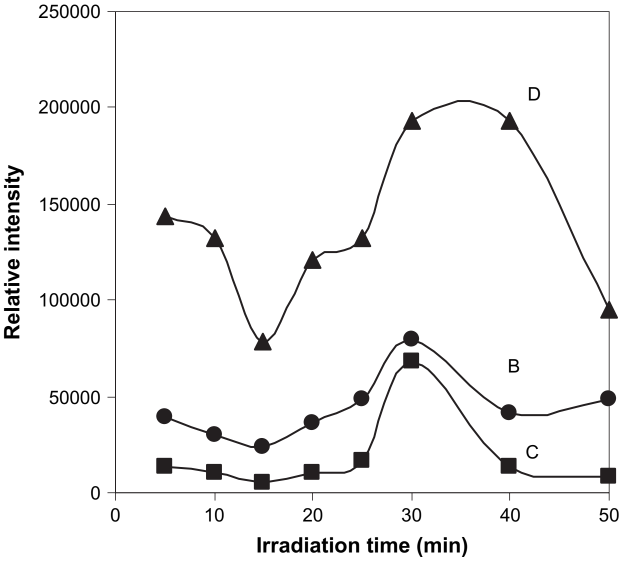


Fig. 6. GC/MS intensities of the degradation products (B, C and D) of C.I. Reactive Orange 16 as a function of irradiation time.

3. Results and discussion

3.1. Photodegradation of dyes

The absorption spectral changes during photooxidation of C.I. Reactive Orange 16 in aqueous solution are shown in Fig. 2. It is observed that the absorption spectrum of C.I. Reactive Orange 16 at pH = 10 is characterised by two bands in the UV region, with their maxima located at 235 and 315 nm, and by a band in the visible region located at 480 nm. The absorbance peaks at 235 and 315 nm are due to the benzene and naphthalene rings, and the absorbance peak at 480 nm is due to the azo linkage of C.I. Reactive Orange 16. The absorbance changes of C.I. Reactive Orange 16 at 235, 315 and 480 nm as functions of irradiation time in aqueous solutions are shown in Fig. 3. It is observed that the absorption of the bands decreases exponentially with time and almost disappears after about 100 min, resulting in complete decolorization of the solution. The absorbance at 235, 315 and 480 nm decreases rather slowly during the first 40 min and continues more rapidly. The slower decrease of the absorbance at 235 can be attributed to the formation of intermediates resulting from the photodegradation of the azo dye, which still contains benzene ring. The complete degradation of C.I. Reactive Orange 16 was observed at 100 min irradiation.

The photooxidation reaction is pseudo-first-order with respect to azo dye concentration. The kinetic constant can be linked to the dye concentration by Eq. (1).

$$\ln \frac{C}{C_0} = -kt \tag{1}$$

where C is the concentration of dye at time t, C_0 is the initial concentration of dye and k is the rate constant. Fig. 4 shows the variation of the normalized dye concentration with irradiation time at 235, 315 and 480 nm. The kinetic constants of C.I. Reactive Orange 16 at these wavelengths are given in Table 1. We may find from these results that the photooxidation rate of azo bond is about four times faster than benzene and naphthalene rings. The results can show that three degradation products were formed during photooxidation of C.I. Reactive Orange 16. There is a correlation between UV/VIS spectral changes of C.I. Reactive Orange 16 (Fig. 2) and kinetic results (Fig. 4) as functions of irradiation time. The plots indicate similar decolorization rate at 100 min of irradiation. The absorbances in UV region after 80 min of irradiation may be related to the products such as aliphatic amines and acids that cannot be identified by GC/MS.

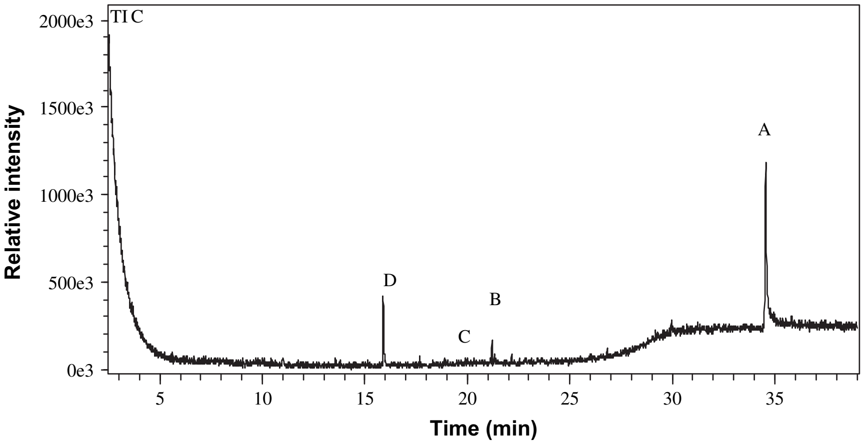


Fig. 7. Chromatogram of C.I. Reactive Orange 16 at 10 min photooxidation.

Photooxidation of C.I. Reactive Orange 16 was monitored by measurement of the pH with irradiation time. The pH of the solution decreases rapidly at the initial stage of the photooxidation, dropping from 6.23 to 4.04 at 40 min (Fig. 5). This drop in the pH indicates the formation of acid compounds with irradiation time. It is interesting to note that the pH of the solution remains almost constant even with prolonged irradiation. The results implied that organic acid compounds are still present after decolorization.

3.2. Identification of degradation products

Degradation products formed during the photooxidation process were analyzed by GC/MS and identified by interpretation of their fragment ions in the mass spectra. Three main compounds detected in the solution were presented in Fig. 1. The evaluation of these compounds during the first 50 min with irradiation time is shown in Fig. 6. It is observed that three degradation products of C.I. Reactive Orange 16 appear during 50 min of irradiation, including 6-acetylamino-3-amino-naphthalene-2-sulfonic acid (B), *N*-(3,4-bis-hydroxymethyl-phenyl)-acetamide (C) and phthalic acid (D). The concentrations of these compounds increase with irradiation time and go through maxima at about 30 min. The degradation products of 6-acetylamino-3-amino-naphthalene-2-sulfonic acid and *N*-(3,4-bis-hydroxymethyl-phenyl)-acetamide appear in small quantity indicates that photooxidation rate of naphthalene ring is slower than benzene ring. The degradation products are detectable for up to 50 min under irradiation.

GC/MS was used to monitor the formation of degradation products of C.I. Reactive Orange 16. The measurement results are shown in Fig. 7. The identified compounds after 10 min of photooxidation are C.I. Reactive Orange 16 (non-degraded form, (A), 6-acetylamino-3-amino-naphthalene-2-sulfonic acid (B),

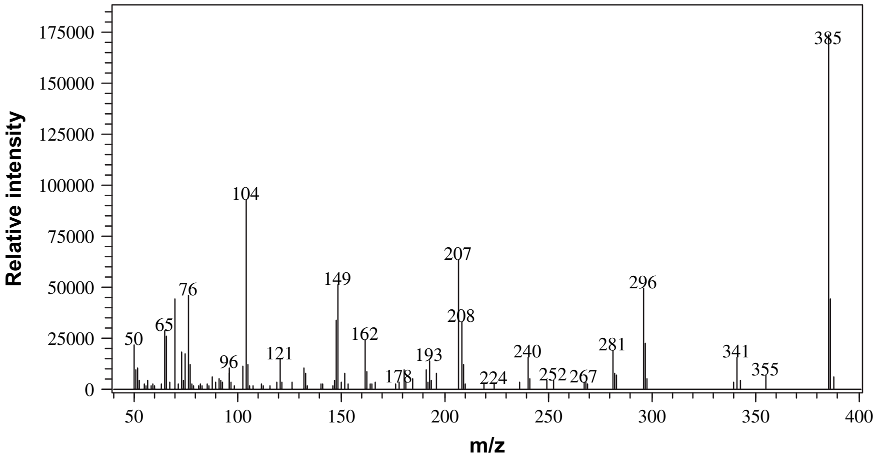


Fig. 8. Mass spectrum of C.I. Reactive Orange 16 (A).

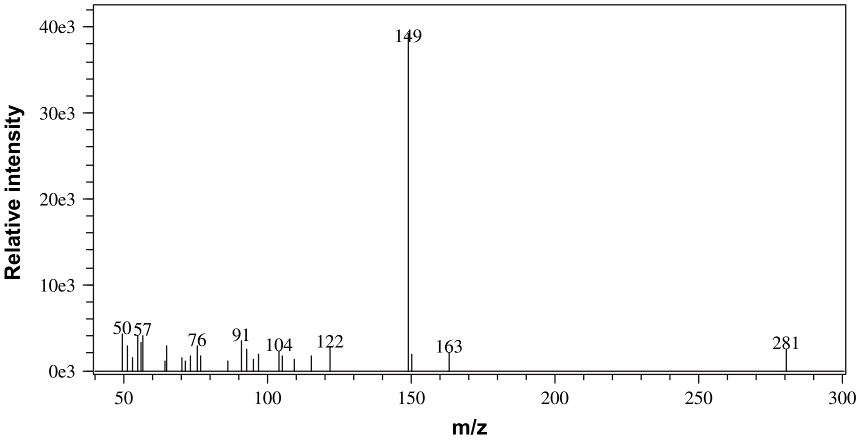


Fig. 9. Mass spectrum of degradation product B.

N-(3,4-bis-hydroxymethyl-phenyl)-acetamide (C) and phthalic acid (D). The degradation products were identified based on their molecular ion and mass spectrometric fragmentation peaks. The mass spectrum of C.I. Reactive Orange 16 is shown in Fig. 8. The mass spectra of three degradation products are shown in Figs. 9–11. The molecular weight of C.I. Reactive Orange 16 is not observed in the spectrum. The degradation products formed by the cleavage of the azo bond of the dye molecule are the primary reaction intermediates. The naphthalene group of the dye molecule was further oxidized to *N*-(3,4-bis-hydroxymethyl-phenyl)-acetamide and phthalic acid. The intermediates were detected by GC/MS in methanol. The degradation products are in methylated form because methanol prefers to react with carboxyl group to produce ester at a higher temperature during the GC/MS measurement. Therefore, the molecular weight of dimethylated phthalic acid is 194 as is seen in mass spectrum (Fig. 11). The other primary intermediate originating from the initial cleavage of the dye was not detected in the solution. This intermediate may undergo further degradation to form lower molecular weight acids. It should be noted that the lower molecular weight products were formed at 20 min of the photooxidation, as indicated by the sharp decrease of the pH (Fig. 5). The possible mechanism for the formation of these degradation products in the photooxidation system is proposed in Scheme 1. The results have confirmed the formation of substituted benzene.

4. Conclusions

The photodegradation of aqueous solutions of C.I. Reactive Orange 16 was investigated with UV irradiation. It was found that the sulfonated azo dyes can be destroyed by UV photooxidation process. The kinetics of the degradation depends on the azo,

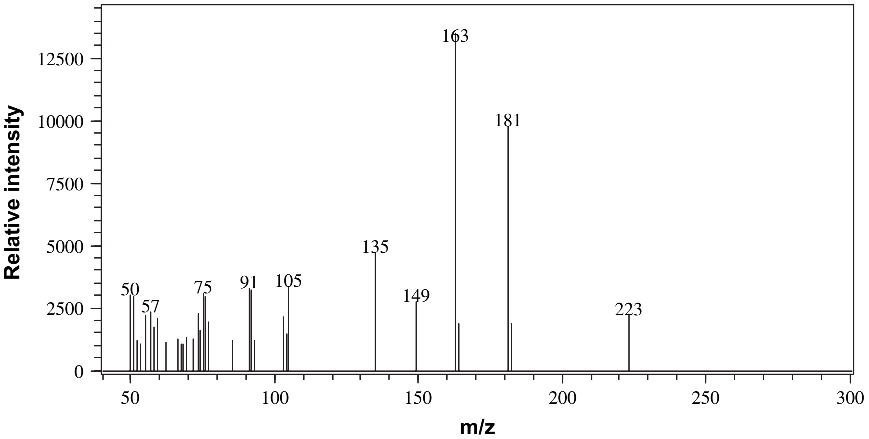


Fig. 10. Mass spectrum of degradation product C.

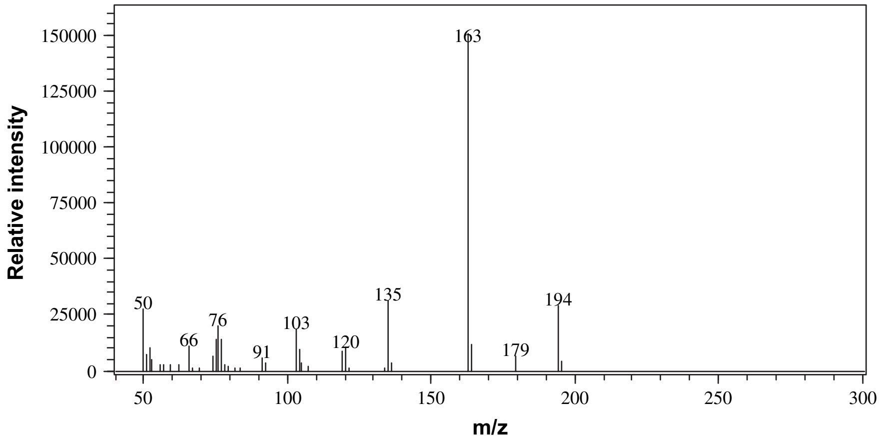
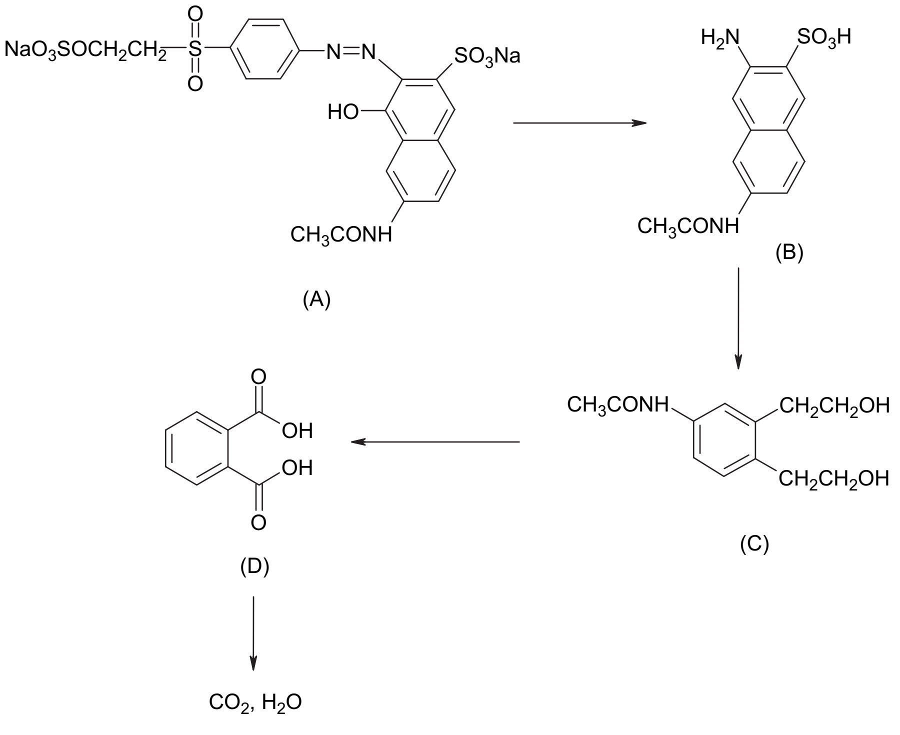


Fig. 11. Mass spectrum of degradation product D.

benzene and naphthalene groups of the dyes. We found that the first step of the degradation is related to cleavage of azo bond of the molecule and naphthalene ring which leads to further degradation until complete mineralization. Kinetic considerations may allow us to understand the mechanism of the degradation.

The primary degradation products undergo successive oxidation steps which lead to formation of aromatic and aliphatic acids. This results in decrease of pH of the solution. GC/MS analysis showed that three degradation products were detected during photooxidation process. The results are comparable with kinetic studies.

Although the degradation rate and formation of degradation products depend on the type of the dye, the UV photooxidation technique seems to be applicable to any industrial wastewater containing azo dyes. The results can be taken as a starting step for the next application of the wastewater.



Scheme 1. Possible mechanism of photodegradation of C.I. Reactive Orange 16 under UV irradiation.

Acknowledgements

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