



## Ozonation of reactive dye, Procion red MX-5B catalyzed by metal ions

K. Pachhade, S. Sandhya\*, K. Swaminathan

National Environmental Engineering Research Institute (NEERI), CSIR Complex, Taramani, Chennai 600113, India

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### ABSTRACT

Ozonation of aqueous solution of Procion red MX-5B, a commercial azo reactive dye was investigated. The effect of various experimental variables on decolorization and degradation of the dye has been studied. Color removal was faster than organic removal. Dye mineralization was evident by the generation of sulphate, chloride, nitrate, oxalic and acetic acid during ozonation. The decolorization and organic removal followed pseudo-first-order kinetics. Among the metal ions studied, manganese catalyzed ozonation showed better decolorization and organic removal. Fourier transform infrared (FTIR) spectroscopy results indicated the disappearance of bands for aromatics and appearance of bands due to carboxylic acids in the ozonated samples. Acetyl benzoic acid, diethyl phthalate and phthalic anhydride were identified as intermediates by gas chromatography mass spectra (GC/MS). Based on these findings a tentative pathway for the degradation MX-5B was postulated.

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### 1. Introduction

The more than 60% of the world dyes production is consumed by textiles industries and more than half of this quantity is discharged into receiving water bodies more or less without treatment hampering thus the function of the ecological process. Among the used dyes, azo-dyes are the most commonly utilized reagents owing to the presence of the azo-group which confers to these chemicals a certain resistance to light, acids, bases and oxygen, the desired properties for clothes' makers. The major limitation in treating the wastewater containing azo-dyes is their resistance to conventional biological treatment processes [1,2]. Traditional physical and chemical methods such as coagulation, adsorption, ion exchange or ultra-filtration, though, can generally be used efficiently, result in the generation of solid waste which needs further disposal [3]. Although these methods resulted in a significant color removal, they were either costly to apply in the actual field or enable to meet the discharge criteria of wastewater in term of chemical oxygen demand (COD). Adsorbent regeneration, excess sludge production and the rapid fouling of the used membranes are some of other handicaps of these processes. Advanced oxidation processes (AOP), which are based on in situ generation of very powerful oxidizing agent such as hydroxyl radicals, are highly effective for the removal of recalcitrant organics from the wastewater. Most common AOP techniques involve the use of ultra-violet light in presence

of H<sub>2</sub>O<sub>2</sub>, ozone and Fenton's reagent. Among the AOP, application of ozone for color and COD removal for many types of wastewater and in combination of biological treatment is an emerging process [4]. Ozonation has excellent potential in decolorization as decolorization and degradation occur in one step; danger to humans is minimal; no sludge remains; all residual ozone can be decomposed easily into oxygen and water; little space is required and ozonation is easily performed [5].

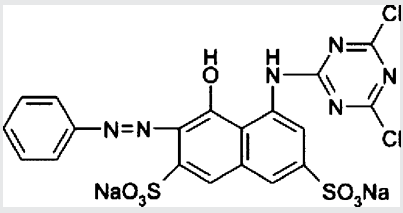
Studies have shown that ozone cleaves the conjugated bonds of azo-dyes and converts high molecular weight compounds of the dye into lower molecules of organic acids leading to color removal and enhancement in biodegradability [4–6]. An increase in the ratio of biochemical oxygen demand (BOD)/COD indicates an improved biodegradability of recalcitrant substrate [7,8].

Oxidation potential of ozone is 2.07 V, and it allows degradation of most organic compounds. Depending upon the molecular selectivity and decay rates, ozone and hydroxyl radicals (OH<sup>•</sup>) generated in aqueous solution are able to open the aromatic rings and oxidize inorganic and organic compounds to their highest oxidation state [9]. It has been shown that the cleavage of dye takes place both by direct ozonation and radical pathways, mainly involving the generation of hydroxyl radicals which can be activated by H<sub>2</sub>O<sub>2</sub>, UV light and reduced transition metals [3,10]. Transition metals such as iron, manganese, zinc, copper and lead have been tried for the enhancement of degradation of organic compounds [11–13]. Metal organic complexes easily oxidize organic compounds or form intermediate oxidation products, which are easily oxidized via ozonation [14].

In the present work, the ozonation of a commercial azo reactive dye, Procion red (MX-5B) was carried out. The dye was selected due

\* Corresponding author. Tel.: +91 44 22541964; fax: +91 44 22541964.  
E-mail address: [sswami.in@yahoo.com](mailto:sswami.in@yahoo.com) (S. Sandhya).

**Table 1**  
Characteristics of Procion red MX-5B.

Structure of MX-5B	$\lambda_{\max}$ (nm)	MW	pH	COD (mg l <sup>-1</sup> )	TOC (mg l <sup>-1</sup> )
	230,311,538	615	3.90	150	32

to its complex chemical structure, high molecular weight, high solubility in water and its persistence one it is discharged into natural environment. The effect of decolorization and degradation under various reaction conditions, the intermediate products formed during ozonation and the catalytic effect of transition metals on color and COD removal were studied.

## 2. Materials and methods

### 2.1. Chemicals

Commercial grade dye was used for all studies. The dye concentration used for the study was 250 mg l<sup>-1</sup>. Reagent grade FeSO<sub>4</sub>·7H<sub>2</sub>O, CuSO<sub>4</sub>·5H<sub>2</sub>O, COCl<sub>2</sub>·7H<sub>2</sub>O and MnO<sub>2</sub> was used for catalytic ozonation experiments. Table 1 presents the characteristics of the dye.

### 2.2. Ozonation procedure

Ozone was generated from dry air in a laboratory model ozone generator with a maximum capacity of 20 g h<sup>-1</sup>. Ozonation experiments were conducted in 1 l boro-silicate glass reactor. Ozone was supplied at the bottom of the reactor through a glass diffuser. All connections from the ozone generator to the reaction vessel were made through teflon tubing. Airflow rate was set at 75 l h<sup>-1</sup> with an ozone production of 260 mg h<sup>-1</sup>. The ozone concentration in the feed gas stream and outlet gas stream was measured by iodometric method. The un-reacted ozone leaving the column was collected in gas washing bottles filled with 4% KI solution. The KI solution reacts with ozone liberating I<sub>2</sub> and the resulting I<sub>2</sub> was titrated against standard thiosulphate using starch as indicator. All the experiments were performed at room temperature (25 ± 2 °C), and in semi batch mode by sparging ozone continuously into the solution. Samples were withdrawn at definite time intervals and analyzed for all parameters.

### 2.3. Analytical methods

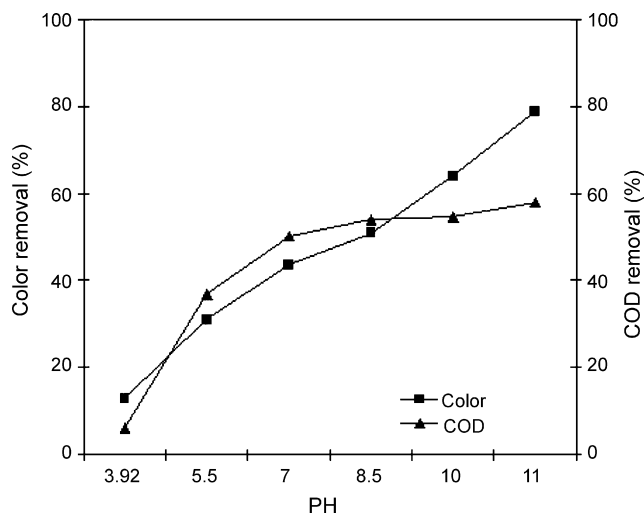
pH, conductivity, COD, chloride, nitrate and sulphate were determined as per Standard Methods [15]. UV-vis spectra of dye solution were recorded between 200 and 600 nm using double beam UV/vis spectrophotometer (Shimadzu Model UV/VIS 160A) equipped with 10 mm quartz corvettes. Decolorization of dye was monitored by measurement of the absorbance of the samples at 538 nm. Total organic carbon (TOC) was measured by TOC analyzer (Shimadzu Model 2000). Ion chromatograph (Model Dionex LC20) employed to analyze organic acids was equipped with an Anion Ion 12 (AS-4) column and operated in suppressed conductivity detection mode. The eluent used was Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub> (3.3 mM, 1.0 mM<sup>-1</sup>) at a flow rate of 0.7 ml min<sup>-1</sup>. Fourier Transform Infrared (FTIR) analysis was carried out using a Bruker Vector 22 FTIR spectrometer. The samples were dried at 70 °C and pelleted with KBr and the absorbance spectra recorded over 700–4000 cm<sup>-1</sup> domain. Gas chromatogra-

phy/mass spectra (GC/MS) analysis was carried out using Hewlett Packard integrated gas chromatography equipped with a capillary column DB-1 (30 m × 0.25 mm × 0.25 m). Helium was used as a carrier gas at a flow rate of 1.0 ml min<sup>-1</sup>. The GC column was operated in a temperature programming mode with an initial temperature of 70 °C held for 5 min, ramp at 10 °C min<sup>-1</sup> rate to 260 °C, and held at this temperature for 5 min. The compounds were identified on the basis of mass spectra stored in National Institute of Standards and Technology (NIST) library.

## 3. Results and discussion

### 3.1. Effect of initial pH on ozonation

Reaction pH is an important parameter influencing the ozonation process. Ozonation of the dye sample was performed for 5 min at different pHs such as 3.9, 5.5, 7.0, 8.5, 10, 11.0 and the data are presented in Fig. 1. Increase in color and COD removal was observed as the pH was increased from acidic to alkaline range. At pH 11.0, color and COD removal observed were 79 and 58%, respectively. Ozone decomposes quickly at high pH and forms hydroxyl radicals, and this shift is fast at alkaline pH values [6,16]. Azbar et al. [17] reported that higher removal of COD of polyester dye effluent at alkaline pH. Degradation of dyes are either due to direct oxidation of ozone or radical oxidation by OH radical. The oxidizing agent in acidic solution is ozone, while in neutral and basic solution it is the hydroxyl radicals [18]. The reaction involves the opening of aromatic ring by electrophilic attack of ozone to form aldehydes and organic acids. This reaction step is formed by the alkaline pH of the incoming effluent [19]. Since oxidation potential of OH radicals is higher than that of the ozone molecule, the decomposition reaction is faster in basic condition [5,6].



**Fig. 1.** Effect of pH on color and COD removal of MX-5B by ozonation.

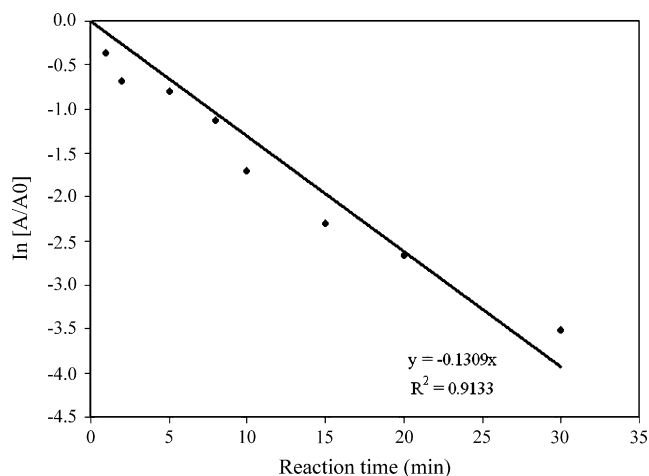


Fig. 2. Pseudo-first-order rate constant for decolorization of MX-5B during ozonation.

### 3.2. Decolorization of MXB by ozonation

During ozonation, the absorbance peaks in the visible region of the dye decreased gradually with time and disappeared at 10 min ozonation indicating the destruction of chromophore structure in the vicinity of azo linkage. The solution turned from dark pink to colorless. Selcuk [4] could remove 98% of color from cotton mill wastewater in 20 min ozonation. Zhang et al. [6] have reported that Reactive red 120 was completely decolorized during 150 min ozonation. The reaction kinetics of dye ozonation was studied and rate constants were determined at various initial dye concentration and time. Fig. 2, the results of dye concentration at different time have showed that the reaction followed a pseudo-first-order reaction. Since the oxidizing ability of ozone comes from either molecular ozone or hydroxyl free radical. The decolorization was found to fit pseudo-first-order kinetics with rate constant of  $-0.13 \text{ min}^{-1}$ . Chu and Ma [20] have also reported similar results of pseudo-first-order kinetics for decolorization of dye by ozonation.

### 3.3. COD and TOC removal during ozonation

Results of color, COD and TOC removal during ozonation are presented in Table 2. It was observed that COD and TOC removal increased with ozonation time. COD removal was 58 and 80%, respectively, at 5 and 30 min of ozonation with corresponding TOC removals of 60.4 and 75%. Color removal was faster than COD and TOC removal indicating that the chromophoric group was destroyed during ozonation and were partially mineralized to small fragments. Koch et al. [2] have reported 50% COD and 38% TOC removal during ozonation of Reactive yellow RY 84. Wang et al. [21] reported that COD removal was more efficient than TOC removal for the ozonation of Remazol Black 5.

Table 2  
Color COD and TOC removal of MX-5B on ozonation.

Time (min)	Color (absorbance)	Color removal (%)	COD ( $\text{mg l}^{-1}$ )	COD removal (%)	TOC ( $\text{mg l}^{-1}$ )	TOC removal (%)
1	1.12	31.0	141	16.0	24	14.5
2	0.82	50.0	103	31.3	21	34.4
5	0.73	55.0	63	58.0	13	60.4
8	0.52	68.0	60	60.0	11	65.6
10	0.29	82.0	55	63.4	9	71.9
15	0.16	90.0	36	76.0	8	75.0
20	0.11	93.0	36	76.0	8	75.0
30	0.05	97.0	30	80.0	8	75.0

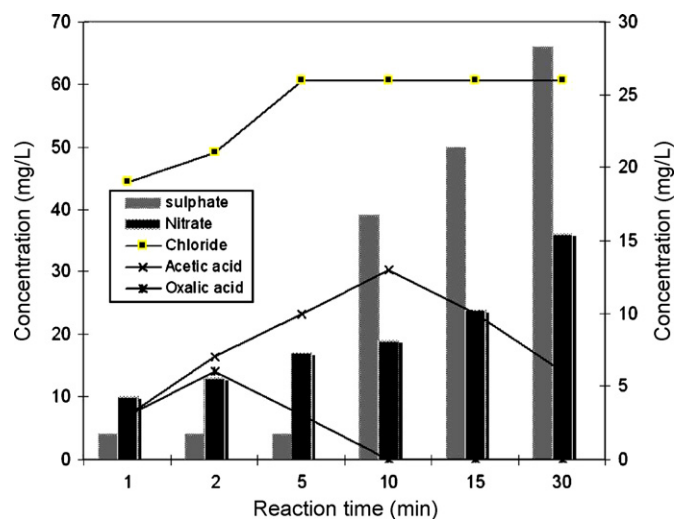


Fig. 3. Release of Inorganic anions and organic acids during ozonation of MX-5B.

### 3.4. Mineralization of MX-5B during ozonation

During the ozonation, the pH of the solution decreases rapidly at the early stage of the experiment, dropping from the initial solution (pH 11 at  $t=0$  min) to about 7.6 after nearly 15 min and to 3.52 at 30 min of ozonation. Conductivity also increased from 630 to  $1280 \mu\text{S cm}^{-1}$  indicating the formation of organic and inorganic ions during ozonation as presented in Fig. 3. Chloride concentration increased from beginning of the experiment and was  $26 \text{ mg l}^{-1}$  at 5 min ozonation and remained stable indicating initial cleavage of triazine group. Gul et al. [22] have observed sharp increase of chloride concentration in the initial stages of ozonation of C.I. Reactive Red 194 and Reactive yellow 145 indicating that the C–Cl bond on the triazine ring is the weakest bond and is susceptible for the hydroxyl radical attack. Concentration of sulphate increased with time of ozonation and was  $66 \text{ mg l}^{-1}$  at 30 min ozonation. He et al. [23] reported that chloride and sulphate concentration increased during sonolytic ozonation of Reactive Yellow 84. Oxidation and cleavage of sulphonic acid group from the naphthalene ring leads to the accumulation of sulphate during ozonation [24]. Nitrate concentration at 5 min and at 30 min ozonation was 17 and  $36 \text{ mg l}^{-1}$ , respectively, indicating the cleavage of triazine and azo-groups. Concentration of acetic acid increased initially and decreased on further ozonation. Oxalic acid was detected initially and disappeared after 10 min ozonation. Formation of fatty acids and inorganic ions during ozonation was reported by others also [2,21]. These results clearly indicate that during ozonation, the dye structure is broken and degraded into smaller fragments of inorganic ions and organic acids.

### 3.5. Degradation kinetics

The process of ozonation is as a result of oxidation by ozone molecules and by generation of hydroxyl radicals, which react with

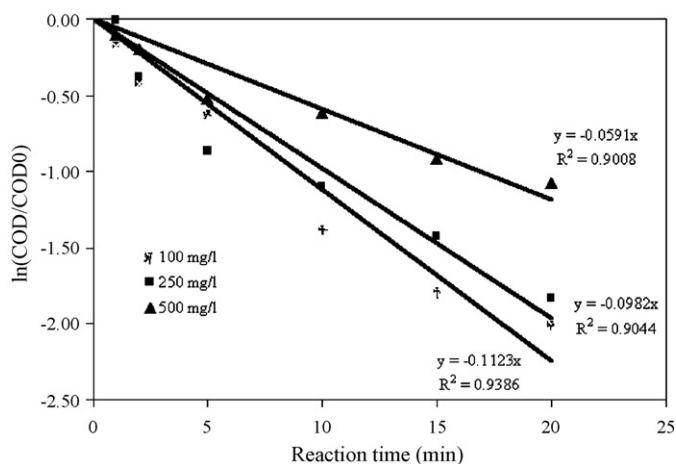


Fig. 4. Kinetics of ozonation for different dye concentration of MX-5B.

initial compound and intermediates. At higher pH, radical oxidation predominates since oxidation potential of OH radical is much higher than that of ozone molecule. The direct reaction of ozone is assumed to be first order with respect to dye and ozone, respectively [25]. When the amount of ozone is in excess or when the ozone concentration is assumed to reach a stationary state at the interface, the oxidation rate follows a pseudo-first-order kinetics with respect to the concentration of the organic substance in terms of degradation and the rate equation is as follows [26]:

$$-\frac{dC_A}{dt} = K' dC_A$$

where  $K'd$  is pseudo-first-order rate constant and  $C_A$  is concentration of organic substance. In the present study data on COD removal for different dye concentration was used:

$$-\frac{dCOD}{dt} = K[COD_0]$$

On integration, the above equation is as follows:

$$\ln\left(\frac{COD_t}{COD_0}\right) = -Kt$$

The plot of  $\ln(COD/COD_0)$  vs. reaction time ( $t$ ), for different initial dye concentration is presented in Fig. 4. The data used were average of five experimental values. The correlation coefficients obtained were between 0.90 and 0.94. The observed pseudo-first-order rate constants calculated by linear regression were  $-0.112$ ,  $-0.098$  and  $-0.059$ , for dye concentrations of 100, 250 and 500  $\text{mg l}^{-1}$ , respectively. Pseudo-first-order trend was reported by Swaminathan et al. [27] for ozonation of H-acid. Shiyun et al. [28] reported that COD degradation of naphthalene sulphonic acids by ozonation followed pseudo-first-order kinetics. The rate of reaction decreases as the concentration of dye increases, which is in accordance with other studies [19,29].

### 3.6. Effect of transition metals

Catalytic ozonation is emerging as a new area in the degradation of organic compounds. Legube and Leitner [14] have reported that the efficiency of ozonation can be enhanced by the presence of transition metals such as Fe, Ni, Mn, and Zn. These metals are easily obtainable, inexpensive, and relatively low in toxicity. Cortes et al. [12] studied the ozonation of chlorobenzene by  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  ions as catalysts and found that addition of metallic ions improved the overall efficiency of ozonation. Fig. 5 presents the data on ozonation of MX-5B with metal ions. Among the metal ions studied,  $\text{MnO}_2$  was effective in color and COD removal. Complete decolorization and

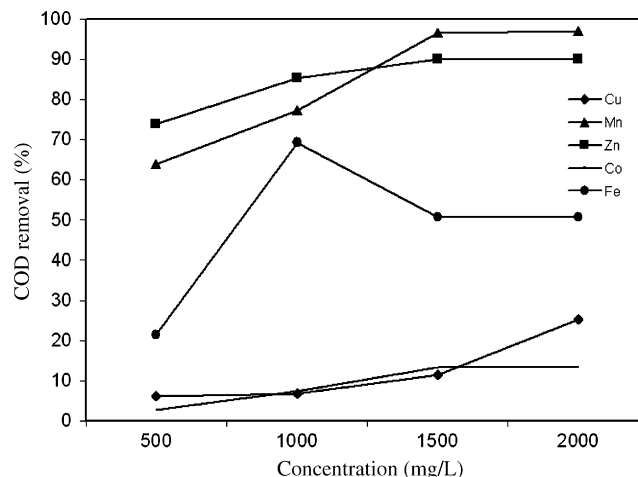


Fig. 5. Effect of metal ions on ozonation of MX-5B.

COD removal (94%) was obtained with  $\text{MnO}_2$  dose of  $1.0 \text{ g l}^{-1}$  at 15 min ozonation. Thus in presence of catalyst, the ozone dose and power consumption can be minimized. Decolorization of Reactive Red and Acid Orange 6 was accelerated by  $\text{MnO}_2$  to the  $\text{O}_3$  system [22]. Andreozzi et al. [30] reported significant improvement of ozonation of oxalic acid with  $\text{MnO}_2$ .

### 3.7. FTIR spectra analysis

FTIR spectra of Procion red MX-5B during ozonation are shown in Fig. 6. Majority of absorption peaks present prior to ozonation were either shifted or disappeared during ozonation. The bands characteristic of azo-bond in the region of  $1500\text{--}1550 \text{ cm}^{-1}$  of MX 5B (a) was absent in the ozonated samples (b and c) indicating that  $-\text{N}=\text{N}-$  may be oxidized with the disappearance of the parent dye. Hu et al. [31] reported that the peak stretching at  $1500 \text{ cm}^{-1}$  is a characteristic due to azo-bond ( $-\text{N}=\text{N}-$ ) and the  $1400\text{--}1600 \text{ cm}^{-1}$  due to benzene ring. Bands observed after ozonation in the range of  $3379\text{--}3437 \text{ cm}^{-1}$  may be attributed to carboxylic acids. New absorption peak at  $1640\text{--}1642 \text{ cm}^{-1}$  appeared after 20 min of ozonation, is characteristic of the  $\text{C}=\text{C}$  may be formed from alkenes of carboxylic acid. The observations were further verified by ion analysis data. Shift in the bands from  $1216$  to  $1046\text{--}1000 \text{ cm}^{-1}$  in the treated samples corresponds to the disappearance of stretching

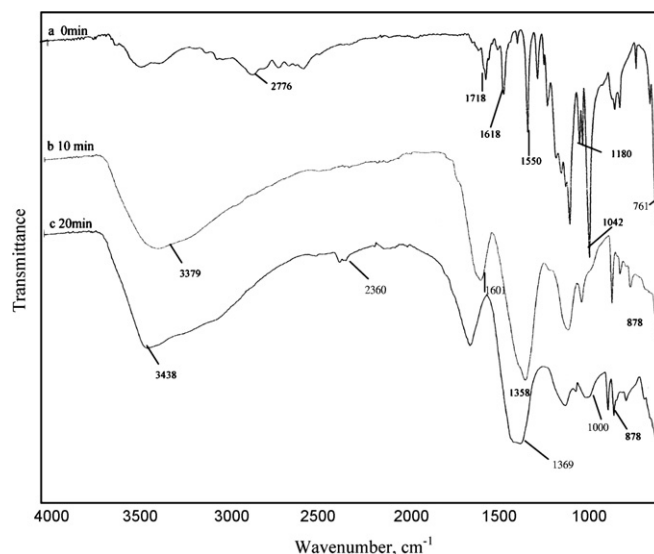
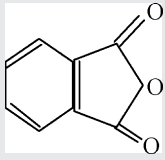
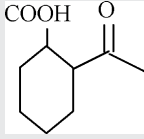
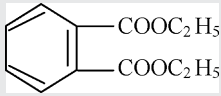


Fig. 6. Changes of FTIR spectra of MX-5B during ozonation.

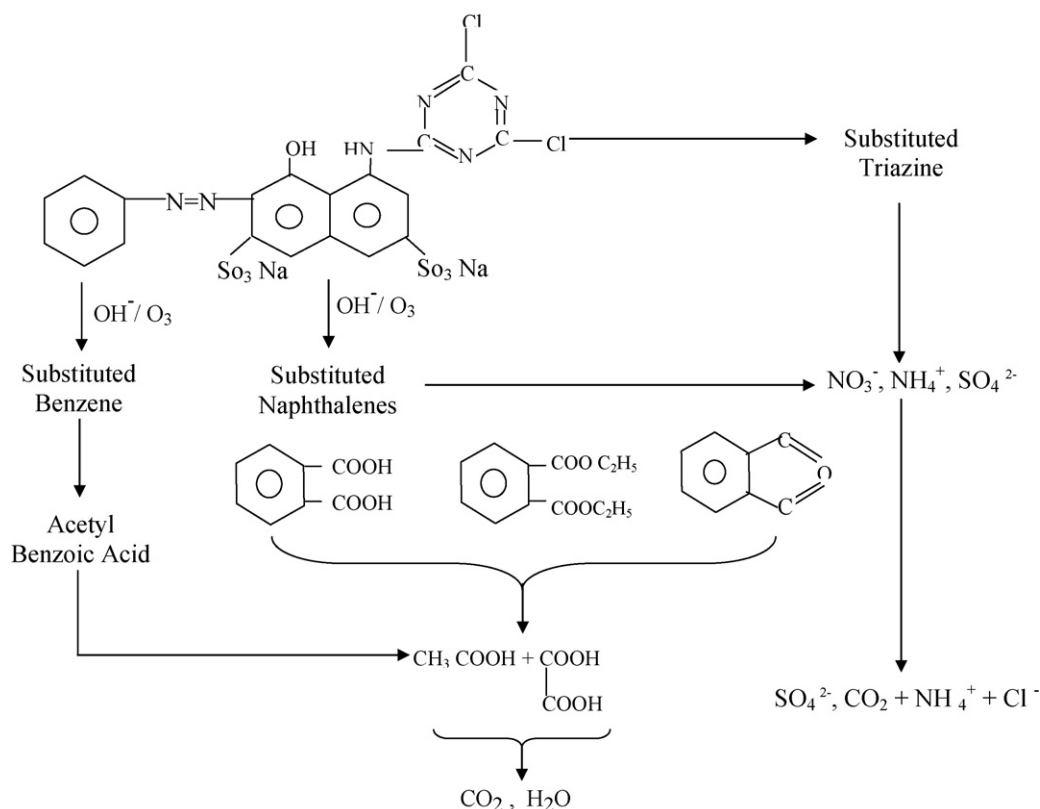
**Table 3**  
Compounds identified by GC/MS during ozonation of MX-5B.

Sl. no.	Name of the compound	Molecular formula	Mol. wt.	Structure
1.	Phthalic anhydride	C <sub>8</sub> H <sub>4</sub> O <sub>3</sub>	148	
2.	2-Acetyl benzoic acid	C <sub>9</sub> H <sub>8</sub> O <sub>3</sub>	164	
3.	1,2-Benzene dicarboxylic acid diethyl ester	C <sub>12</sub> H <sub>14</sub> O <sub>4</sub>	222	

vibrations in sulphonate groups. New peak observed at 878 cm<sup>-1</sup> at 30 min of ozonation could be due to stretching vibrations of C–O [32]. Bands located at 1180 cm<sup>-1</sup> may be due to sulphonate group, which almost disappeared after ozonation. This indicates the mineralization of sulphonate group during ozonation of dye. Chen et al. [33] have shown that IR characteristic peak of the phenyl group disappeared after reaction with •OH proving that carboxylic acid intermediates were generated. The above observations indicate that during ozonation, the sulphonic acid groups of the dye may be substituted by hydroxyl groups followed by oxidation and cleavage of naphthalene ring with the formation of low molecular weight carboxylic acids.

### 3.8. Degradation mechanism of MX-5B

In order to elucidate the mechanism of Procion red MX-5B degradation, GC/MS analysis was carried out to identify the intermediates formed during ozonation of the dye. Table 3 presents some of the compounds identified by GC/MS. Degradation of the dye occurs through direct ozone oxidation/ or radical mechanism. The primary oxidizing species in ozonation is hydroxyl radicals. As the decolorization is very fast, the attack of hydroxyl radicals takes place first at the carbon atoms with the chromophore azo-linkage. Hence the fragments produced by the cleavage of the dye molecule may be the primary reaction intermediates. The compounds identified are



**Fig. 7.** Proposed pathway for the degradation of MX-5B by ozonation.

phthalic acid ester, phthalic anhydride, acetyl benzoic acid. Phthalic acid and other substituted aromatic compounds have been reported during photocatalytic and ozonation of dyes [34,35]. The aromatic rings open and yield carboxylic acids, which are confirmed by ion chromatography data. Mineralization leads to the formation of carbon dioxide, sulphate, chloride and nitrate as end products. Based on these observations and CC/MS data a pathway is postulated as presented in Fig. 7.

#### 4. Conclusions

In this work, ozonation of Procion red MX-5B has been studied under different experimental conditions. Optimum pH of 11.0 resulted in maximum color and COD removal. Both color and COD removal could be achieved at 30 min ozonation and an ozone dose of 260 mg h<sup>-1</sup>. Color removal was faster than COD removal. Maximum color, COD and TOC removal observed was 97, 80 and 75%, respectively. Chloride, sulphate, nitrate, oxalic acid and acetic acid were formed during ozonation indicating that the dye is mineralized by ozonation. Decolorization and COD removal followed pseudo-first-order kinetics. Among the metal ions studied Mn<sup>2+</sup> was effective in color and COD removal. FTIR data indicated evidence for the cleavage of the dye structure and formation of lower fatty acids. Based on the intermediates identified by GC/MS, a pathway for MX-5B degradation has been postulated. The results of the study show that catalyzed ozonation of dye can be effectively applied for the treatment of dye wastewater resulting in color and COD removal.

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