Supporting Information

Influence of solution pH on degradation of atrazine during UV and UV/H$_2$O$_2$ oxidation: Kinetics, mechanism, and degradation pathways

Yucan Liu$^{a*}$, Kai Zhu$^{b*}$, Miaomiao Su$^a$, Huayu Zhu$^c$, Jianbo Lu$^a$, Yuxia Wang$^d$, Jinkun Dong$^a$, Hao Qin$^a$, Ying Wang$^a$ and Yan Zhang$^a$

$^a$School of Civil Engineering, Yantai University, Yantai 264005, China.
$^b$College of resources and environment, Linyi University, Linyi 276000, China.
$^c$School of chemistry & chemical engineering, Linyi University, Linyi 276000, China.
$^d$School of Environmental and Municipal Engineering, North China University of Water Resources and Electric Power, Zhengzhou, 450046, China

Corresponding author:

Yucan Liu Ph.D.
School of Civil Engineering, Yantai University
30 Qingquan Road, Yantai, 264005, China
E-mail: liuyucan@ytu.edu.cn
Tel: +86 0535 6902606
Fax: +86 0535 6902606
Mobile: +86 15853588482

Kai Zhu Ph.D.
College of resources and environment, Linyi University
Shuangling Road, Linyi, 276000, China
E-mail: zhukai@lyu.edu.cn
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Table S4 Retention time (RT) and MS spectral information in full scan modes of ATZ and its intermediates. .................................................................................................................................................................. 42
**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 μL. 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.

\[ C_{\text{Total}} = C_{\text{Deprotonated form}} + C_{\text{Protonated form}} \]
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)

![Molecular structure of P1](image)

**ESI+ mode**

![MS/MS spectrum of P1](image)

**Fig. S5** Molecular structure and MS/MS spectrum of P1 (ESI+, CE=22 eV).
**P2** (2-Methoxy-4-methylamino-6-isopropylamino-s-triazine)

![Molecular structure of P2](image)

**ESI+ mode**

![MS/MS spectrum of P2](image)

**Fig. S6** Molecular structure and MS/MS spectrum of P2 (ESI+, CE=22 eV).
**P3** (2-Hydroxy-4-isopropylamino-6-vinylamino-s-triazine)

![Molecular structure of P3](image)

**ESI+ mode**

![Mass Spectrometer Image](image)

*Fig. S7* Molecular structure and MS/MS spectrum of P3 (ESI+, CE=0 eV).
**P4** (2-Hydroxy-4-ethylamino-6-isopropylamines-triazine)

**ESI+ mode**

**ESI- mode**

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)

![Molecular structure](image)

ESI+ mode

![MS/MS spectrum](image)

**Fig. S11** Molecular structure and MS/MS spectrum of P7 (ESI+, CE=26 eV).
**P8** (2-Methoxy-4-isopropylamino-6-ethylamino-s-triazine)

![Chemical structure of P8](image)

**ESI+ mode**

![MS/MS spectrum of P8](image)

**Fig. S12** Molecular structure and MS/MS spectrum of P8 (ESI+, CE=22 eV).
P9 (2-Chloro-4-ethylamino-6-isopropylamino-s-triazine)

ESI+ mode

Fig. S13 Molecular structure and MS/MS spectrum of P9 (ESI+, CE=22 eV).
**P10** (2-Hydroxy-4-vinylamino-s-triazine)

![Molecular structure of P10](image)

ESI+ mode

![Mass spectrum of P10](image)

**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$_2$O$_2$ process.
Fig. S17 Degradation of H₂O₂ in UV/H₂O₂ process and the dark controls at pH of 7.0.
**Fig. S18** Effect of H$_2$O$_2$ dose 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 H₂O₂ dose 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$_2$O$_2$ process.
Fig. S21 UV-vis absorbance spectra of ATZ and its products in aqueous solutions at pH of 10.0 during UV/H$_2$O$_2$ process.
Fig. S22 Degradation of H$_2$O$_2$ in UV/H$_2$O$_2$ process and the dark controls at pH of 4.0.
Fig. S23 Degradation of H$_2$O$_2$ in UV/H$_2$O$_2$ 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$_2$O$_2$ process under different H$_2$O$_2$ dose.

(A) pH=7.0, 0 mg L$^{-1}$ H$_2$O$_2$; (B) pH=7.0, 5 mg L$^{-1}$ H$_2$O$_2$; (C) pH=7.0, 15 mg L$^{-1}$ H$_2$O$_2$; (D) pH=7.0, 30 mg L$^{-1}$ H$_2$O$_2$; (E) pH=7.0, 50 mg L$^{-1}$ H$_2$O$_2$; (F) pH=4.0, 30 mg L$^{-1}$ H$_2$O$_2$; (G) pH=10.0, 30 mg L$^{-1}$ H$_2$O$_2$. 

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**P12** (2-Hydroxy-4-acetamido-6-isopropenylamino-s-triazine)

![Molecular structure of P12](image)

**ESI+ mode**

![MS/MS spectrum of P12](image)

**Fig. S25** Molecular structure and MS/MS spectrum of P12 (ESI+, CE=20 eV).
**P13** (4-acetamido-s-triazine)

![Molecular structure of P13](image)

**ESI+ mode**

![MS/MS spectrum of P13](image)

**Fig. S26** Molecular structure and MS/MS spectrum of P13 (ESI+, CE=15 eV).
**P14** (2-Hydroxy-4-acetamido-6-(2-hydroxyisopropylamino)-s-triazine)

![Molecular structure of P14](image)

**ESI+ mode**

![ESI+ MS/MS spectrum](image)

**ESI- mode**

![ESI- MS/MS spectrum](image)

**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)

![Chemical structure of P15](image)

**ESI+ mode**

![MS/MS spectrum of P15 in ESI+ mode](image)

**ESI- mode**

![MS/MS spectrum of P15 in ESI- mode](image)

**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)

![Molecular structure](image)

**ESI+ mode**

![MS/MS spectrum](image)

**Fig. S29** Molecular structure and MS/MS spectrum of P16 (ESI+, CE=15 eV).
**P17** (2-Hydroxy-4-(2-hydroxy-ethylamino)-6-isopropylamino-s-triazine)

![Molecular structure and MS/MS spectrum of P17 (ESI+, CE=18 eV).](image)

**Fig. S30** Molecular structure and MS/MS spectrum of P17 (ESI+, CE=18 eV).
**P18** (2-Hydroxy-4-ethylamino-6-(2-hydroxyisopropylamino)-s-triazine)

![Molecular structure of P18](image)

**ESI+ mode**

![MS/MS spectrum of P18](image)

**Fig. S31** Molecular structure and MS/MS spectrum of P18 (ESI+, CE=17 eV).
**P19** (2-Hydroxy-4-ethylamino-6-isopropenylamino-s-triazine)

![Molecular structure](image)

**ESI+ mode**

![MS/MS spectrum](image)

**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+ spectrum of P20](image)

ESI- mode

![ESI- spectrum of P20](image)

**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)

![Molecular structure and MS/MS spectrum of P21 (ESI+ and ESI-, CE=20 eV).](image)

**Fig. S34** Molecular structure and MS/MS spectrum of P21 (ESI+ and ESI-, CE=20 eV).
**Table S1** Pseudo-first-order reaction rate constants ($k_{obs}$) of ATZ at different pH values in sole-UV process.

| Initial solution pH values | Final solution pH values | Linear correlation coefficient ($r^2$) | 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                          |

*Note: initial ATZ concentration: 5 mg L$^{-1}$.**
Table S2 Retention time (RT) and MS spectral information in full scan modes of ATZ and its intermediates.

| Name | RT/min | MS spectral (ESI+) | MS spectral (ESI-) |
|------|--------|---------------------|--------------------|
| P1   | 7.42   | ![Diagram](image1)  | ![Diagram](image2)  |
| P2   | 9.89   | ![Diagram](image3)  | ![Diagram](image4)  |
| P3   | 11.90  | ![Diagram](image5)  | ![Diagram](image6)  |
| P4   | 12.60  | ![Diagram](image7)  | ![Diagram](image8)  |
| P5   | 14.06  | ![Diagram](image9)  | ![Diagram](image10) |
| P6   | 14.46  | ![Diagram](image11) | ![Diagram](image12) |
| P7   | 14.88  | ![Diagram](image13) | ![Diagram](image14) |
| P8   | 15.20  | ![Diagram](image15) | ![Diagram](image16) |
| P9   | 15.44  | ![Diagram](image17) | ![Diagram](image18) |
| P10  | 5.02   | ![Diagram](image19) | ![Diagram](image20) |
| P11  | 7.54   | ![Diagram](image21) | ![Diagram](image22) |
Table S3 Pseudo-first-order reaction rate constants ($k_{\text{obs}}$) of ATZ (initial pH of 7.0) at different H$_2$O$_2$ does in UV/H$_2$O$_2$ process.

| Initial H$_2$O$_2$ concentration | Final solution pH values | Linear correlation coefficient ($r^2$) | Reaction rate constants $k_{\text{obs}}$ (min$^{-1}$) | Half-life time $t_{1/2}$ (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                     |
| Name | RT/min | MS spectral (ESI+) | MS spectral (ESI-) |
|------|--------|--------------------|--------------------|
| P12  | 6.70   | ![Image]           | ![Image]           |
| P13  | 8.58   | ![Image]           | ![Image]           |
| P14  | 11.38  | ![Image]           | ![Image]           |
| P15  | 11.64  | ![Image]           | ![Image]           |
| P16  | 16.60  | ![Image]           | ![Image]           |
| P17  | 3.92   | ![Image]           | ![Image]           |
| P18  | 7.90   | ![Image]           | ![Image]           |
| P19  | 9.20   | ![Image]           | ![Image]           |
| P20  | 9.77   | ![Image]           | ![Image]           |
| P21  | 9.95   | ![Image]           | ![Image]           |