IJNRD.ORG ISSN : 2456-4184
INTERNATIONAL JOURNAL OF NOVEL RESEARCH AND DEVELOPMENT (IJNRD) | IJNRD.ORG
An International Open Access, Peer-reviewed, Refereed Journal

OZONATION OF SOME AZO DYES: STUDY OF OXIDATION BY-PRODUCTDS FORMED DURING OZONATION

Submitted by

Umesh Kumar Khare[1], Purnendu Bose[2]

[1] Professor in Civil Engineering Department, Government Engineering College Modasa(Gujarat), India and former Ph.D. Research scholar, department of Civil Engineering, Indian Institute of Technology Kanpur, India

[2] Purnendu Bose , Professor, Department of Civil Engineering, Indian Institute of Technology, Kanpur, India

*** Corresponding author: Umesh Kumar Khare, email: ukkhare@gmail.com**

Abstract: Ozonation has been applied to many fields in water and wastewater treatment. The effect of ozonation on the degradation process of azo dyes CI Acid Red14 (AR14), Congo Red (CR), CI Reactive Black 5(RB5), and CI Reactive Violet 5(RV5) has been studied in the semi batch rector with an influent ozone concentration of 58.5 mg/l. and flow of 0.5 l/min. The parameters such as pH, color, absorbance (at maximum wavelength), conductivity, chemical oxygen demand (COD), total organic carbon (TOC) were monitored during the ozonation process at different time intervals. Intermediate by-products formed during the ozonation of synthetic dye solutions were identified by derivatization with O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride(PFBHA) and subsequent extraction follwed by GC/MS analysis. Intermediate ozonation by-products identified are alcohol, aldehydes, acetone, glyoxal, glycodial and organic acids

During the ozonation process the rapid decrease in pH and sharp increase of conductivity indicated the formation of acidic by-products and ions which were identified by high performance ion chromatography. Sulfate, nitrate, formate and oxalate were identified as main oxidation by-products. Formation of nitrate is presumably the result of the oxidation and cleavage of azo and amino groups while sulfate formation is due to oxidation and cleavage of sulfonic acid groups. COD and TOC were seen to decline for all the dyes with ozonation time but reduction in COD was more efficient then reduction in TOC. Results obtained confirm that ozonation is highly effective in removing the color of synthetic dye solutions. COD and TOC removals were however less complete, suggesting production of colorless ozonation by-products.

Keywords: Ozonation; Acid Red 14; Congo Red; Reactive Black 5; Reactive Violet 5

I. INTRODUCTION

India has become a major producer of dyes and pigments to cater to the needs of not only the textile industries but also of other industries such as paper, rubber, plastics, paints, printing inks, art and craft, leather, food, drug and cosmetics . Azo dyes are an abundant class of synthetic, colored, organic compounds, characterized by nitrogen to nitrogen double bonds (N=N).They contain between one and four azo groups usually attached to two radicals of which at least one, but usually both, are aromatic groups (Sarasa et al., 1998; Wu and Wang,2001; Wang et al.,2003). They are most used dyes in textile industry. In general, 40-90% of the dye is fixed to the fabric during the dyeing process, depending on the fixation rate of the applied dyestuff. Large amount of unfixed azo dye remain in effluent after completion of dyeing process, which leads to decrease in transparency of water and inhibition of sunlight if discharged in water body (Gomes et al., 2000; Wang et al., 2003).

Azo dye molecules are highly structured polymers, hence they are very difficult to breakdown biologically and can not be treated efficiently by conventional methods like an activated sludge process (Lin and Lin, 1993; Arslan and Balcioglu, 1999). Under anaerobic conditions, many bacteria reduce azo bond in the dye molecule, to produce colorless aromatic amines which can be toxic and carcinogenic (Shaw et al., 2002; Pearce et al., 2003; Buitron et al., 2004).

Acid dyes are water-soluble anionic dyes and are applied to nylon, wool, silk, and modified acrylics (Tsai et al., 2004). Reactive dyes are highly water soluble and enable to form covalent bond with fibers. They are used to dye cellulose fibers, wool and nylon (Tyagi and yadav, 1998). Direct dyes are applied to the cotton in solution and are held to the fibres by hydrogen bonds and instantaneous dipole-induced dipole forces. Among the various types of dye, Congo Red (CR) dye is used in wool and silk to give red color with a yellow fluorescence (Purkait et al.,2004). It is known that reactive and acid dyes are the most problematic, as they tend to pass through conventional treatment system unaffected (Wang et al, 2003).

Ozone is very effective for complete removal of color, because it attacks conjugated double bonds which are associated with color but provides only partial reduction of COD and TOC (Muthukumar et al., 2004). The mechanism of reaction of ozone follows two main paths: a direct path corresponding to the action of molecular ozone, and an indirect path resulting from the decomposition of ozone to radicals, initiated by hydroxyl ions (Sarasa et al, 1998). Ozone and hydroxyl radicals ($OH^{\cdot}$) generated in the aqueous solution are able to open the aromatic rings (Oguz et al., 2005).

Although ozone is used increasingly to degrade the recalcitrant compounds still little is known about the reaction intermediates and products formed during ozonation of textile effluents. First by-products after short term ozonation are not be underestimated since they might have higher toxic potential than original compound (Koch et al. 2002;Wang et al, 2003).Toxic intermediates formed as first by-products are destroyed by further ozonation. Glaze(1986) noted that ozonation of water form organic peroxides, unsaturated aldehydes. Aliphatic aldehydes, ketones and acids along with nitates and ammonia can be found as final by-products. Chan & Larson described main by-products formed after ozonation of anilines:- nitrobenzene, nitrosobenzene, azobenzene, azoxybenzene, benzidine and phenazine (Sarasa et al. 2002).Dye molecules are oxidized to small molecules such as organic acids, aldehydes, ketones etc, instead of completely mineralized by ozonation (Lin and Lin, 1993; Wang et al., 2003).

It has been confirmed that rate limiting step in the ozonation of dye containing wastewater is the mass transfer of ozone from gas phase to the wastewater. Time for complete decolorization increases with increase in number of azo groups and salt concentration in azo dyes while it decreases with increase in number of sulphonic acid groups in the dye structure (Shu and Hung, 1995; Muthukumar et al., 2005).At higher dye concentrations ozonation may become less efficient because of increased competition for ozone between parent molecules and reaction byproducts (Alvares et al., 2001; Alaton et al., 2002).

This study include the ozonation of aqueous azo dyes AR14 (1000 mg/l), CR (1000 mg/l), RB5 (2000 mg/l) and RV5 (2000 mg/l) solutions in semi batch reactor. The objective of the study was to investigate the ozonation by-products formed during the ozonation of synthetic dye wastewater of mostly used acidic, direct and reactive (monoazo and di-azo) azo dyes and to study the mineralization of these dyes during the ozonation.

II. RESEARCH METHODOLOGY

The azo dyes CI Acid Red 14, Congo Red, CI Reactive Black 5 and CI Reactive Violet 5, used for the experiments were obtained from Colour Chem Ltd. Mumbai (India) as a commercially available dye. Structures of these dyes are as in Figure1 and characteristics are as follows:

C.I. name and number	Azo group	Molecular Weight (g)	λ_{max} (nm)	%Carbon (theoretical)	%Carbon (Average) (actual)
Acid Red 14 (14720)	Mono azo	502	510	47.8	41.232
Congo Red (22120)	Di-azo	696.7	495	55	31.734
Reactive Black 5 (20505)	Di-azo	991.8	597	31.5	19.798
Reactive Violet 5 (18097)	Mono-azo	797	560	32	13.06

Elemental analyzer (CHNOS analyzer, model CE-440, Leemans Lab. Inc. USA) was used to determine actual carbon, hydrogen and nitrogen content. On the bases of carbon content the purity of AR14, CR, RB5 and RV5 were around 86%, 57%, 62% and 43%. All the dyes were used as available without any further purification.

The experimental setup used for ozonation consists of a bubble contactor operated in the semi-batch mode. The shape of the reactor was cylindrical with diameter of 6.4 cm and height 39 cm. The rector was fitted with porous ceramic plate at bottom to form bubbles of 1 mm average size. Ozone was generated in gas phase by passing pure dry oxygen through the ozone generator (INDIZONE, CDS/4C/AF; India). Arrangements were made for applying this gas mixture to the bottom of the reactor, where it bubbled through a porous ceramic plate and moved upwards through the reactor. The gas flow into the reactor was controlled using an on-line mass flow controller (AALBORG, GFC171S; USA). Ozone concentrations in the gas influent and effluent to the reactor were measured using online UV absorbance based ozone monitors (ANSEROS, OZOMAT GM-6000-OEM; Germany).

All components of the experimental setup and the reactor were made of glass, teflon or stainless steel to eliminate ozone consumption due to corrosion of components by ozone.

It was assumed that due to the agitation caused by gas bubbles and due to low reactor height: diameter ratio, the aqueous contents of the reactor were well mixed.

Aqueous solutions of AR14 and CR were prepared in double distilled water of 1000 mg/l strength while relatively high concentrations 2000 mgl^{-1} aqueous solutions were prepared for RB5 and RV5 in order to investigate the effect of ozonation. Mass flow controller and both ozone monitors were switched on for at least 30 minutes for warming up .Rector was filled with 500 ml dye solution and flow of oxygen to ozone generator was set to 0.5 l min^{-1}. At least for 5 min only oxygen was supplied just to make sure that no residual ozone present in cuvette of ozone monitors. Both the monitors were then set for zero reading if required. Ozone generator was then switched on and readings of influent and effluent ozone monitors were recorded at 5 min intervals. Samples (20ml) were collected during ozonation after 10, 20, 30, 40, 60, 80 min intervals. First dye solution without buffer was ozonated to study effect on pH and conductivity. Then dye solutions were suitably buffered with 0.2 M phosphate buffer to keep solutions around neutral pH and samples were prepared for COD, TOC and by-product analysis.

Sample pH was measured using a combination, pH electrode (Toshiwal CL-51, India) connected to a digital pH meter (Toshiwal CL-54, India)and conductivity was measured by digital conductivity meter CC601.COD of the samples were analyzed by using closed reflux method as described in Standard Methods (Method No. 5220 C, APHA et al., 1995).Samples were analyzed for TOC on the Carbon Analyzer, model TOC-V $_{CPN}$, Shimadzu Made, as per Standard Methods (APHA et al., 1995). Analysis of organic and inorganic anions was performed by high performance ion chromatograph (761 compact IC, Metrohm Ltd., CH-9101, Herisau, Switzerland) equipped with C-18 anion column and operating in suppressed conductivity detection mode. Sample injected of 20 µl in volume and flow rate of elluent (sodium bicarbonate and sodium carbonate) was 0.7 mL/min.

Analysis of aldehydes and acetone was based on the method described in EPA556 and by Weinberg et al.(1997). In each sample of 2 ml 25 mg of KHP was added and for derivatization 1 ml PFBHA(6 mg/l) was also added. Such vials were put for 1 hr and 45 min at 50ºC after cooling to room temperature eight drops of concentric H_2SO_4 was added in vial to quench the derivatization reaction.Then samples were extracted into 2 ml of hexane by shaking for three min. After phase separation the hexane layer was drawn off into a 16 ml vial containing 4 ml 0.2N H_2SO_4 for extraction cleanup. After 30 second shaking the hexane phase was transferred into auto sampler vials. GC/MS (Thermo-Finnigan) equipped with 30m x 0.25 mm DB-5 column was used for compound identification The temperature program used was as follows:-Injector temperature was 180ºC, initial temperature 50ºC held for 1 min, 50ºC-220ºCat 4ºC/min then ramping at 50ºC/min to 250ºC to clean off the column.

III. RESULTS AND DISCUSSION

High dye concentrations (2000 mg/l) of reactive dyes and 1000 mg/l for acid and direct dyes were chosen to make sure about availability of organic matter after different ozonation time and due to comparatively low purity of reactive dyes. Generally concentrations of dye in dye bath are considered to be between 0.8 – 2.6 gl^{-1} (Arslan and Balcioglu, 2000). Sharp reduction in pH was observed in samples of all dyes because of the formation of acidic by-products during the ozonation process. Conductivity increases with ozonation due to formation of ions and acids. Variations in pH and conductivity for selected dyes with ozonation time are shown in Figure 2. Conductivity observed for the reactive dyes were high compared to other dyes which may be due to low purity and high concentration of dye taken for ozonation. In prolonged ozonation due to more acidic solutions organic compounds can not be oxidized to carbon dioxide but to carboxylic acids. For the study of mineralization, intermediate by-products and end products formed during ozonation the samples were buffered to have pH around 7.0.

Sulfate, nitrate, formate and oxalate were identified as the main oxidation end products of all selected dyes. Concentrations of sulfate and nitrate increase with ozonation time which may be due to oxidation of sulfonic acid groups, azo and amino groups. Formate and oxalate concentrations also increase but reduction observed towards end which may be due to more mineralization after 60 min of ozonation. Changes in concentrations of formate, oxalate, sulfate and nitrate after different time of ozonation for selected dyes were plotted with ozone consumed in mg of ozone consumed/ mg of initial TOC as shown in Figure3. VFA for different dyes were found to increase with the ozonation time but for CR and RV5 after 40 min ozonation VFA dcreases due to more mineralization. More reduction was observed in VFA after aerobic biodegradation of ozonated dyes due to high mineralization during aerobic biodegradation as shown in Figure 4.

Decolorization was almost complete for all the dyes after 60 min of ozonation. COD was seen to decline for all the compounds with increase in mg of ozone consumed/ mg of initial TOC, which may be partly attributed to mineralization of organic carbon and partly to conversion of the remaining organic carbon to higher average oxidation stage. Further reductions in TOC suggest considerable mineralization of compounds due to ozonation, but the obtained TOC values may not represent actual TOC concentrations due to the losses of volatile compounds (formaldehyde, acetaldehyde) during ozonation. Aerobic biodegradation of ozonated dyes results more than 90% reduction in COD and TOC which suggest considerable mineralization as shown in Table1-4.

PFBHA was used in attempt to derivatize ozonation by-products which were polar compounds and have carbonyl or carboxylic acid groups. PFBHA reacts with the carbonyl functionalities to form the corresponding oxime which should be extractable from the aqueous phase by liquid- liquid extraction. PFBHA oxime have strong mass spectra fragmentation peaks at m/z =181which is confirmed as ($C_6F_5CH_2^-$) the pentafuorobenzyl, PFB ion (Bose et al.1998). The GC/MS analysis of acidic extract of all compounds showed the presence of some major by-products listed in table 5. Chromatograms, showing the presence of listed by-products are shown in Figure 5 and Figure 6. Figure 7 shows matching of mass chromatogram of some identified compounds like Acetaldehyde and Glycodial with main library(mainlb) of GC/MS.

IV. CONCLUSIONS

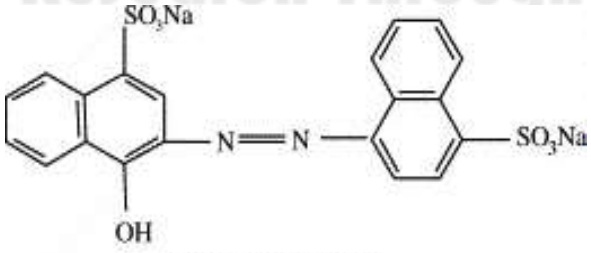
Results obtained indicate that almost complete decolorization took place after 60 min of ozonation for all selected dyes. Experimental study showed that ozone treatment is an effective treatment for color removal and biodegradability enhancement but gives partial reduction of TOC and COD for all the compounds. Sulfate, nitrate, formate and oxalate were identified as the main oxidation end products of ozonation of all selected dyes. Main intermediate ozonation by-products identified by GC/MS analysis were benzyl Alcohol, Acetaldehyde, Acetone, Glycoaldehyde, Benzyldehyde, Glyoxal, and Glycoldial.

REFERENCES

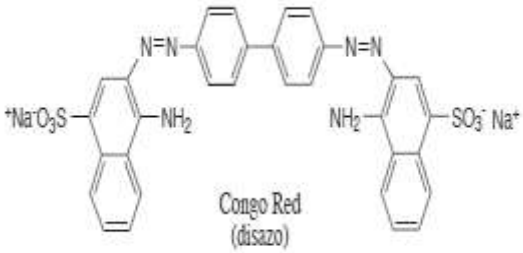
Adams Craig D. and Gorg Steven (2002).Effect of pH and gas phase ozone concentration on the decolorization of common textile dyes.Journal of Env. Engg., 128(3), 293-297.

Alaton Idil Arslan; Kornmuller Anja; and Jakel M. R. (2002) .Ozonation of spent reactive dye baths: effect of HCO3-/CO3- Alkalinity.Journal of Env. Engg., 128(8), 689-696.

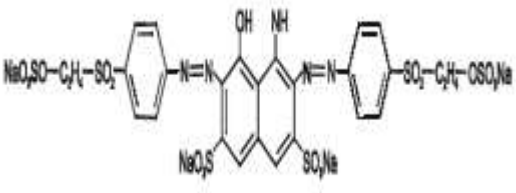
Alvares, A.B.C. Diaper,C. and Parsons,S.A.(2001). Partial oxidation by ozone to remove recalcitrance from W.W.- a review. Environ. Technol., 22, 409-427.
APHA (1995) Standard methods for the examination of water and wastewater, 18th edition, Washington D.C., USA.
Arslan,I.,Akmehmet Balcroglu,I and Tuhkanen T.(1999).Oxidative treatment of simulated dyehouse effluent by UV and near-UV light assisted Fenton's Reagent. Chemosphere, 39, 2767-83.
Arslan I. and Balcioglu, I.A. (2000). Effects of common reactive dye auxiliaries on the ozonation of dyehouse effluents containing vinylsulphone and aminochlorotriazine dyes. Desalination 130, 61–71.
Buitrón Germán, Maribel Quezada and Gloria Moreno (2004) Aerobic degradation of the azo dye acid red 151 in a sequencing batch biofilter. Bioresource technology,92(2),143-149.
Chu,W.,and Ma,C.W.(2000) .Quantitative prediction of direct and indirect ozonation kinetics. Water Research, 34(12), 3153-3160.
Gomes de Moraes Sandra, Renato Sanches Freire and Nelson Durán (2000).Degradation and toxicity reduction of textile effluent by combined photocatalytic and ozonation processes . Chemosphere, 40(4), 369-373.
Gurol Mirat D, Singer Philip C. (1982). Kinetics of ozone decomposition: A dynamic Approach.Environ. Sci. Technol., 16(7),377-383.
Koch M., Yediler A., Lienert D ., G. Insel and A. Kettrup(2002).Ozonation of hydrolyzed azo dye reactive yellow 84 (CI).Chemosphere,46(1),109-113.
Lin S.H. and Lin C. M.(1993).Treatment of textile waste effluents by ozonation and chemical coagulation.WaterResearch,27(12),1743-1748.
Muthukumar M. , Sargunamani D., Selvakumar N. (2005). Statistical analysis of the effect of aromatic, azo and sulfonic acid groups on decolorization of acid dye effluents using advanced oxidation processes. Dyes and Pigments 65, 151-158.
Muthukumar M. and Selvakumar N. (2004). Studies on the effect of inorganic salts on decolouration of acid dye effluents by ozonation . Dyes and Pigments 62(3), 221-228.
Oguz Ensar,Keskinler Bulent , Celik Zeynep (2005) Ozonation of aqueous Bomplex Red CR-L dye in a semi-batch reactor. Dyes and pigments 64, 101-108.
Pearce C. I., Lloyd J. R. and Guthrie J. T. (2003). Removal of colour from textile wastewater using whole bacterial cells: a review. Dyes and Pigments,58(3),179-196.
Purkait M. K., Vijay S. S., Dasgupta S. and De S.(2004). Separation of congo red by surfactant mediated cloud point extraction. Dyes and Pigments 63(2), 151-159.
Robinson T.,McMullan G.,merchant R.,Nigam P.(2001)Remediation of dyes in textile effluent : a critical review on current treatment technologies with a proposed alternative. Biosource Technology, 77,247-255.
Sarasa J., Roche M. P., Ormad M. P., Gimeno E., Puig A and Ovelleiro J.L.(1998). Treatment of a wastewater resulting from dyes manufacturing with ozone and chemical coagulation . Water Research,32(9) 2721-2727.
Shaw C. B., Carliell C . M. and Wheatley A. D.(2002). Anaerobic/aerobic treatment of coloured textile effluents using sequencing batch reactors .Water Research 36(8),1993-2001.
Shu Hung-Yee and Chang Ming-Chin (2005). Decolorization effects of six azo dyes by O_3, UV/O_3 and UV/H_2O_2 processes . Dyes and Pigments 65(1), 25-31.
Shu Hung-Yee and Huang Ching-Rong (1995). Degradation of commercial azo dyes in water using ozonation and UV enhanced ozonation process . Chemosphere, 31(8)3813-3825.
Tsai W. T., Chang C. Y., Ing C. H. and Chang C. F. (2004). Adsorption of acid dyes from aqueous solution on activated bleaching earth. Journal of colloid and interface science, 275(1), 72–78.
Tyagi O.D. and Yadav M.(1990).A text book of synthetic dyes, Anmol Publication, New Delhi.
Wang Chunxia, Ayfer Yediler, Doris Lienert, Wang Zijian and Antonius Kettrup (2003).Ozonation of an azo dye C.I. Remazol Black 5 and toxicological assessment of its oxidation products .Chemosphere,52(7),1225-1232.
Wu J.N. and Wang T.W.(2001). Ozonation of aqueous azo dye in a semi-batch reactor. Water Research. 35 (4),1093–1099.
Zhang Feifang, Ayfer Yediler ,Xinmiao Liang and Antonius Kettrup (2004). Effects of dye additives on the ozonation process and oxidation by-products: a comparative study using hydrolyzed C.I. Reactive Red 12. Dyes and Pigments 60(1), 1-7.
Weinberg H. S. and Glaze W. H. 1997. A unified approach to the analysis of polar organic by-products of oxidation in aqueous matrices. Wat. Res. 31, 1555-1572.



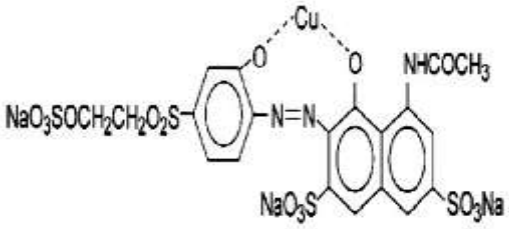
Acid Red 14 (AR14)
C. I. 14720



Congo Red
(disazo)



Reactive Black 5 (RB5)



Reactive Violet 5 (RV5)

Figure 1. Chemical structures of the Acid Red 14, Congo Red, Reactive Black 5 and Reactive Violet 5.

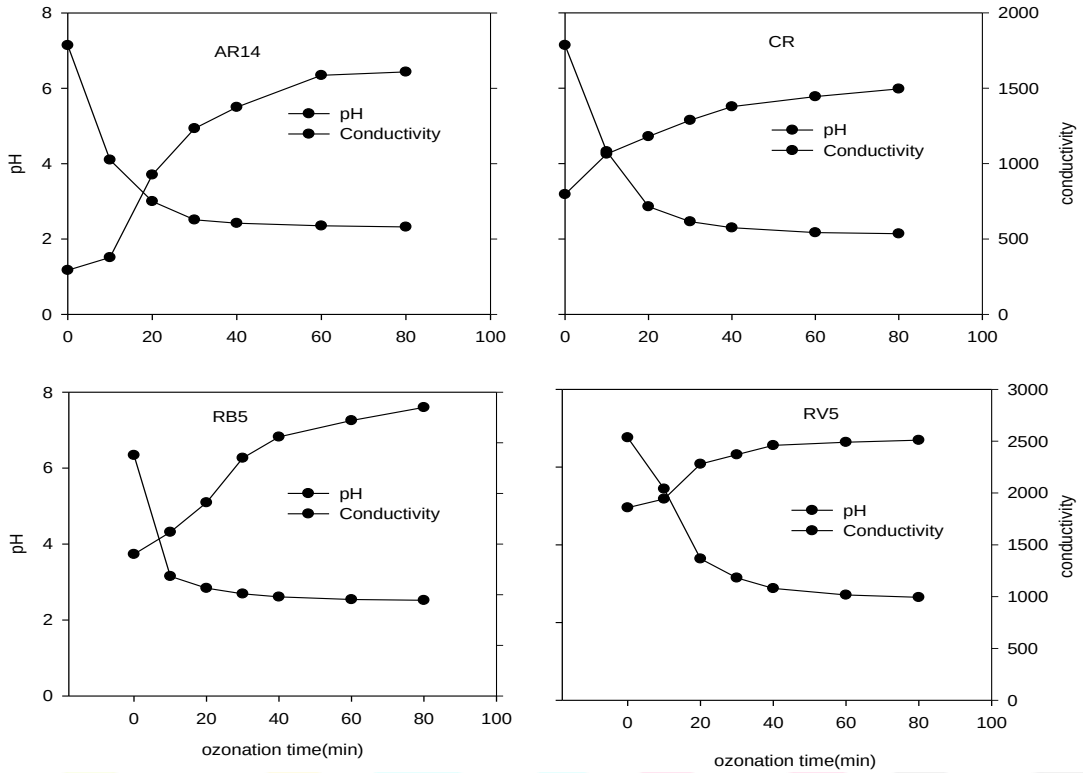


Figure 2 Effects on pH and Conductivity during ozonation of dyes (sample prepared without buffer).

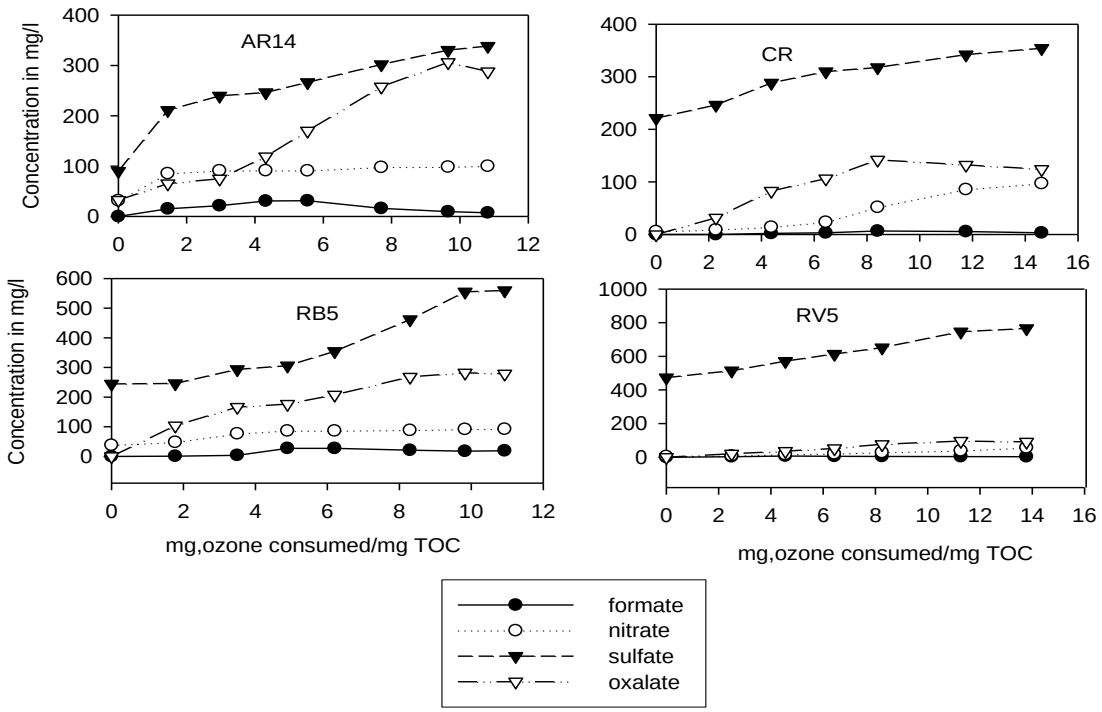


Figure 3 Effects on concentration of end products during ozonation of different dyes.

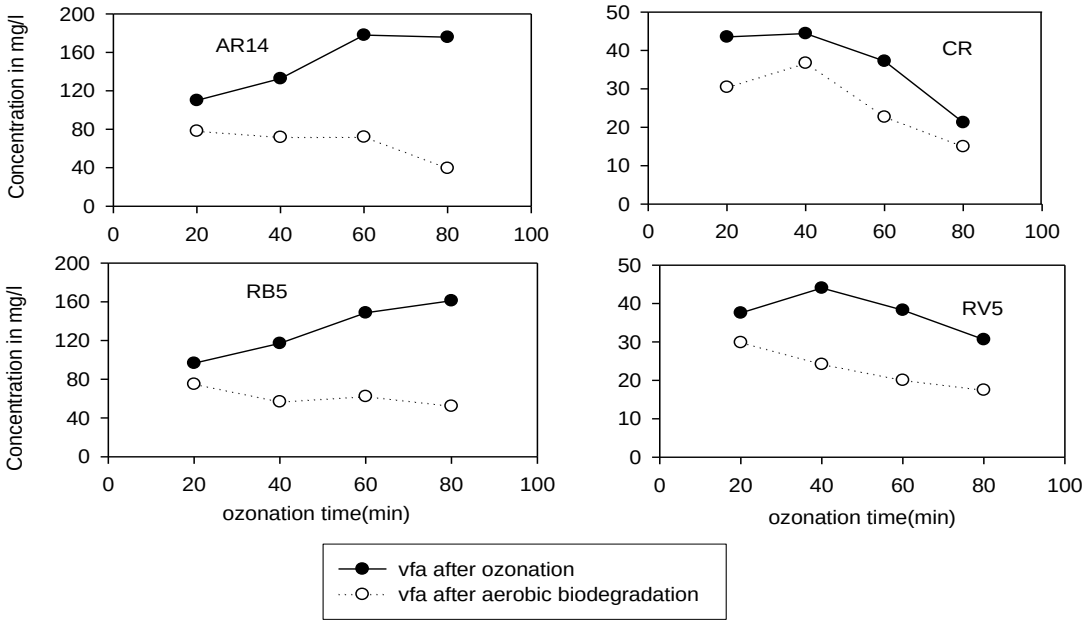


Figure 4 Variation in VFA during ozonation and after biodegradation of ozonated samples of dyes.

Table 1. Summary of Treatment of Acid Red-14 (AR-14) Dye by Ozonation–Aerobic Biodegradation

Ozone dose (mg Ozone Absorbed per mg Initial TOC)	Initial COD	COD After Ozonation	COD After Aerobic Treatment	Overall COD Removal (Percent)	Initial TOC	TOC After Ozonation	TOC After Aerobic Treatment	Overall TOC Removal (Percent)	Color (Pt-Co Units)
2.97	1083 --	728 *32.78*	572 *21.43*	47.18	403 --	349 *13.40*	230 *34.10*	42.93	1500
5.54	1083 --	488 *54.94*	353 *27.66*	67.41	403 --	283 *29.78*	177 *37.46*	56.08	200
7.7	1083 --	374 *65.47*	196 *47.59*	81.90	403 --	242 *39.95*	101 *58.26*	74.94	100
9.66	1083 --	259 *76.08*	80 *69.11*	92.61	403 --	189 *53.10*	37 *80.42*	90.82	15

Note: Underlined numbers represent COD or TOC in mg/L
Numbers in *italics* represent percent COD or TOC removal efficiency of the operation

Table 2. Summary of Treatment of Congo Red (CR) Dye by Ozonation–Aerobic Biodegradation

Ozone dose (mg Ozone Absorbed per mg Initial TOC)	Initial COD	COD After Ozonation	COD After Aerobic Treatment	Overall COD Removal (Percent)	Initial TOC	TOC After Ozonation	TOC After Aerobic Treatment	Overall TOC Removal (Percent)	Color (Pt-Co Units)
4.37	681 --	439 *35.54*	335 *23.69*	50.81	240 --	213 *11.25*	132 *38.3*	45.00	1750
8.40	681 --	237 *65.20*	152 *35.86*	77.68	240 --	167 *30.42*	68 *59.28*	71.67	125
11.75	681 --	118 *8267*	45 *61.86*	93.39	240 --	106 *55.83*	18 *83.02*	92.50	25
14.63	681 --	83 *87.81*	34 *59.04*	95.01	240 --	66 *72.50*	14 *78.79*	94.17	5

Note: Underlined numbers represent COD or TOC in mg/L
Numbers in *italics* represent percent COD or TOC removal efficiency of the operation

Table 3. Summary of Treatment of Reactive Black-5 (RB-5) Dye by Ozonation–Aerobic Biodegradation

Note: Underlined numbers represent COD or TOC in mg/L
Numbers in *italics* represent percent COD or TOC removal efficiency of the operation

Table 4. Summary of Treatment of Reactive Violet-5 (RV-5) Dye by Ozonation–Aerobic Biodegradation

Ozone dose (mg Ozone Absorbed per mg Initial TOC)	Initial COD	COD After Ozonation	COD After Aerobic Treatment	Overall COD Removal (Percent)	Initial TOC	TOC After Ozonation	TOC After Aerobic Treatment	Overall TOC Removal (Percent)	Color (Pt-Co Units)
3.50	929 --	613 *34.0*	383 *37.5*	58.77	329 --	260 *21.0*	162 *37.7*	50.45	875
6.20	929 --	376 *59.5*	218 *42.0*	76.53	329 --	203 *38.3*	78 *61.6*	76.29	75
8.30	929 --	321 *65.4*	107 *66.7*	88.37	329 --	178 *45.9*	42 *76.4*	87.23	40
9.82	929 --	281 *69.7*	78 *72.2*	91.60	329 --	171 *48.0*	40 *76.6*	87.84	5

Ozone dose (mg Ozone Absorbed per mg Initial TOC)	Initial COD	COD After Ozonation	COD After Aerobic Treatment	Overall COD Removal (Percent)	Initial TOC	TOC After Ozonation	TOC After Aerobic Treatment	Overall TOC Removal (Percent)	Color (Pt-Co Units)
4.56	603 --	341 *43.45*	201 *41.06*	66.67	218 --	159 *27.06*	74 *53.46*	66.06	125
8.26	603 --	228 *62.19*	105 *53.95*	82.59	218 --	108 *50.46*	41 *62.04*	81.19	50
11.27	603 --	164 *72.80*	71 *56.71*	88.23	218 --	78 *64.22*	26 *66.67*	88.07	10
13.79	603 --	132 *78.11*	56 *57.58*	90.71	218 --	65 *70.18*	21 *67.69*	90.37	5

Note: Underlined numbers represent COD or TOC in mg/L
Numbers in *italics* represent percent COD or TOC removal efficiency of the operation

Table 5. Summary of by-products idenified

By-product	Retention time, min	Molecular weigh of PFBHA abduct	Identified compound by GC/MS using mainlb	Molecular weight of parent pound	Parent compoud
A	6.73	198	Pentaflurobenzyl Alcohol	108	$C6H_5CH_2OH$
B	9.75,9.99	239	Acetaldehyde oxime,	44	CH_3CHO
C	11.81	253	Acetone	58	CH_3COCH_3

D	12.43	253	Propionaldehyde	58	CH_3CH_2CHO
E	17.66,18.48	255	Glycoaldehyde	61	CH_3OHCHO
F	24.99	285	1,3 Dihydroxypropanone oxime	76	$C_3H_8O_2$
G	27.18	301	Benzyldehyde	106	C_6H_5CHO
H	33.97,34.17	448	Glycoldial	58	$C_2H_2O_2$
I	35.06	462	Glyoxal di oxime	88	$C_2H_4N_2O_2$
J	25.01	225	Formaldehyde oxime	30	HCHO

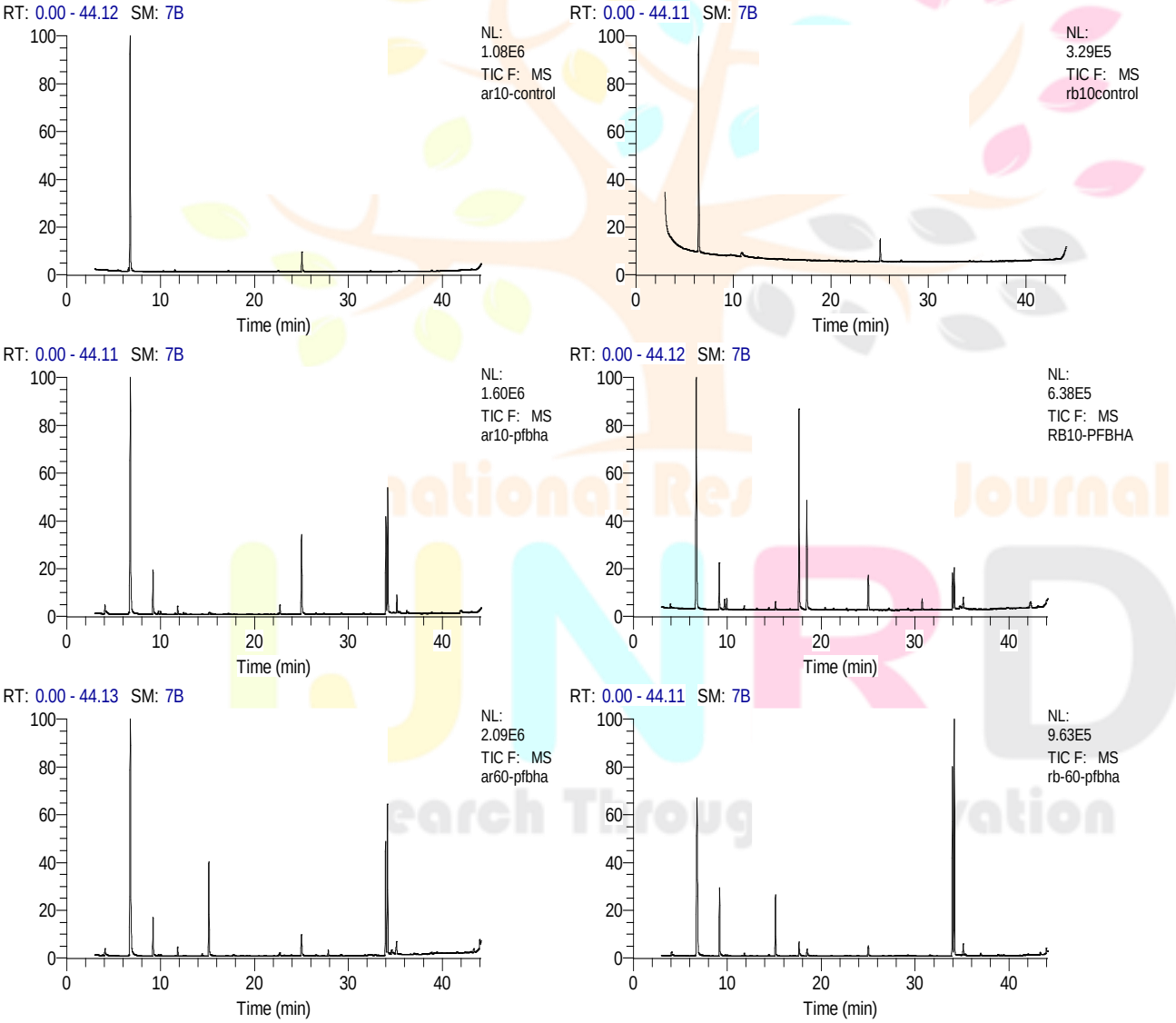


Figure 5 Chromatogram of GC/MS analysis of acidic extract of AR14 and RB5 showing the presence of some major by-products listed in table 5.

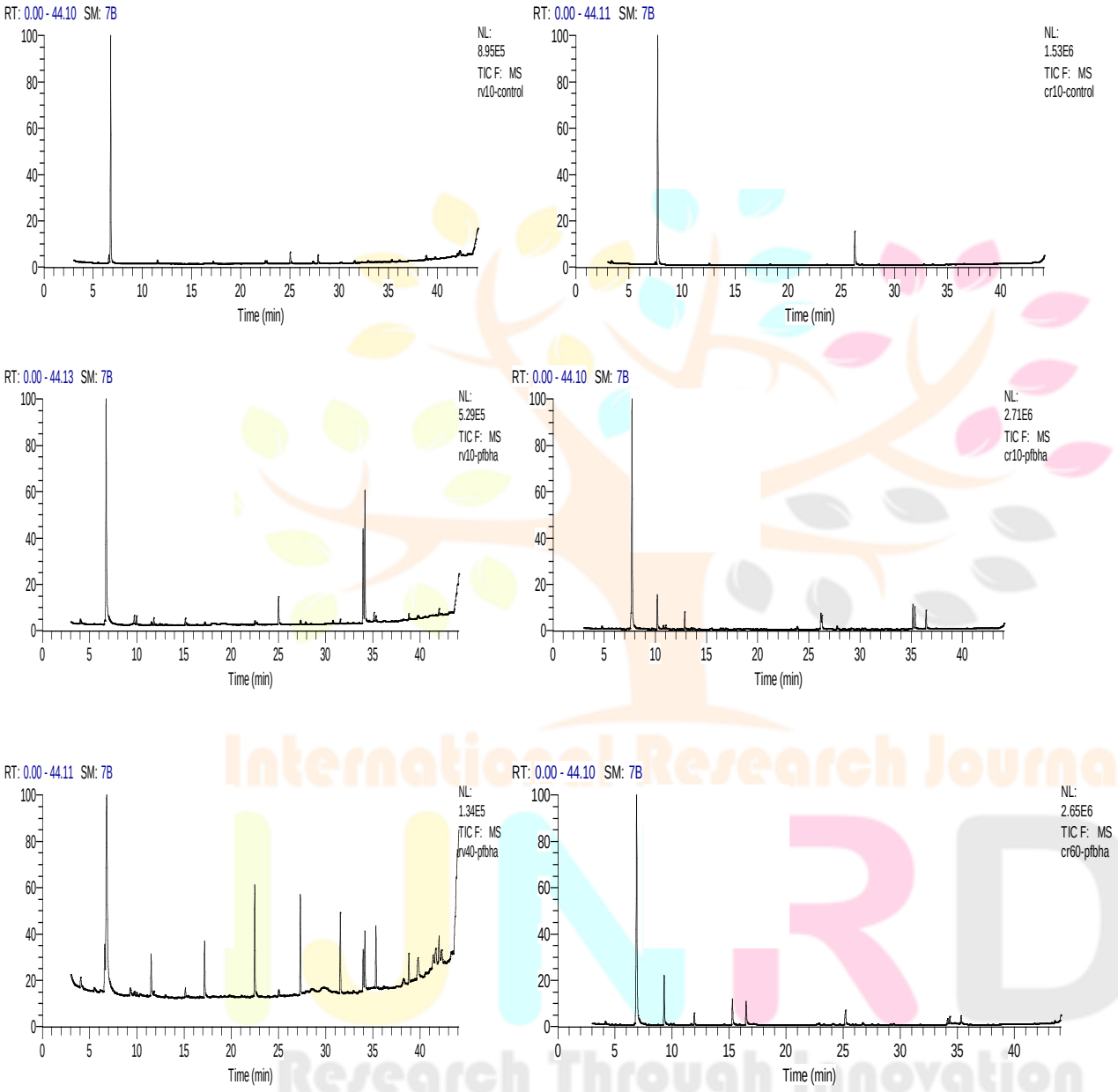


Figure 6 Chromatogram of GC/MS analysis of acidic extract of RV5 and CR showing the presence of some major by-products listed in table 5.

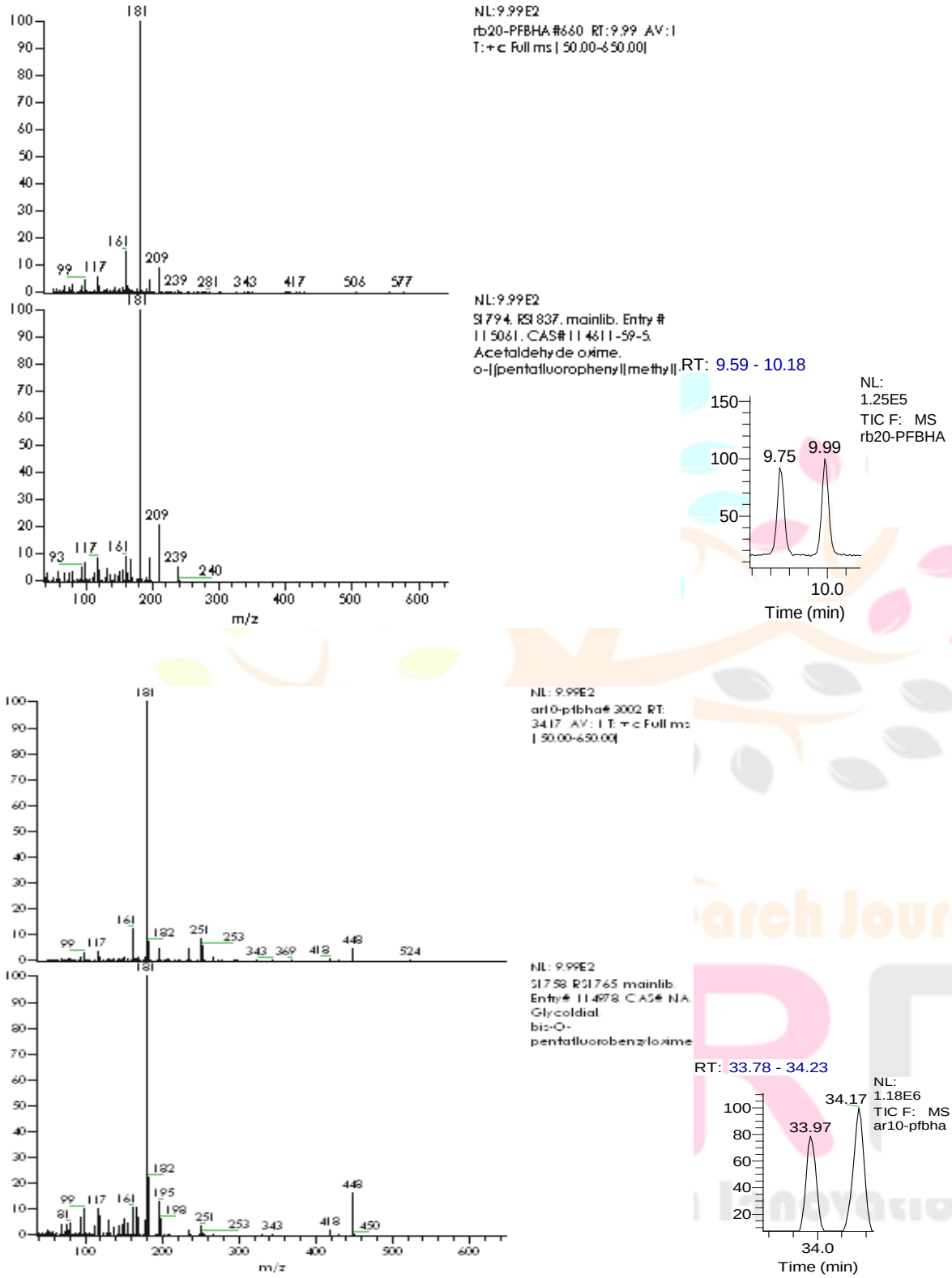


Figure 7 MS/MS matching of identified compound(Acetaldehyde and Glycodial) from mainlb.