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Degradation Mechanism of Cationic Red X-GRL by Ozonation

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Abstract: The degradation mechanism of Cationic Red X-GRL was investigated when the intermediates, the nitrate ion and the pH were analyzed in the ozonation. The degradation of the Cationic Red X-GRL includes the de-auxochrome stage, the decolour stage, and the decomposition of fragment stage. During the degradation process, among the six nitrogen atoms of Cationic Red X-GRL, one is transferred into a nitrate ion, one becomes the form of an amine compound, and the rest four are transformed into two molecules of nitrogen. In the course of the ozonation of Cationic Red X-GRL, the direct attack of ozone is the main decolour effect.

Keywords: Ozonation, cationic Red X-GRL, mechanism, intermediates, dye, decolourization.

The treatment of textile wastewater is an environmental concern. Some dyes may have carcinogenic and/or teratogenic effects that would be detrimental to public health. The conventional treatment can not readily remove dyes from textile wastewater, because of their stability to light and biological degradation[1,2]. Ozone and hydroxyl radicals (·OH) generated in the aqueous solution are able to open the aromatic rings by the oxidative cleavage of the chromophores of dye, and hence the absorption spectra of dye is displaced out of the visible region[3,4]. Although the role of ozonation (and its related oxidation processes) in treating several organic substances has been examined by different authors[5,6], most of these works paid little attention to the intermediates and degradation pathways.

Cationic Red X-GRL, which is broadly used in the textile industry, was selected for the study, is nonbiodegradable by the conventional activated sludge process. Cationic Red X-GRL was recrystallized from methanol. It has a molecular weight of 356.84 g/mol, and mole extinction coefficient of 6.31×10^6 L/(mol·m) at 530 nm.

The ozonation system consisted of an ozone generator and a semi-batch bubble column reactor (3.5 L) installed in thermostatic water-bath.

A TU1800 UV-VIS spectrophotometer was used to measure the concentration of dye. A TRACE 2000 GC/MS was used to characterize the degradation products. An Agilent 6890N GC was used to measure the peak areas of intermediates. A Metrohm 792 Basic IC was used to measure the concentration of nitrate ion. The pH-value of the solution was measured by pHS-25.

3.5 L unbuffered dye solution of 500 mg/L reacted with ozone at pH 3 and 25 °C.

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200 mL reaction mixture was taken out periodically. The extraction of the samples, under pH 3 and 11, was done four times by adding 5 mL CH_2Cl_2 each time. Extraction phase was converged and purged to 1 mL by pure nitrogen at 25°C. 1 mL 3-methoxy-1-thiophenol (1.006 ‰) was added and then diluted to 5 mL with CH_2Cl_2. For GC/MS analysis, 1 mL samples of 15, 30, 45 and 60 min solution were concocted. The solution that did not undergo the ozonation was used as blank. The residual samples were used for GC analysis.

Table 1 shows three main results of this reaction: (1) the pH-value decreased with the reaction time that indicated the formation of organic acids; (2) the molar ratio of nitrate ion and initial dye increased to 0.963, which indicated only one of the six nitrogen atoms of dye is transformed into nitrate ion; (3) the maximum absorbance wavelength of dye shifted from 530 nm at 0 min to 522 nm at 10 min, which indicated that the auxochrome is cleaved from dye.

Table 1 The variation of the pH, λ_{max}, and NO_3^- during the ozonation

Time, min	pH	NO_3^-, mg/L	C_{dye}, mol/L	λ_{max}, nm	$NO_3^-/ C_{dye,0}$
0	5.82	0.000	1.278×10^{-4}	530	0.000
2	4.15	0.860	7.850×10^{-5}	528	0.108
4	3.68	2.190	3.705×10^{-5}	526	0.276
6	3.41	4.890	1.626×10^{-5}	524	0.616
8	3.23	7.595	3.180×10^{-6}	522	0.957
10	3.14	7.642	5.820×10^{-7}	522	0.963

Experimental conditions: Q_{oxygen}=100 L/h; T=25°C.

Figure 1 The GC/MS chromatogram of sample

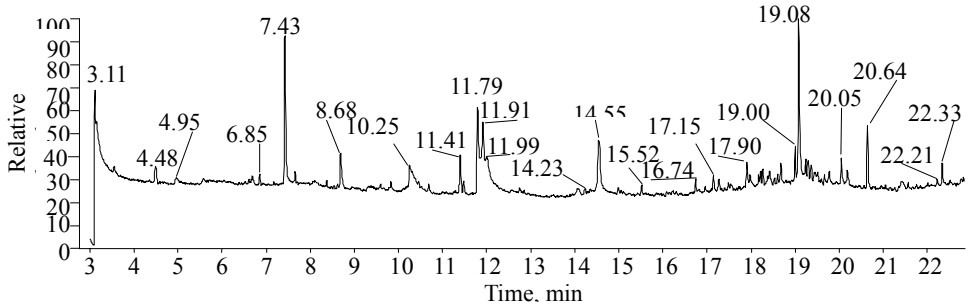

Table 2 The intermediates determined *via* GC/MS

No.	Retention time, min	Molecular formula	Molecular weight	Structural formula
1	4.95	$C_3H_5NO_2$	87	D_4 in Figure 3
2	7.43	C_7H_6O	106	D_1 in Figure 3
3	8.68	$C_7H_8O_2$	124	D_3 in Figure 3
4	10.25	$C_4H_7N_3O$	113	D_2 in Figure 3

Figure 2 The intermediates peak areas determined *via* GC

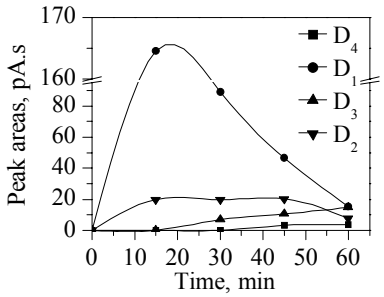

Figure 3 The presumable pathways and intermediates of Cationic Red X-GRL during the ozonation

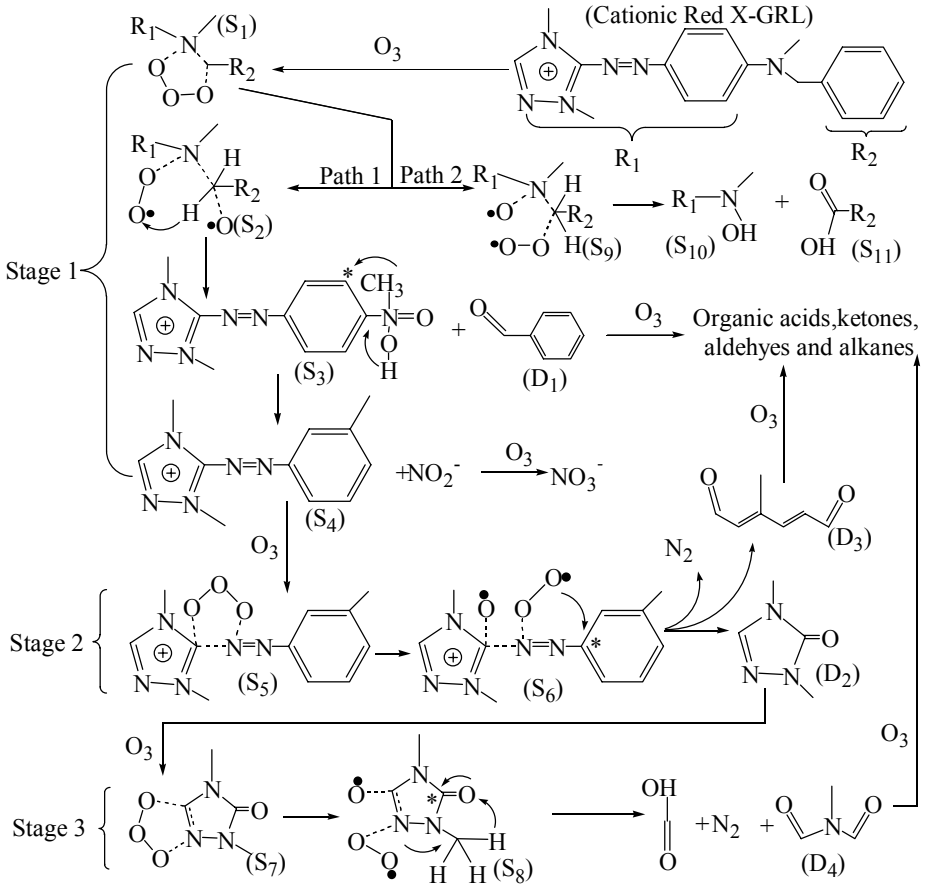

Figure 1 shows the GC/MS chromatogram of the sample. Retention time of 3~4.5 min is the peak of dichloromethane. The peak of 3-methoxy-1-thiophenol appears at 11.79 min. **Table 2** tabulates the intermediates discerned by GC/MS.

The GC peak areas of intermediates in **Figure 2** shows two characteristics: (1) the formation sequence of intermediates is $\mathbf{D_1 \rightarrow D_2 \rightarrow D_3 \rightarrow D_4}$; (2) the auxochrome, $\mathbf{R_2\text{-}CH_2\text{-}}$, leaves from the dye first, making the maximum absorbance wavelength to shift (**Table 1**).

After a careful review of the above results, the probable degradation pathways and intermediates of dye can be presumed as depicted in **Figure 3**. There are two possible cleavage paths of O-O band in state $\mathbf{S_1}$. Because GC and GC/MS detected compound $\mathbf{D_1}$ instead of compound $\mathbf{S_{11}}$, the Path 1 is more predominant than Path 2. The same result in ozonation of curcumin was found by Grosjean *et al.*[7]. The steric hindrance of methyl[8] and the presence of C=C double bond made compound $\mathbf{D_2}$ not to be polymerized, but it can be oxidized to acids or ketones by ozone.

The proposed degradation mechanism in **Figure 3** shows three major stages of the reactions: (1) the de-auxochrome stage which makes the maximum absorbance wavelength of Cationic Red X-GRL to shift from 530 to 522 nm; (2) the decolour stage which makes the cleavage of the chromophore; (3) and the decomposition of fragment stage which makes the intermediates split into various organic acids, ketones, aldehydes, and alkanes[4,9]. During the degradation process, among the six nitrogen atoms of Cationic Red X-GRL, one is transferred into a nitrate ion, one becomes the form of an amine compound, and the rest four are transformed into two molecules of nitrogen. In the course of the ozonation of Cationic Red X-GRL, the direct attack of ozone is the main decolour effect.

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