

Electronic supplementary information

Non-Hydroxyl Radical Mediated Photochemical Processes for Dye Degradation

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Table S1. Mobile phase gradient for the LC-MS/MS experiments.

Time (min)	Flow (ml/min)	0.1% HCOOH/H ₂ O (%)	CH ₃ OH (%)
0	0.2	90	10
38	0.2	10	90
42	0.2	90	10
55	0.2	90	10

Table S2. Degradation products of AO7 in the UV/diketone and UV/H₂O₂ processes.

No.	RT ^a	m/z	MS ² fragments	Detectability ^b			
				AA	BD	HD	H ₂ O ₂
A1	7.36	172	- ^c	√	√	√	ND
A2	9.20	173	146, 80	√	√	√	√
A3	13.64	214	-	√	√	√	ND
A4	8.22	189	125, 109	√	√	√	√
A5	30.30	343	325, 219, 170	√	√	√	ND
A6	32.05	391	-	ND	ND	ND	√
A7	39.92	427	410, 385, 370, 328, 283, 240, 172	√	ND	ND	ND
A8	43.84	299	235, 219	√	√	√	√

^a RT: retention time. ^b √: detected, ND: not detectable. ^c -: not available.

Table S3. Degradation products of MO in the UV/diketone and UV/H₂O₂ processes.

No.	RT	m/z	MS ² fragments	Detected or not			
				AA	BD	HD	H ₂ O ₂
M1	7.36	172	-	√	ND	√	ND
M2	9.20	173	-	√	√	√	√
M3	13.64	214	172, 150, 134	√	ND	√	ND
M4	14.43	228	184, 171	√	ND	√	ND
M5	19.57	390	372, 213, 198	√	ND	ND	ND
M6	20.92	404	386, 362, 213, 198	√	ND	ND	ND
M6'	24.98	404	-	ND	√	√	ND
M7	20.61	362	-	√	ND	ND	ND
M8	23.49, 25.01	320	304	√	√	√	√
M9	35.95	360	316, 296, 156	√	ND	ND	ND
M10	37.20	290	275, 226, 156	√	√	√	√
M11	39.95	346	317, 282, 156	√	ND	√	ND
M12	0.99	193	-	√	ND	ND	ND

Table S4. The toxicology of the three diketones and H₂O₂.

	BD* ^a	AA ^b	HD ^c	H ₂ O ₂ ^d
LD ₅₀ (oral, rat) (mg/kg)	1580	570-760	1600	910
LD ₅₀ (dermal, rabbit) (mg/kg)	> 5000	790-1370	N.A.	> 2000
LC ₅₀ (inhalation, rat, 4 hour) (mg/L)	2.25-5.2	5.1	2000	2

*: BD is a byproduct of fermentation. It occurs naturally in alcoholic beverages and is used as additive for some foods to impart a buttery flavor.

^a *Diacetyl*; MSDS No. D3634 [online]; Sigma-Aldrich: Saint Louis, MO, 18 Mar, 2013.

<http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=D3634&brand=SIGMA&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Fsigma%2Fd3634%3Flang%3Den> (accessed September 16, 2013)

^b *Acetylacetone*; MSDS No.00900 [online]; Sigma-Aldrich: Saint Louis, MO, 19 Sept 2012.

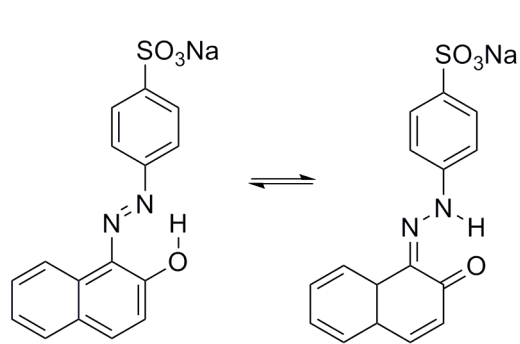
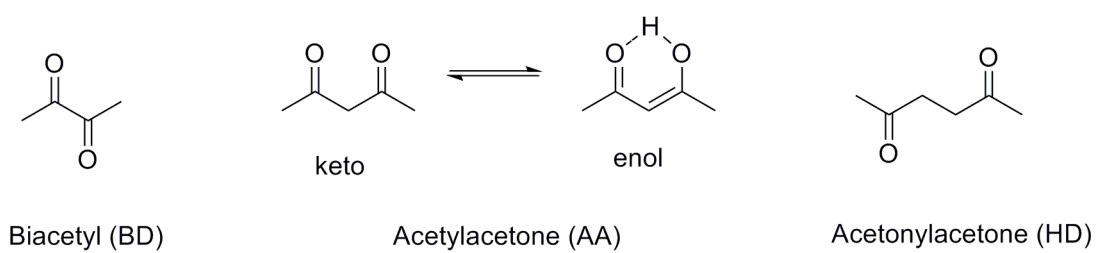
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^c *Acetylacetone*, MSDS No. 00770[online]; Sigma-Aldrich: Saint Louis, MO, 13 Jul 2012.

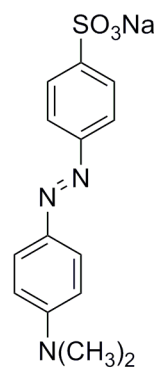
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^d *Hydrogen Peroxide*, MSDS No. H1009 [online]; Sigma-Aldrich: Saint Louis, MO, 26 Jan 2013.

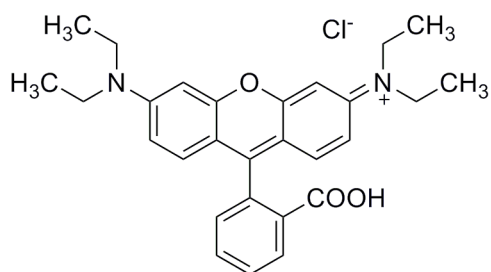
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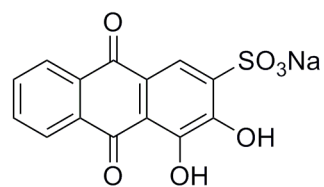
Acid Orange 7 (AO7)



Methyl Orange (MO)

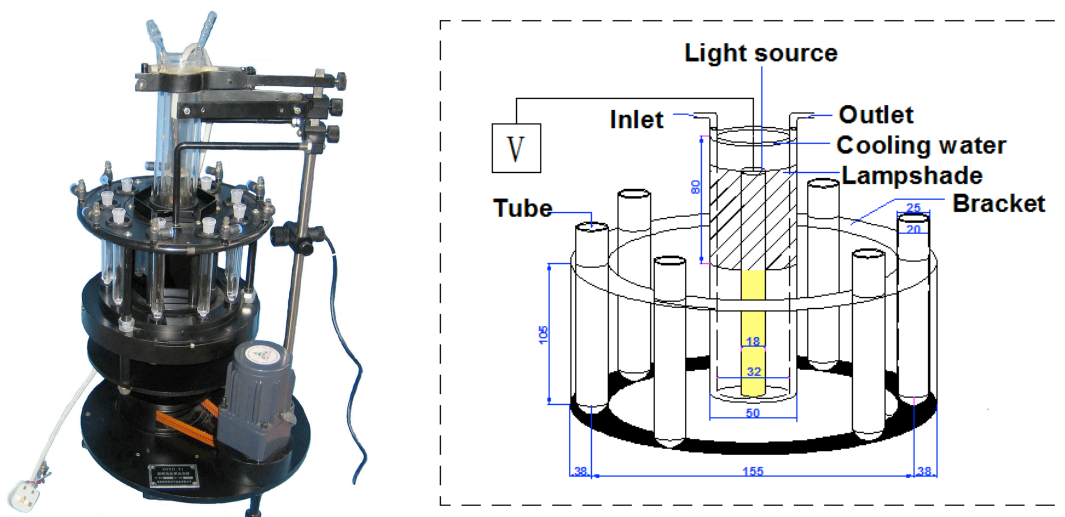


Rhodamine B (RB)



Alizarin Red (AR)

Scheme S1. Molecular structures of the three diketones and the four dyes.



Scheme S2. The picture and a schematic illustration of the photoreactor rig.

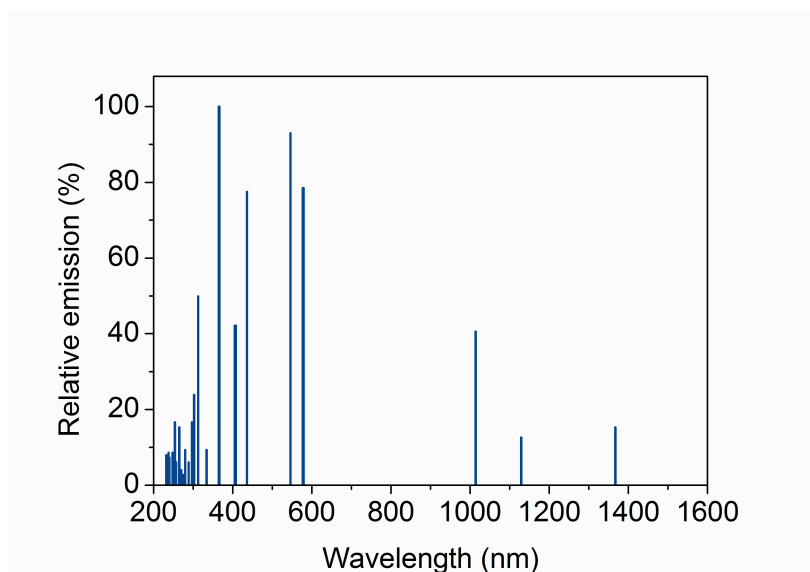


Fig. S1. The light spectrum of the medium-pressure mercury lamp.

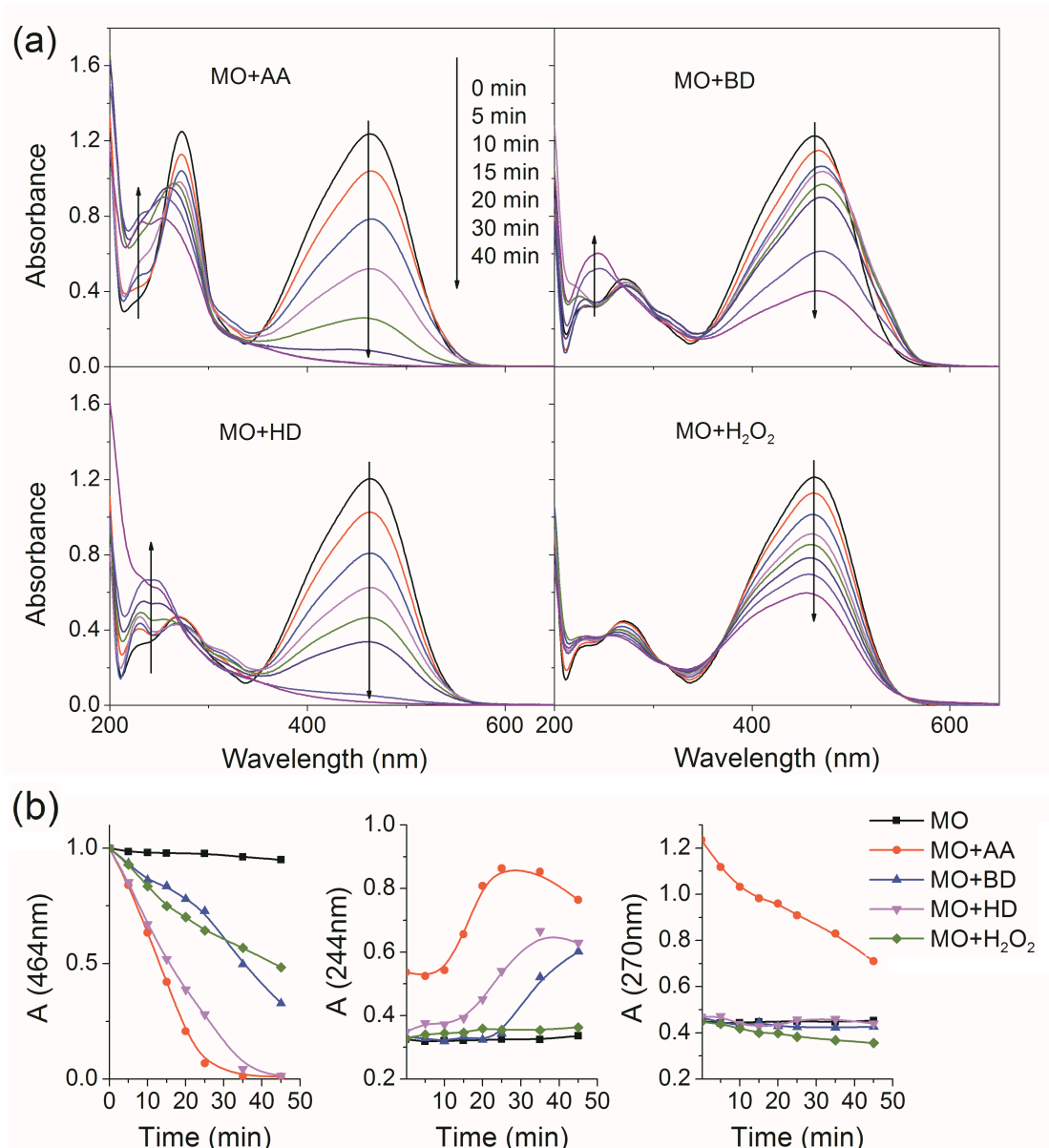


Fig. S2. (a) Evolution of the UV-Vis spectra of MO in the UV/diketone and UV/H₂O₂ processes. (b) Intensities of the three main UV/Vis absorption peaks of MO plotted as a function of irradiation time. The absorption intensity at 464 nm was normalized, and the intensities at 244 and 270 nm were the original absorption values. [MO] = 0.12 mM, [Activator] = 1 mM. Light intensity: 7.0 mW cm⁻². Samples were diluted for 2.5 times prior to analysis.

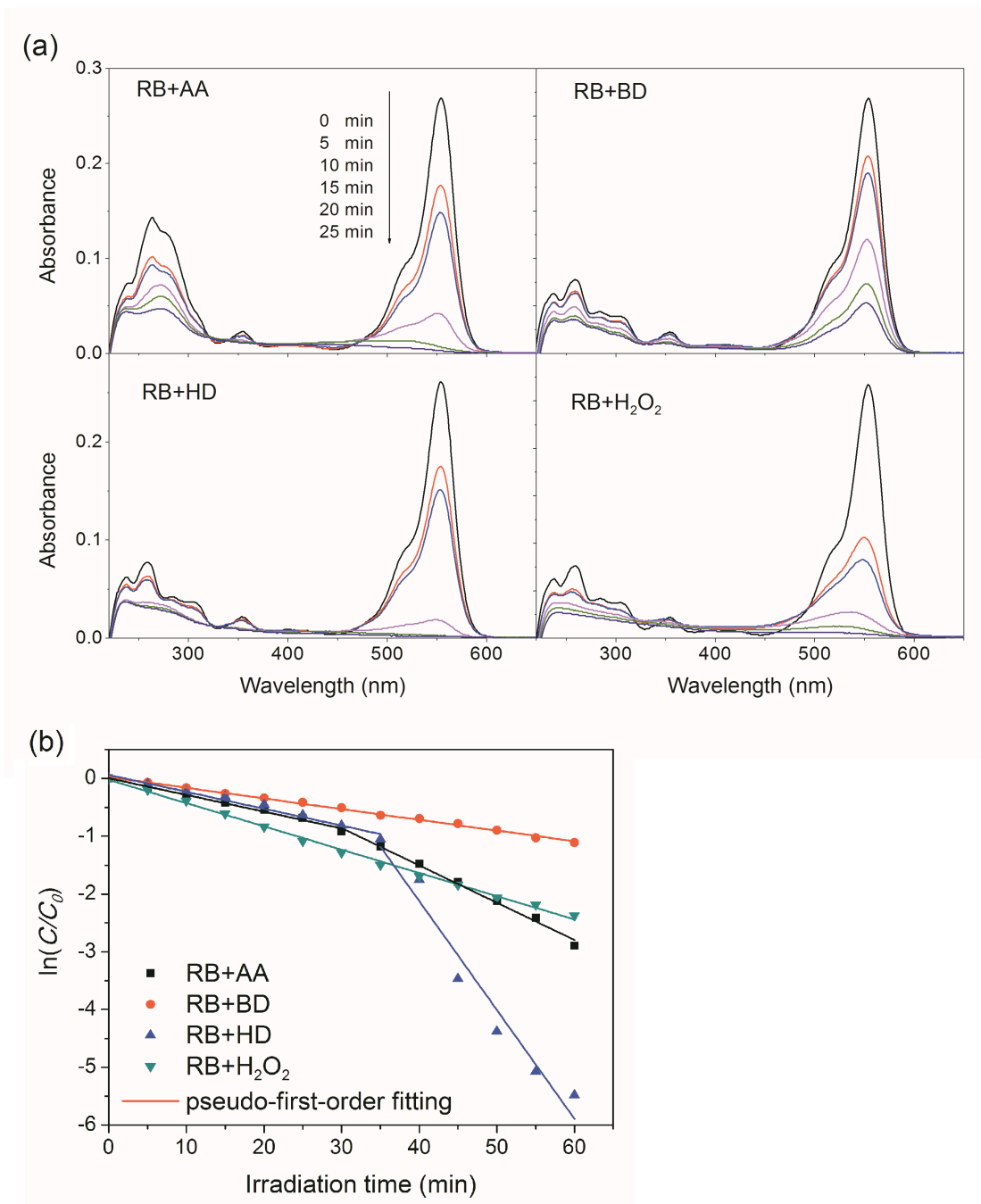


Fig. S3. (a) Evolution of the UV-Vis spectra of RB in the UV/diketone and UV/H₂O₂ processes. [RB] = 0.03 mM, [Activator] = 0.5 mM. (b) Degradation kinetics of RB in the UV/diketone and UV/H₂O₂ processes. [RB] = 0.05 mM, [Activator] = 0.5 mM.

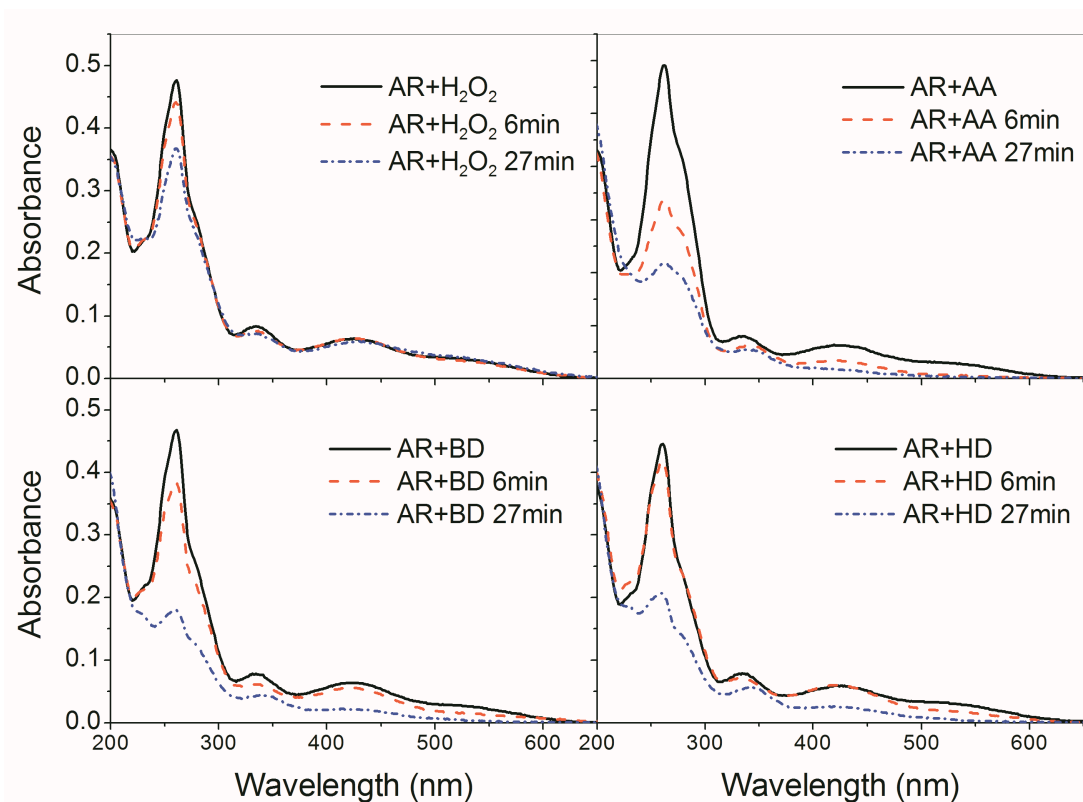


Fig. S4. Evolution of the UV-Vis spectra of AR in the UV/diketone and UV/H₂O₂ processes. [AR] = 0.1 mM, [Activator] = 0.5 mM, Light intensity: 5.3 mW cm⁻². Samples were diluted for 5 times prior to analysis.

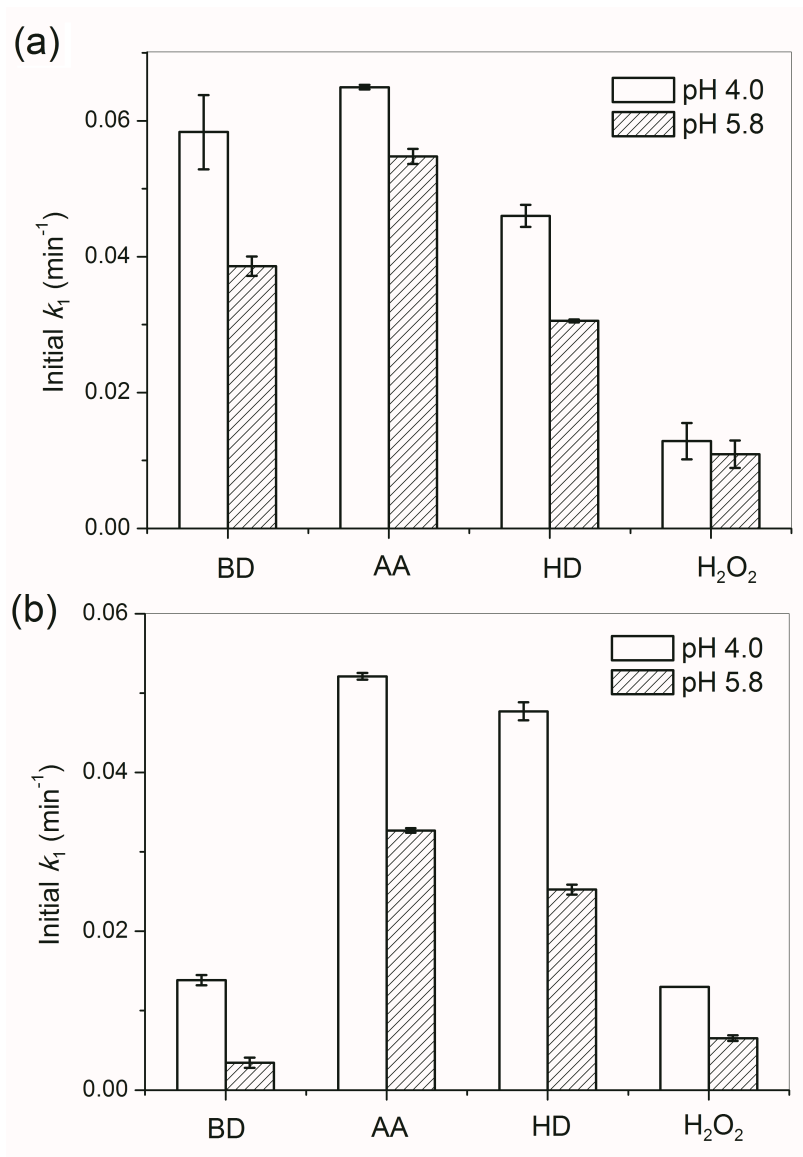


Fig. S5. The initial pseudo-first order decoloration rate constants of AO7 (a) and MO (b) in 0.2 mol/L NaAc/HAc buffer solutions of pH 4.0 and 5.8. (a) $[\text{AO7}] = 0.16 \text{ mM}$, $[\text{Activator}] = 0.5 \text{ mM}$. (b) $[\text{MO}] = 0.12 \text{ mM}$, $[\text{Activator}] = 1 \text{ mM}$. Error bar represents the standard deviation of duplicates.

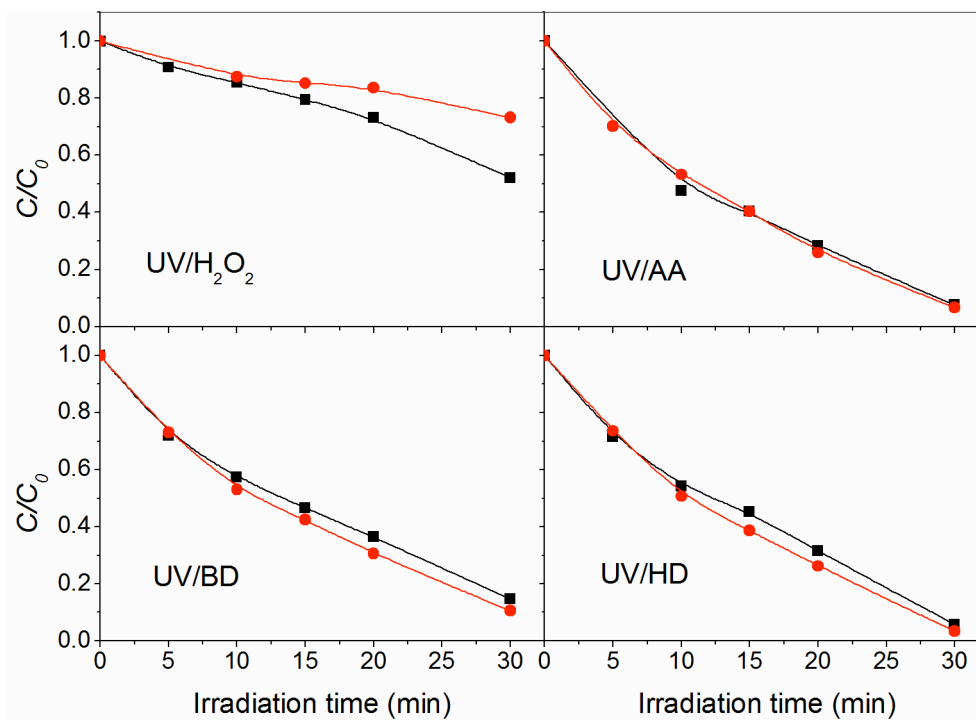


Fig. S6. Effect of ethanol on the decoloration of AO7 in the UV/diketone and UV/ H_2O_2 processes (Black: no ethanol, red: with ethanol).

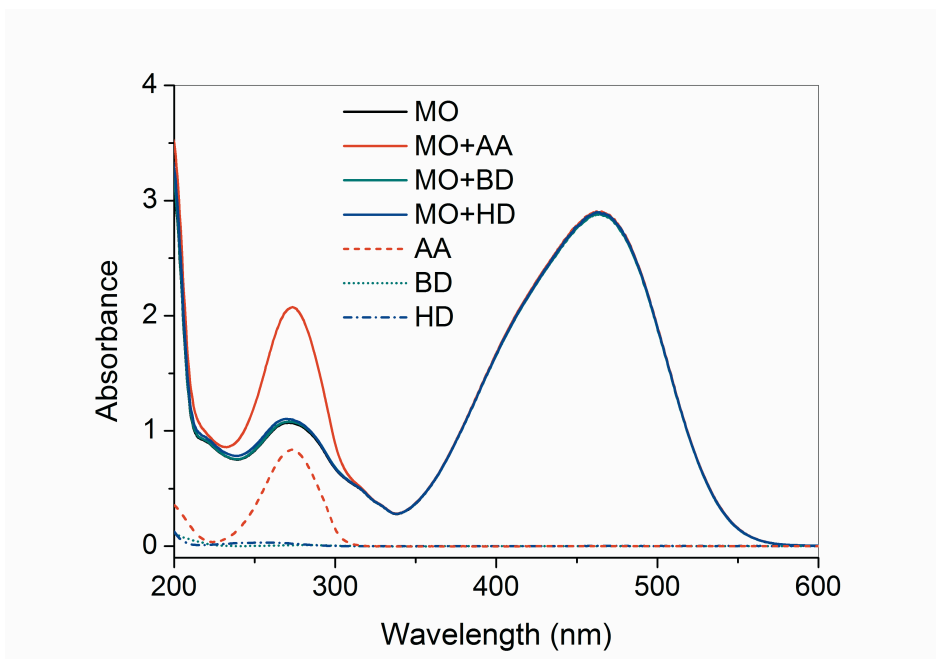


Fig. S7. UV-Vis spectra of MO, diketones and the mixture of MO and diketones.

*: The spectra of MO-diketone solution were exactly the sum of the individual spectra of MO and diketones.