Supporting Information

Influence of solution pH on degradation of atrazine during UV and UV/H₂O₂ oxidation: Kinetics, mechanism, and degradation pathways

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Text S1 Parameters of UPLC and MS for identifying UV photo-oxidation products.

The binary mobile phase was composed of methanol (mobile phase A) and ultrapure water (mobile phase B), and the flow rate was 0.2 mL min⁻¹. The elution started with 10% A for 3 minutes, the concentration of A was increased to 70% within 18 minutes, and then the concentration of A was increased to 100% within 22 minutes and retained for 3 minutes, finally it was dropped back to 10% and run for 3 minutes for equilibrium before the next injection. A total acquisition time of one run analysis was 28 min. The column temperature was maintained at 35 °C and the injection volume was 10 μ L. The source temperature and desolvation temperature were 110 °C and 350 °C, the capillary voltage was 3.3 kV, and the cone voltage was 35 V. Desolvation gas (nitrogen gas) and cone gas (nitrogen gas) flows were set at 500 L h⁻¹ and 30 L h⁻¹, respectively. Full scan data were acquired from m/z 50 to 300 at an acquisition rate of 0.2 sec scan⁻¹ in both positive electrospray ionization (ESI+) mode and negative electrospray ionization (ESI-) mode. In order to obtain further information for analyzing the structure of intermediates, collision induced dissociation (CID) experiments in daughter scan were also conducted. Argon was used as collision gas in daughter scan model and its flow rate was at 0.12 mL min⁻¹. The collision energy for each product was optimized in the range from 15 to 35 eV.



Fig. S1 Emission spectrum of the low-pressure mercury UV lamp.



Fig. S2 Schematic diagram of photochemical reactor.

(1) low-pressure mercury UV lamp; (2) quartz glass well; (3) sampling point; (4) magnetic stirrer; (5) magnetic stirrer apparatus; (6) thermostatic water recirculation system; (7) silicone tube. All dimensions are in millimeter (mm).



Fig. S3 Distribution for protonated and deprotonated ATZ species as a function of solution pH.

 $C_{Total} = C_{Deprotonated form} + C_{Protonated}$.



Fig. S4 The EIC of photo-degradation intermediates of ATZ in solution during sole-UV treatment. Raw ATZ solution: 5 mg L⁻¹; irradiation time: 120 min. (A) pH 4.0; (B) pH 5.5; (C) pH 7.0; (D) pH 8.5; (E) pH 10.0.

P1 (4-Isopropylamino-6-amino-*s*-triazine)





Fig. S5 Molecular structure and MS/MS spectrum of P1 (ESI+, CE=22 eV).

P2 (2-Methoxy-4-methylamino-6-isopropylamino-s-triazine)





Fig. S6 Molecular structure and MS/MS spectrum of P2 (ESI+, CE=22 eV).

P3 (2-Hydroxy-4-isopropylamino-6-vinylamino-*s*-triazine)



ESI+ mode



Fig. S7 Molecular structure and MS/MS spectrum of P3 (ESI+, CE=0 eV).

P4 (2-Hydroxy-4-ethylamino-6-isopropylamines-s-triazine)







Fig. S8 Molecular structure and MS/MS spectrum of P4 (ESI+ and ESI-, CE=23 eV).

P5 (2-Hydroxy-4-acetamido-6-ethylamino-*s*-triazine)



ESI+ mode



ESI- mode



Fig. S9 Molecular structure and MS/MS spectrum of P5 (ESI+ and ESI-, CE=16 eV).

P6 (2-Hydroxy-4-(2-hydroxy-ethylamino)-6-vinylamino-s-triazine)



ESI+ mode



Fig. S10 Molecular structure and MS/MS spectrum of P6 (ESI+ and ESI-, CE=24 eV).

P7 (2-Hydroxy-4-acetamido-6-isopropylamino-s-triazine)





Fig. S11 Molecular structure and MS/MS spectrum of P7 (ESI+, CE=26 eV).

P8 (2-Methoxy-4-isopropylamino-6-ethylamino-s-triazine)





Fig. S12 Molecular structure and MS/MS spectrum of P8 (ESI+, CE=22 eV).

P9 (2-Chloro-4-ethylamino-6-isopropylamino-s-triazine)





Fig. S13 Molecular structure and MS/MS spectrum of P9 (ESI+, CE=22 eV).

P10 (2-Hydroxy-4-vinylamino-s-triazine)





Fig. S14 Molecular structure and MS/MS spectrum of P10 (ESI+, CE=12 eV).



Fig. S15 UV-vis absorbance spectra of ATZ and its products in aqueous solutions at different pH values during sole-UV process.



Fig. S16 UV-vis absorbance spectra of ATZ and its products in aqueous solutions at pH of 7.0 during UV/H_2O_2 process.



Fig. S17 Degradation of H_2O_2 in UV/ H_2O_2 process and the dark controls at pH of 7.0.



Fig. S18 Effect of H_2O_2 does and irradiation time on degradation of ATZ (5 mg L⁻¹) in aqueous solution at pH of 4.0 during UV irradiation treatment.



Fig. S19 Effect of H_2O_2 does and irradiation time on degradation of ATZ (5 mg L⁻¹) in aqueous solution at pH of 10.0 during UV irradiation treatment.



Fig. S20 UV-vis absorbance spectra of ATZ and its products in aqueous solutions at pH of 4.0 during UV/H_2O_2 process.



Fig. S21 UV-vis absorbance spectra of ATZ and its products in aqueous solutions at pH of 10.0 during UV/H_2O_2 process.



Fig. S22 Degradation of H_2O_2 in UV/ H_2O_2 process and the dark controls at pH of 4.0.



Fig. S23 Degradation of H_2O_2 in UV/ H_2O_2 process and the dark controls at pH of 10.0.



Fig. S24 The EIC of photo-degradation intermediates of ATZ in aqueous solution at 90 min of UV irradiation in UV/ H_2O_2 process under different H_2O_2 dose. (A) pH=7.0, 0 mg L⁻¹ H_2O_2 ; (B) pH=7.0, 5 mg L⁻¹ H_2O_2 ; (C) pH=7.0, 15 mg L⁻¹ H_2O_2 ; (D) pH=7.0, 30 mg L⁻¹ H_2O_2 ; (E) pH=7.0, 50 mg L⁻¹ H_2O_2 ; (F) pH=4.0, 30 mg L⁻¹ H_2O_2 ; (G) pH=10.0, 30 mg L⁻¹ H_2O_2 .

P12 (2-Hydroxy-4-acetamido-6-isopropenylenylamino-s-triazine)





Fig. S25 Molecular structure and MS/MS spectrum of P12 (ESI+, CE=20 eV).

P13 (4-acetamido-s-triazine)





Fig. S26 Molecular structure and MS/MS spectrum of P13 (ESI+, CE=15 eV).

P14 (2-Hydroxy-4-acetamido-6-(2-hydroxyisopropylamino)-s-triazine)





Fig. S27 Molecular structure and MS/MS spectrum of P14 (ESI+ and ESI-, CE=20 eV).

P15 (2-Hydroxy-4-ethylimine-6-(2-hydroxyisopropylamino)-s-triazine)





Fig. S28 Molecular structure and MS/MS spectrum of P15 (ESI+ and ESI-, CE=20 eV).

P16 (2-Chloro-4-vinylamino-6-acetamido-s-triazine)





Fig. S29 Molecular structure and MS/MS spectrum of P16 (ESI+, CE=15 eV).

P17 (2-Hydroxy-4-(2-hydroxy-ethylamino)-6-isopropylamino-s-striazine)



ESI+ mode



Fig. S30 Molecular structure and MS/MS spectrum of P17 (ESI+, CE=18 eV).

P18 (2-Hydroxy-4-ethylamino-6-(2-hydroxyisopropylamino)-s-triazine)



ESI+ mode



Fig. S31 Molecular structure and MS/MS spectrum of P18 (ESI+, CE=17 eV).

P19 (2-Hydroxy-4-ethylamino-6-isopropenylenylamino-s-triazine)



ESI+ mode



Fig. S32 Molecular structure and MS/MS spectrum of P16 (ESI+, CE=15 eV).

P20 (2-Hydroxy-4-(2-hydroxy-ethylamino)-6-amino-s-triazine)



ESI+ mode



ESI- mode



Fig. S33 Molecular structure and MS/MS spectrum of P20 (ESI+ and ESI-, CE=20 eV).

P21 (2-Chloro-4-vinylamino-6-amino-s-triazine)



ESI+ mode



Fig. S34 Molecular structure and MS/MS spectrum of P21 (ESI+ and ESI-, CE=20 eV).

Initial solution pH values	Final solution pH values	Linear correlation coefficient (<i>r</i> ²)	Reaction rate constants k_{obs} (min- 1)	Half-life time t _{1/2} (min)
4.0	4.03	0.989	0.0076	91.2
5.5	5.51	0.986	0.0113	61.3
7.0	6.98	0.987	0.0150	46.2
8.5	8.46	0.989	0.0140	49.5
10.0	9.95	0.985	0.0134	51.7

Table S1 Pseudo-first-order reaction rate constants (k_{obs}) of ATZ at different pH values in sole-UV process.

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Note: initial ATZ concentration: 5 mg L^{-1} .

Name	RT/min	MS spectral (ESI+)	MS spectral (ESI-)
P1	7.42	100 154 65 71 74 89 102 121 183 187 198 221 183 187 198 221 183 20 220 m/z	
P2	9.89	100 5765 717689.97 115 119 133 153 171 0 4.14 457 717689.97 115 119 133 153 171 187 206 60 80 100 120 140 160 180 200 220	
Р3	11.90	100 58 65 71 65 71 67 1 89 97 104 121 129 145 153 181183 0 80 100 120 140 160 180 200 220 1/2	
Ρ4	12.60	100 198 395 220 417 50 100 150 200 250 300 350 400 450 500 ¹ /2	100 393 0 50 100 150 200 250 300 350 400 450 500
Р5	14.06	100 220 100 417 198 417 71 113 252 318 395 433 0 71 10 150 200 250 300 350 400 450 500 ¹ / ₂	100 196 111 218 250 393 415 0 100 150 200 250 300 350 400 450 500
Р6	14.46	100 198 220 417 417 65 127 242,252,300,318 395 50 100 150 200 250 300 350 400 450 500	100 125 125 125 125 125 128 250 100 150 200 250 300 350 400 450 500 ^{1/2}
Ρ7	14.88	100 100 100 198 198 198 198 198 198 198 198	210 210 210 223_236 259 0 75 83 99 112 136 166 178 1 1 23 236 259 50 75 100 125 150 175 200 225 250 m/z
Ρ8	15.20	100 6574 97 121 129 193 198 6574 97 121 129 193 198 50 75 100 125 150 175 200 225 250 m/z	
Р9	15.44	100 216 218 238 0 50 75 100 125 150 175 200 225 250 m/z	214 75 60 84 ⁸⁹ 111 127 143 168 196 216 50 75 100 125 150 175 200 225 250 m/z
P10	5.02	100 96 129 151 1/2 139 151 1/2 100 100 100 110 120 130 140 150 1/2	
P11	7.54	100 198 38 71 128 154 220 395 417 0 71 128 154 220 395 417 50 100 150 200 250 300 350 400 m/z	100 196 38 123 151 181 199 245 284 321 381 393 0 150 150 200 250 300 350 400

Table S2 Retention time (RT) and MS spectral information in full scan modes of ATZ and its intermediates.

Initial H_2O_2	Final solution	Linear correlation	Reaction rate constants	Half-life time
concentration	pH values	coefficient (r ²)	k_{obs} (min ⁻¹)	t _{1/2} (min)
0	6.98	0.983	0.0145	46.2
5	6.95	0.979	0.0165	42.0
15	6.88	0.988	0.0118	58.7
30	6.82	0.991	0.0108	64.2
50	6.68	0.995	0.0097	71.5

Table S3 Pseudo-first-order reaction rate constants (k_{obs}) of ATZ (initial pH of 7.0) at different H₂O₂ does in UV/H₂O₂ process.

Name	RT/min	MS spectral (ESI+)	MS spectral (ESI-)	
P12	6.70	100 57 71 57 71 174 89 107 121 135141 160 173 179 207 232 243 258 0 75 100 125 150 175 200 225 250 m/z		
P13	8.58	100 100 100 100 100 100 100 100		
P14	11.38	100 3 ² 0 50 75 100 125 150 175 200 225 250 m/z	100 3 ⁶ 0 0 50 75 100 125 150 175 210 210 210 210 210 210 210 210	
P15	11.64	100 58 60 74 89 105 131 50 75 100 125 150 175 200 225 250 m/z	100 58 62 85,89 101 0 4.45,144 50 75 100 125 150 175 200 225 250 100 121 121 121 121 121 213 248 m/z	
P16	16.60	100 58 74 58 74 74 74 75 75 75 100 125 150 155 150 155 150 155 150 155 150 155 150 155 150 155 155		
P17	3.92	100 196 129 214 214 215 236 0 115 150 177 203 215 236 0 115 150 175 200 225 250 m/z		
P18	7.90	100 214 20 60 74 76 89 118 130 155 171 179 196 217 250 256 01 50 75 100 125 150 175 200 225 250 m/z		
P19	9.20	100 3 ⁸ 0 0 50 75 100 125 150 175 196 200218 200218 254 m/z		
P20	9.77	100 3 ² 60 74 88 101 114 130 140 160 50 75 100 125 150 175 200 225 250 m/z	100 170 56 61 75 85 99 117 147 164 183 202207 241 0 144 14 14 14 14 14 14 14 14 14 14 14 14	
P21	9.95	100 172 100 194 60 74 89.92 119 133.151170 183 212 223 0 40 44 89.92 119 133.151170 183 212 223 50 75 100 125 150 175 200 225 250 m/z	100 56 61 56 75 50 75 100 15 122 150 175 170 171 190 260 0 125 150 175 200 225 250 175 260 175 200 255 250 175 200 255 250 175 200 255 250 250 255 250	

Table S4 Retention time (RT) and MS spectral information in full scan modes of ATZ and its intermediates.