

**Oxygen as a Promoter for Efficient Degradation of Organic Pollutants by High
Temperature and High Pressure Electrochemistry**

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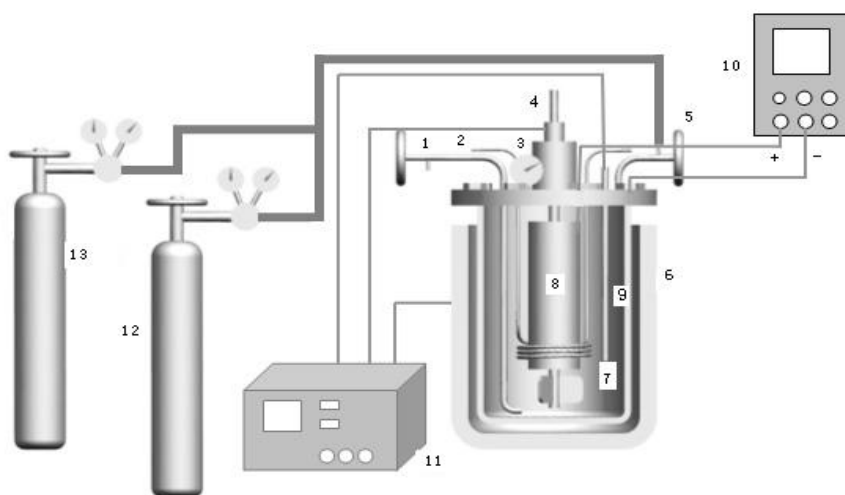


Figure S1. The experiment set-up

1 sample inlet and sampling pipe; 2 cooling water inlet; 3 pressure gauge; 4 stirring system;
5 gas outlet; 6 electric heating jacket; 7 temperature sensor; 8 anode; 9 cathode;
10 DC supply; 11 reactor controller; 12 oxygen; 13 nitrogen.

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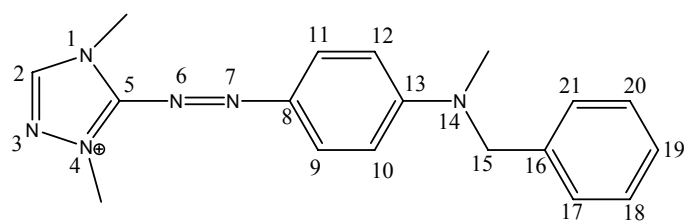


Figure S2. Structural of cationic red X-GRL

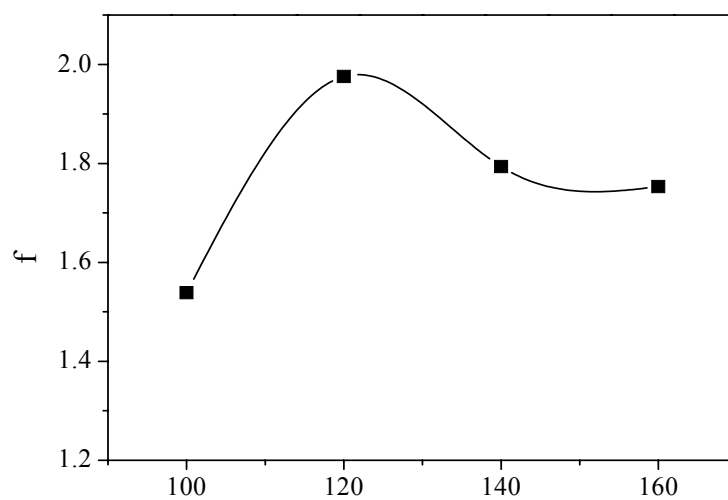


Figure S3. The synergetic factors at different temperatures.

Conditions: PNP 1000 mg L⁻¹, 160 °C, oxygen 0.5 MPa, current 0.5 A, Na₂SO₄ 3 g L⁻¹, treated time 120 min.

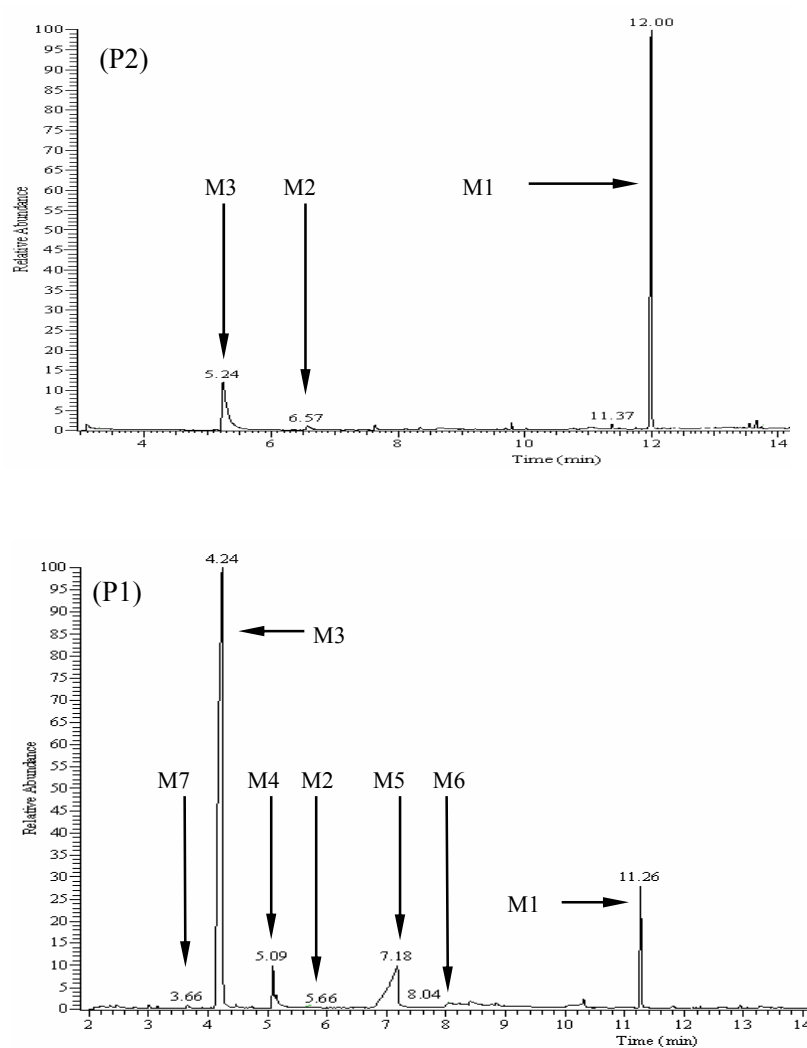


Figure S4. The GC/MS spectra for two processes.

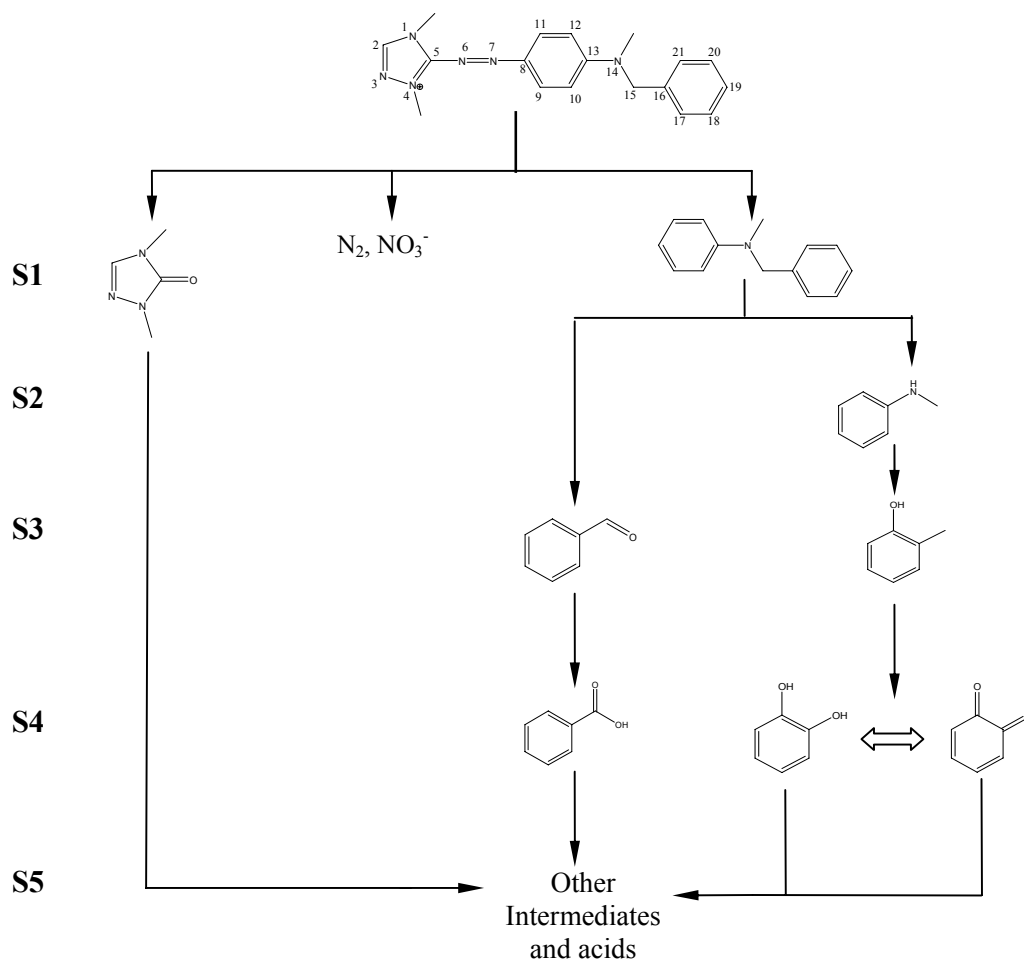


Figure S5. The degradation pathway for two processes.

In P2, the attack of the azo bond would be the initial step of dye degradation, which led to the rapid removal of color. In the bond (-C-N=N-), the length of the bond of C(5)-N(6), N(6)-N(7) and N(7)-C(8) is 1.456 Å, 1.362 Å and 1.404 Å, respectively, which indicated C(5)-N(6) would be the first potential broken among the three as for stability. The radical would attack this site and result in the release of nitrogen element and the formation of 2,4-dimethyl-2,4-dihydro-[1,2,4] triazol-3-one, which was identified in our previous work though it might be missed in the analysis

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in the present work. However, it was confirmed that NO_2^- was not detected in the solution, while NO_3^- was very low (below 2 mg/L), which was much less than the theoretic calculation from the broken of azo bond. In literatures, it reported a degradation pathway for azo dye through the formation of molecular nitrogen (1). In the present work, we deduced that the degradation might also proceed in this way. The broken of azo group from the parent substance would result in the formation of the benzenamine, N-phenylmethlene diazene radical, which would be unstable and then turned into benzenamine, N-phenylmethlene by release of molecular nitrogen. After the broken of the azo dye to form M1, the hydroxyl radical attack would lead to the broken down of N(14)-C(15), which led to the formation of M2 and M3. Due to the relatively lower COD removal, it could be deduced that the decolorization of azo bond broken was relatively easy but the further degradation intermediates to organic acids would be rather difficult. According to the products and their amounts, the P2 goes forward to at most stage 2 or 3 (S3).

In P1, the formed products of M3 further oxidized to Benzoic acid (M5) by hydroxyl radical replacement. The attack of hydroxyl radical on the N(14), would led to the rearrangement of methyl to the activated sites of C(10) or C(12) while release the nitrogen to the final formation of nitrate in the aqueous solution. In this way, the product of 2-methyl-phenol (M4) formed. The attack of hydroxyl radical would take instead of methyl group to form hydroquinone (M6), which would be converted to benzoquinone (M7) by hydrogen addict. These products would be further degraded to form other intermediates and organic acids. In this way, the P1 goes forward to stage 5 (S5), which lead to a much deeper degradation.

References:

- (1) Spadaro, J. T.; Isabelle, L.; Renganathan V. Hydroxyl radical mediated degradation of azo dyes: evidence for benzene generation. *Environ. Sci. Technol.* **1994**, *28*, 1389-1393.

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Table S1. Effect of initial dye concentration on dye and COD removal.

Initial concentration	P2	P1	
dye*	500 mg/L	20.1	98.5
	1000 mg/L	9.1	96.5
	2000 mg/L	3.5	95.8
COD**	500 mg/L	15.8	43.2
	1000 mg/L	9.2	39.1
	2000 mg/L	5.1	36.4

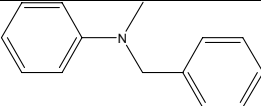
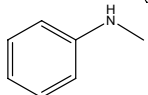
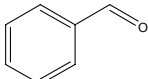
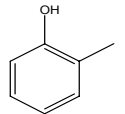
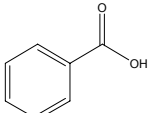
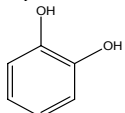
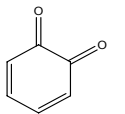
Conditions: P1: pH 5.0, I 0.5 A, Na₂SO₄ 3 g/L, O₂ 0.5 MPa, T 160 °C;

P2: pH 5.0, I 0.5 A, Na₂SO₄ 3 g/L, O₂ 0.5 MPa, T 25 °C.

* treatment time: 30 min

** treatment time: 120 min.

Table S2. The main degradation intermediates of X-GRL by two processes

Code	m/z	Molecular formula	Name	Structure	1	2
M1	197	C ₁₄ H ₁₅ N	Benzenamine,N-phenylmethylene		√	√
M2	106	C ₇ H ₈ N	N-methyl-aniline		√	√
M3	106	C ₇ H ₆ O	Benzaldehyde		√	√
M4	108	C ₇ H ₈ O	2-methyl-phenol		√	
M5	122	C ₇ H ₆ O ₂	Benzoic acid		√	
M6	122	C ₇ H ₆ O ₂	<i>o</i> -hydroquinone		√	
M7	122	C ₇ H ₆ O ₂	<i>o</i> -benzoquinone		√	