Supporting Information

For

Enhanced degradation of atrazine by microbubble ozonation

Yunsi Liu[a], Shuo Wang[a], Lifang Shi[a], Wanmeng Lu[a], Pan Li[a, b]*

\

[a] *School of Environmental Science and Engineering, Tongji University, 1239 Siping Road, Shanghai, PR China*

[b] *School of Environmental Science and Engineering, State Key Laboratory of Control and Resource Reuse, Tongji University, 1239 Siping Road, Shanghai, PR China*

1. Degradation of atrazine by ozone microbubble and macrobubble aeration at pH 5, 7 and 9

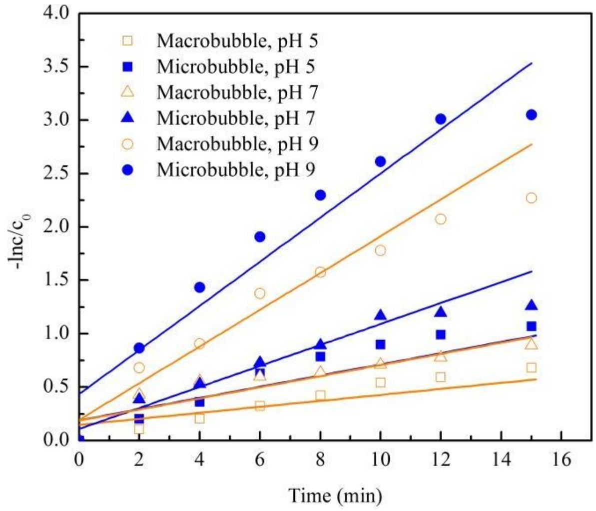

Figure S1. Degradation of atrazine by ozone microbubble and macrobubble aeration at pH 5, 7 and 9. (semi-batch experiment; initial conditions: $[O_3]$ = 1mg/L, $[Atra]_0$=1.16 μmol/L, gas flow: 0.5 L/min, T = 20 ± 1℃)

Table S1. The pseudo-first-order kinetic equations and correlation coefficients between atrazine and macrobubble and microbubble ozone at pH 5, 7 and 9. (semi-batch experiment; initial conditions: $[O_3]$ = 1mg/L, $[Atra]_0$=1.16 μmol/L, gas flow: 0.5 L/min, T = 20 ± 1℃).

Condition	Regression equation	R^2	k_{obs} (min^{-1})
Microbubble, pH 5	y=0.0531x-0.1895	0.973	0.053
Microbubble, pH 7	y=0. 1008x+0.1091	0.951	0.101
Microbubble, pH 9	y=0.2410x+0.298	0.983	0.241
Macrobubble, pH 5	y=0.0281x+0.1503	0.990	0.028
Macrobubble, pH 7	y=0.0530x+0.186	0.841	0.053
Macrobubble, pH 9	y=0.1740x+0.1935	0.957	0.174

2. Degradation of atrazine in the presence of TBA

The reaction rate of t-butanol and · OH is equal to 6.0 $\times 10^8$ L/mol·s [1], and the reaction rate of atrazine and · OH is equal to 3.0 $\times 10^9$ L/mol·s [2]. Therefore, as formula (1) show, 0.06 mM TBA was used as hydroxyl radical scavenger in our experiment.

$$\frac{k_{TBA}[TBA]}{k_{Atra}[Atra]} = \frac{6.0\times10^{8}\times0.06\times10^{-3}}{3\times10^{9}\times1.16\times10^{-6}} = 10.34 \geq 10 \qquad (1)$$

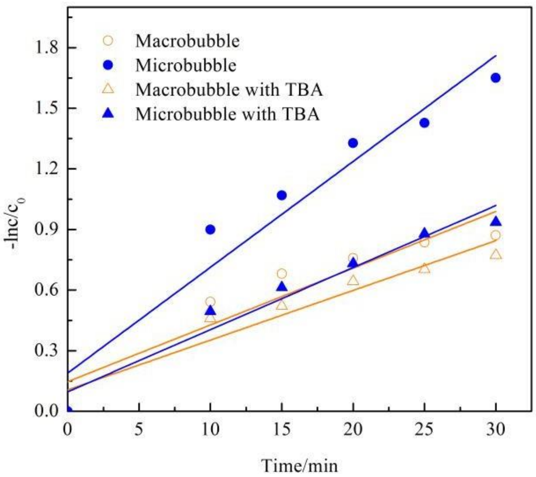

Figure S2. Degradation of atrazine by ozone microbubble and macrobubble aeration at pH 5 in the presence of TBA (semi-batch experiment; initial conditions: $[O_3]$ = 1mg/L, [TBA] = 0.06 mM, $[Atra]_0$ = 1.16 µmol/L, gas flow: 0.5 L/min, T = 20 ± 1℃).

Table S2. The pseudo-first-order kinetic equations and correlation coefficients between atrazine and macrobubble and microbubble ozone at pH 5 in the presence of TBA (semi-batch experiment; initial conditions: $[O_3]$ = 1mg/L, [TBA] = 0.06 mM, $[Atra]_0$ = 1.16 µmol/L, gas flow: 0.5 L/min, T = 20±1℃).

Condition	Regression equation	R^2	k_{obs} (min^{-1})
Microbubble	y=0.0524x-0.1895	0.938	0.052
Microbubble with TBA	y=0.0307x+0.097	0.950	0.031
Macrobubble	y=0.0279x+0.1503	0.901	0.028

Macrobubble with TBA	y=0.0246x+0.1063	0.922	0.025

3. Size distribution of microbubbles

During our experiment, a large amount of macroscopic microbubbles appeared white and thick at the beginning of aeration, however disappeared within three minutes. In our previous study [3], we examined the concentration of the microbubbles in the solution, in which above 90% of microbubbles disappeared within 1 minute and only nanobubbles left in the solution afterwards as shown in Figure S3.

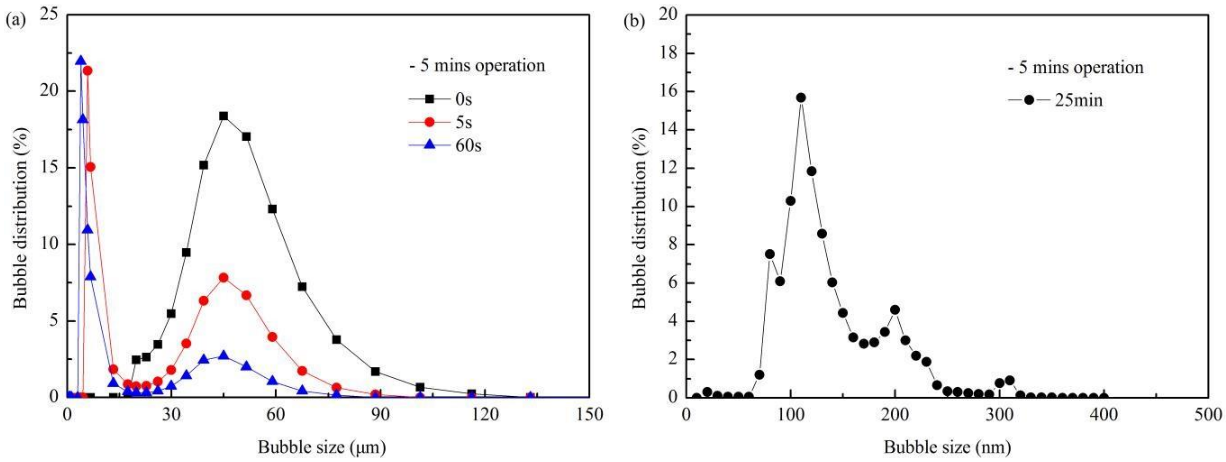

Figure S3. Size distribution of micro- and nanoscale bubbles during a 30 min cycle of aeration.

References

1 M. Kuosa, J. Kallas and A. Häkkinen, Ozonation of p-nitrophenol at different pH values of water and the influence of radicals at acidic conditions, *J. Environ. Chem. Eng.*, 2015, **3**, 325–332.

2 J. L. Acero, K. Stemmler and U. von Gunten, Degradation Kinetics of Atrazine and Its Degradation Products with Ozone and OH Radicals: A Predictive Tool for Drinking Water Treatment, *Environ. Sci. Technol.*, 2000, **34**, 591–597.

3 S. Wang, Y. Liu, P. Li, Y. Wang, J. Yang and W. Zhang, Micro-nanobubble aeration promotes senescence of submerged macrophytes with low total antioxidant capacity in urban landscape water, *Environ. Sci. Water Res. Technol.*, 2020, **6**, 523–531.