Supplementary Information

Photolysis of Fungicides on Simulated Leaf Surfaces vs. Aqueous Solutions: Pathways, Kinetics, and Environmental Detoxification Insights

Chenyang Zhang[a], Xuewei Zhang[a], Xuerui Yang[a,b], Guangli Xiu[a,b,c], Jean-Marc Chovelon[d], Lei Zhou[a,b,c*]

[a]State Environmental Protection Key Lab of Environmental Risk Assessment and Control on Chemical Processes, School of Resources & Environmental Engineering, East China University of Science and Technology, Shanghai 200237, China
[b]Shanghai Environmental Protection Key Laboratory for Environmental Standard and Risk Management of Chemical Pollutants, School of Resources & Environmental Engineering, East China University of Science and Technology, Shanghai 200237, China
[c]Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, China
[d]Univ Lyon, Université Claude Bernard Lyon 1, CNRS, IRCELYON, Villeurbanne F-69626, France

* Corresponding author.
E-mail addresses: zhoulei@ecust.edu.cn (Lei Zhou)

Text S1. HR-MS Instrument parameters.

The HR-MS (*Q-Exactive plus, Thermo Fisher) was coupled to an HPLC Waters Alliance system for compound separation, and performed in positive ion mode with a scan range of m/z 50-750. The electrospray ionization source parameters were: capillary temperature 350 ℃, spray voltage 3.2 kV, capillary voltage 49 V and aux gas 10 Arb. An ACQUITY UPLC C18 2.1*100 mm column with a particle size of 1.7 mm was used for separation. The flow rate was 0.3 mL/min; the injection volume was 2 μL.

The mobile phase of KM, PAS and CRL was a mixture of water (0.1% formic acid) and acetonitrile (ACN). The gradient elution program was as follows: 0.0-0.5 min, 30% ACN; 0.5-4.5 min, 30-60% ACN; 4.5-5.5 min, 60-95% ACN; 5.5-7 min, 95% ACN; 7-7.1 min, 95-30% ACN; 7.1-10 min, 30% ACN.

Text S2. UV absorption spectrum

In this study, we used a UV-Vis spectrophotometer (Hach, DR6000) to measure the UV absorption spectra of the fungicides. A full spectrum scan mode was employed, with a scanning wavelength range of 290-600 nm. The concentration of fungicides was 50 μM. Measurements were taken in a 1 cm quartz cuvette.

The UV absorption spectra of the fungicides contained in the carnauba wax were measured by UV-vis DRS spectrophotometer with an integral sphere (Shimadzu, UV-2600). The powdered samples were loaded in a quartz flow cell and were measured in the wavelength range of 290 to 800 nm at room temperature.

Text S3. Photolysis Kinetics and Quantum Yield

(1) Photolysis Kinetics

The dynamics of fungicides degradations in aqueous solution and on the carnauba wax film were analyzed by plotting the residue concentration of fungicides against time using a pseudo-first-order reaction equation (Eq. (1)).

$$\ln([FUN]_t / [FUN]_0) = k_{obs}t \quad (1)$$

$$t_{1/2} = \ln 0.5 / k_{obs} \quad (2)$$

where $[FUN]_0$ was the initial concentration of fungicides, $[FUN]_t$ was the concentration of fungicides at t time (μM), k_{obs} was the photolysis rate constant (min-1), and t was the degradation time (min). Besides, $t_{1/2}$ was the half-life of fungicides.

(2) Quantum Yield

The photolysis quantum yields (Φ) of direct photolysis of three fungicides in aqueous solution was determined according to following equation[1].

$$\phi = \frac{-(dC/dt) \times 10^{-3}}{\int_{290}^{600} \frac{I_{0,\lambda}}{l}(1 - e^{-2.303\varepsilon_\lambda lC})d\lambda} \quad (3)$$

where C (mol L^{-1}) is the fungicides concentration, t (s) is the radiation time, $I_{0,\lambda}$ (Einstein cm^{-2} s^{-1}) is the wavelength-specific incoming light intensity, ε_{λ}(L mol^{-1} cm^{-1}) is the wavelength-specific molar absorption coefficient for the fungicides, and l (cm) is the optical path length.

Table S1. Detailed HPLC detection conditions for each fungicide.

Compound	A	B	C	D	Column temperature (℃)	Detection wavelength (nm)	Retention time (min)
Kresoxim-methyl (KM)	0	0	30	70	25	230	8.60
Cyprodinil (CRL)	40	0	0	60	30	270	5.50
Pyraclostrobin (PAS)	40	0	0	60	30	278	6.20

The mobile phase A was pure water, phase B was methanol, phase C was 0.1% (v/v) aqueous acetic acid and acetonitrile in phase D.

Table S2. Acute and chronic toxicity evaluation criteria.[a]

acute toxicity (mg/L)	chronic toxicity (mg/L)	category
$LC_{50}/EC_{50} < 1$	ChV < 1	very toxic
$1 < LC_{50}/EC_{50} < 10$	1 < ChV < 10	toxic
$10 < LC_{50}/EC_{50} < 100$	10 < ChV < 100	harmful
$100 < LC_{50}/EC_{50}$	100 < ChV	not harmful

[a] Globally Harmonized System of Classification and Lablling of Chemicals, GHS

Table S3. Identification major intermediate photoproducts of KM on wax film and in aqueous solution.

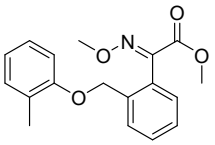
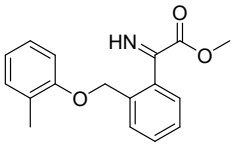
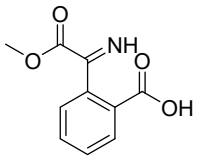
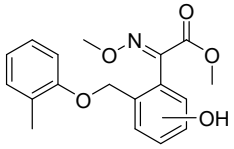
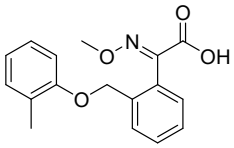
Label	RT (min)	Measured exact mass [M+H]+	Theoretical exact mass [M+H]+	Δppm	Formula of neutral structure	Propose structure	media
KM	6.73	314.1385	314.1387	-0.64	$C_{18}H_{19}NO_4$		-
KM isomers	5.02; 6.06; 6.30; 7.17	314.1385	314.1387	-0.64	$C_{18}H_{19}NO_4$	/	Both wax and water
KP1	3.49	284.1282	284.1282	0.00	$C_{17}H_{17}NO_3$		Both wax and water
KP2	1.54	208.0604	208.0605	-0.48	$C_{10}H_9NO_4$		Both wax and water
KPA1	4.21	330.1337	330.1336	0.30	$C_{18}H_{19}NO_5$		Water
KPA2	5.36	300.1230	300.1231	-0.33	$C_{17}H_{17}NO_4$		Water

Table S4. Identification major intermediate photoproducts of PAS on wax film and in aqueous solution.

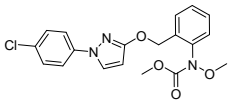
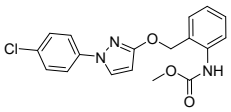
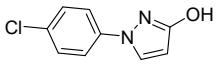
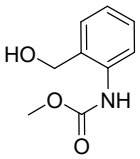
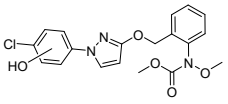
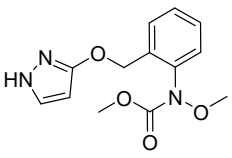
Label	RT (min)	Measured exact mass [M+H]+	Theoretical exact mass [M+H]+	Δppm	Formula of neutral structure	Propose structure	media
PAS	6.91	388.1054	388.1059	-1.29	$C_{19}H_{18}O_4N_3Cl$		-
PAS isomer	6.60	388.1054	388.1059	-1.29	$C_{19}H_{18}O_4N_3Cl$	/	Both wax and water
PP1	6.89	358.0953	358.0953	0.00	$C_{18}H_{16}O_3N_3Cl$		Both wax and water
PP2	4.12	195.0320	195.0320	0.00	$C_9H_7ON_2Cl$		Both wax and water
PP3	4.01	182.0811	182.0812	-0.55	$C_9H_{11}NO_3$		Both wax and water
PPA1	6.87	404.1009	404.1008	0.25	$C_{19}H_{18}O_5N_3Cl$		Water
PPA2	3.32	278.1135	278.1136	-0.36	$C_{13}H_{15}N_3O_4$		Water

Table S5. Identification major intermediate photoproducts of CRL on wax film and in aqueous solution.

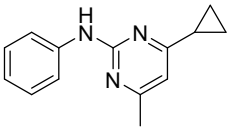
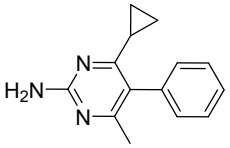
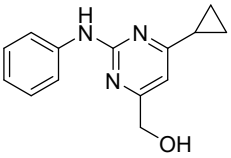
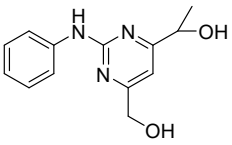
Label	RT (min)	Measured exact mass [M+H]+	Theoretical exact mass [M+H]+	Δppm	Formula of neutral structure	Propose structure	media
CRL	5.16	226.1334	226.1339	-2.21	$C_{14}H_{15}N_3$		-
CP1	5.87	226.1338	226.1339	-0.44	$C_{14}H_{15}N_3$		Both wax and water
CPA1	1.53	242.1288	242.1288	0.00	$C_{14}H_{15}N_3O$		Water
CPA2	5.03	246.1237	246.1238	-0.41	$C_{13}H_{15}N_3O_2$		Water

Table S6. Acute and chronic toxicity of KM, PAS, CRL and their photoproducts.

Compound	Acute toxicity LC_{50}/EC_{50} (mg/L)			Chronic toxicity ChV (mg/L)		
	Fish	Daphnid	Green Algae	Fish	Daphnid	Green Algae
KM	0.084	0.069	0.225	0.013	0.018	0.131
KP1	44.8	27.4	27.6	4.77	3.28	8.53
KP2	1.06E5	5.03E4	1.74E4	8.37E3	2.93E3	3.03E3
KPA1	0.239	0.186	0.508	0.034	0.043	0.267
KPA2	0.146	0.115	0.339	0.021	0.028	0.186
PAS	0.254	0.198	0.551	0.036	0.047	0.293
PP1	1.78	1.27	2.43	0.228	0.234	1.06
PP2	34.8	21.2	20.9	3.69	2.49	6.37
PP3	1.66E3	846	404	143	61.1	83.2
PPA1	0.714	0.533	1.23	0.096	0.112	0.595

Compound	Acute toxicity LC_{50}/EC_{50} (mg/L)			Chronic toxicity ChV (mg/L)		
	Fish	Daphnid	Green Algae	Fish	Daphnid	Green Algae
PPA2	26.4	16.5	18.3	2.89	2.11	5.94
CRL	3.05	2.08	3.30	0.370	0.338	1.30
CP1	7.75	5.07	6.78	0.895	0.733	2.43
CPA1	67.5	40.2	36.5	6.98	4.48	10.6
CPA2	1.34E3	699	367	118	53.9	79.6

Table S7. k_{obs}, $t_{1/2}$ of KM, PAS and CRL with different SDBS concentrations.

Fungicide	Concentration ratio (fungicide : SDBS)	k_{obs} (min^{-1})	$t_{1/2}$ (min)
Kresoxim-methyl (KM)	1:0	$(60.66 \pm 2.74) \times 10^{-3}$	11.43 ± 0.49
	1:0.5	$(69.11 \pm 0.99) \times 10^{-3}$	10.02 ± 0.14
	1:2	$(93.52 \pm 1.39) \times 10^{-3}$	7.41 ± 0.11
	1:5	$(123.25 \pm 7.25) \times 10^{-3}$	5.62 ± 0.31
	1:10	$(130.28 \pm 3.71) \times 10^{-3}$	5.32 ± 0.15
Pyraclostrobin (PAS)	1:0	$(51.67 \pm 1.59) \times 10^{-3}$	13.41 ± 0.40
	1:0.5	$(58.83 \pm 4.05) \times 10^{-3}$	11.78 ± 0.76
	1:2	(92.23 ± 1.94) × 10-3	7.52 ± 0.15
	1:5	$(268.60 \pm 6.36) \times 10^{-3}$	2.58 ± 0.06
	1:10	$(493.36 \pm 7.62) \times 10^{-3}$	1.40 ± 0.02
Cyprodinil (CRL)	1:0	$(17.53 \pm 1.99) \times 10^{-3}$	39.54 ± 4.03
	1:0.5	$(20.75 \pm 1.15) \times 10^{-3}$	33.40 ± 1.75
	1:2	$(70.92 \pm 1.91) \times 10^{-3}$	9.77 ± 0.26
	1:5	$(101.92 \pm 6.37) \times 10^{-3}$	6.80 ± 0.40
	1:10	$(44.97 \pm 4.07) \times 10^{-3}$	15.41 ± 1.28

Table S8. k_{obs}, $t_{1/2}$ of KM, PAS and CRL with different Tween-20 concentrations.

Fungicide	Concentration ratio (fungicide : SDBS)	k_{obs} (min^{-1})	$t_{1/2}$ (min)
Kresoxim-methyl (KM)	1:0	$(52.10 \pm 4.85) \times 10^{-3}$	13.30 ± 1.13
	1:0.5	$(49.72 \pm 2.23) \times 10^{-3}$	13.94 ± 0.60
	1:2	$(60.44 \pm 5.13) \times 10^{-3}$	11.47 ± 0.90
	1:5	$(71.66 \pm 3.59) \times 10^{-3}$	9.67 ± 0.46
	1:10	$(94.70 \pm 4.86) \times 10^{-3}$	7.32 ± 0.36
Pyraclostrobin (PAS)	1:0	$(46.62 \pm 1.56) \times 10^{-3}$	14.87 ± 0.48
	1:0.5	$(68.52 \pm 5.52) \times 10^{-3}$	10.12 ± 0.75
	1:2	$(156.37 \pm 20.02) \times 10^{-3}$	4.43 ± 0.50
	1:5	$(172.38 \pm 11.09) \times 10^{-3}$	4.02 ± 0.24
	1:10	$(243.73 \pm 5.06) \times 10^{-3}$	2.84 ± 0.06
Cyprodinil (CRL)	1:0	$(19.38 \pm 1.76) \times 10^{-3}$	35.77 ± 2.98
	1:0.5	$(4.90 \pm 1.05) \times 10^{-3}$	141.46 ± 24.96
	1:2	$(5.31 \pm 1.37) \times 10^{-3}$	130.54 ± 26.77
	1:5	$(8.38 \pm 1.26) \times 10^{-3}$	82.71 ± 10.81
	1:10	$(11.28 \pm 1.26) \times 10^{-3}$	61.45 ± 6.17

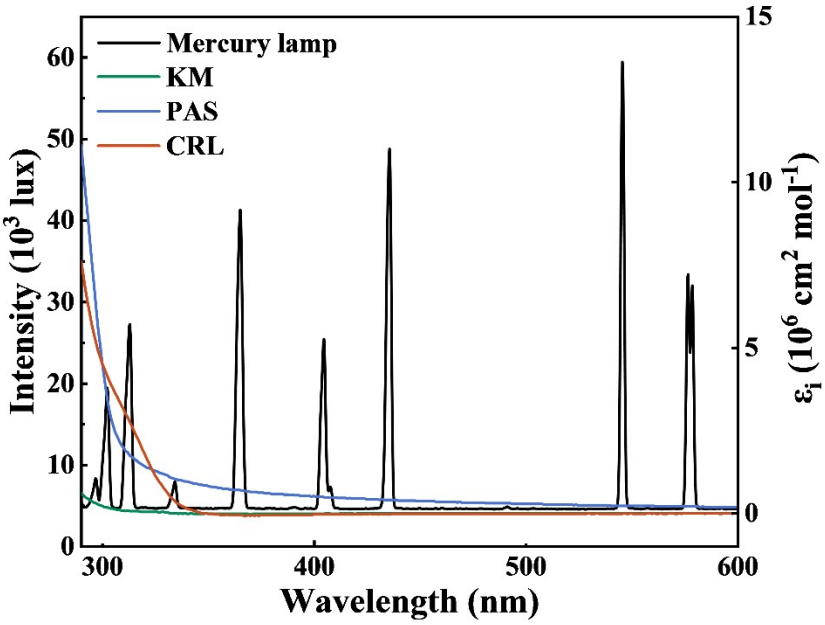


Fig. S1. Emission spectrum of a 500W high-pressure mercury lamp (supplied by the manufacturer) and the molar absorption coefficient of KM, PAS and CRL.

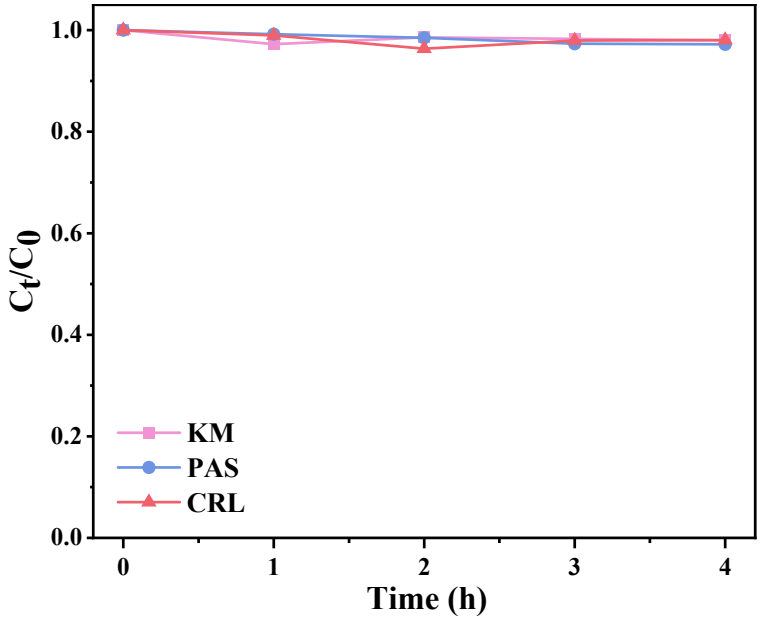


Fig. S2. Dark control experiments of KM, PAS and CRL in aqueous solution (50 mL fungicides with 1 μM level was used).

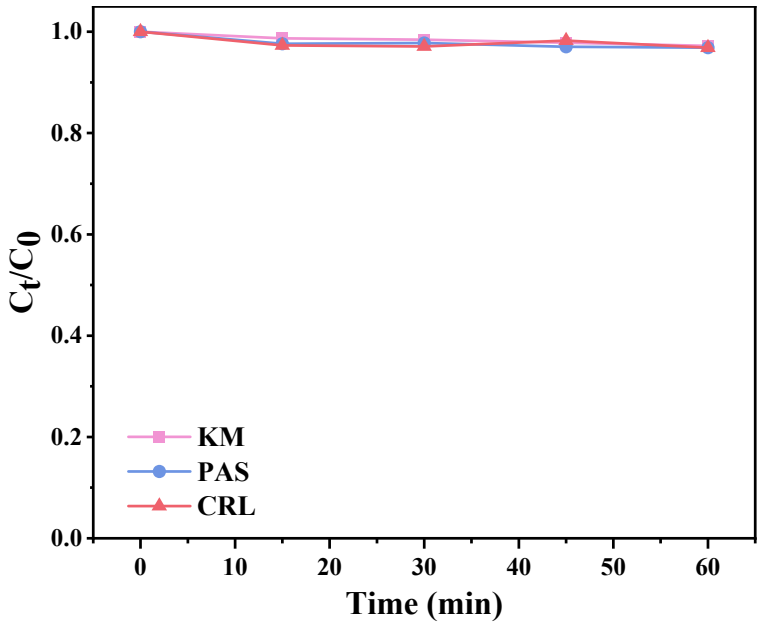


Fig. S3. Dark control experiments of KM, PAS and CRL on the carnauba wax film (0.1 mL fungicides with 500 µM level was used).

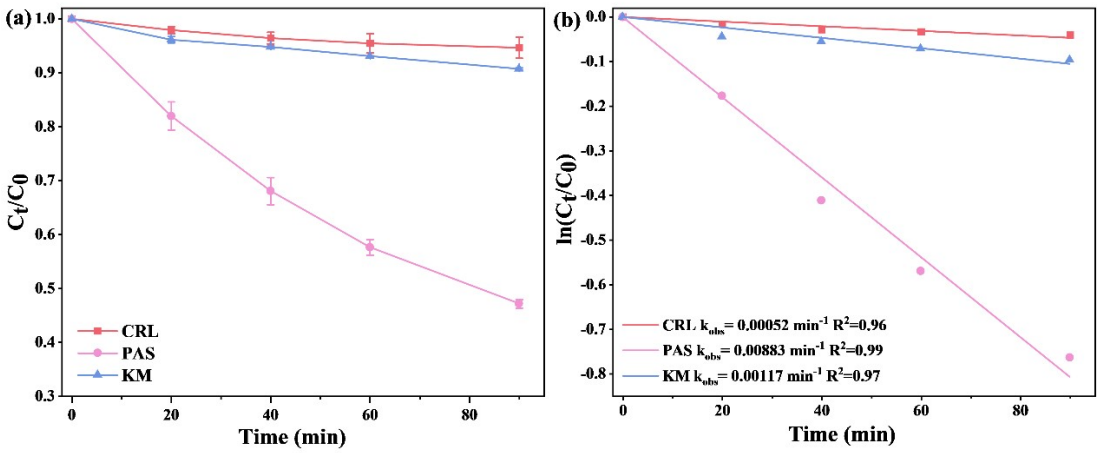


Fig. S4. Photodegradation experiments of KM, PAS and CRL in aqueous solution (50 mL fungicides with 1 µM level was used). (a) The concentration decay curves. (b) Photodegradation rate constants of three fungicides.

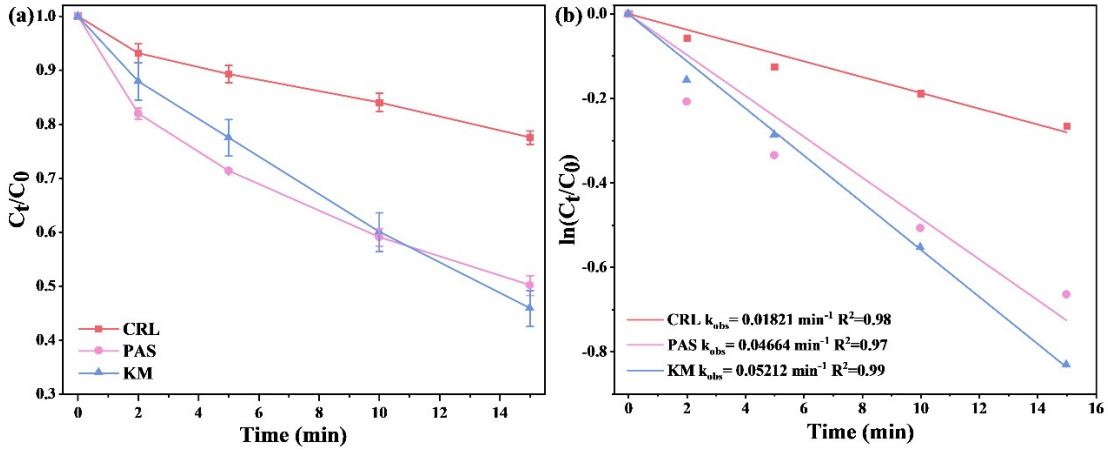


Fig. S5. Photodegradation experiments of KM, PAS and CRL on the carnauba wax film (0.1 mL fungicides with 500 μM level was used). (a) The concentration decay curves. (b) Photodegradation rate constants of three fungicides.

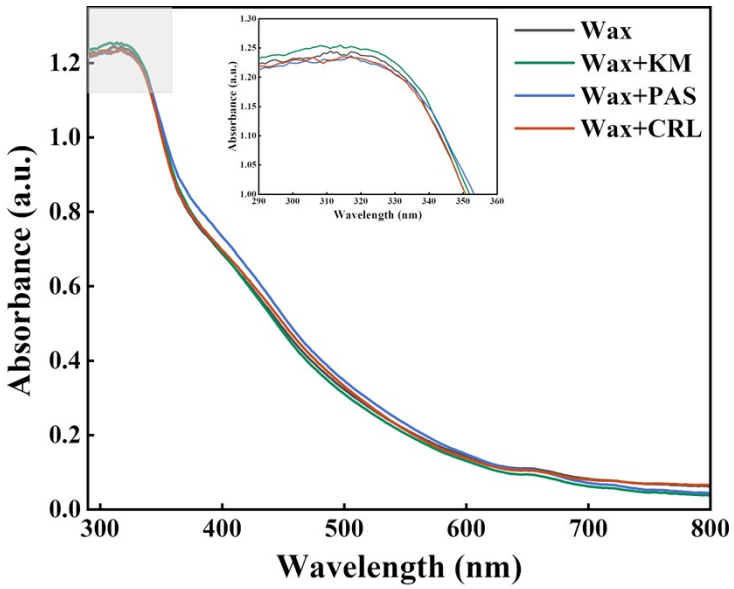


Fig. S6. UV-Vis absorption spectra of KM, PAS and CRL (5 μmol/g) contained in the carnauba wax.

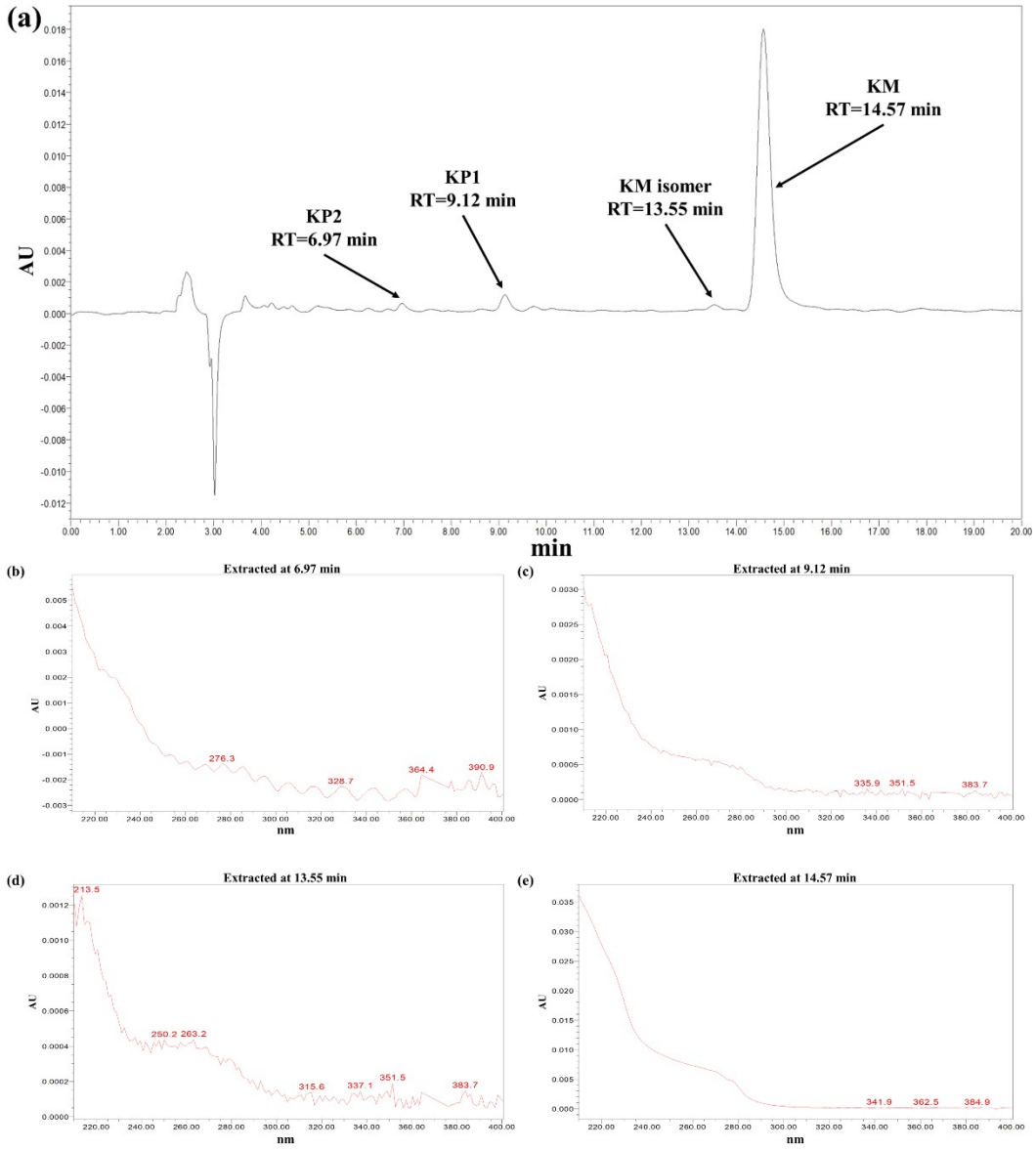


Fig. S7. The characteristic HPLC chromatograms and the UV absorption spectra of KM and its photoproducts on wax film. (a) The characteristic HPLC chromatograms of KM and its photoproducts on wax film. (b) The UV absorption spectra extracted from the peak at 6.97 min. (c) The UV absorption spectra extracted from the peak at 9.12 min. (d) The UV absorption spectra extracted from the peak at 13.55 min. (e) The UV absorption spectra extracted from the peak at 14.57 min.

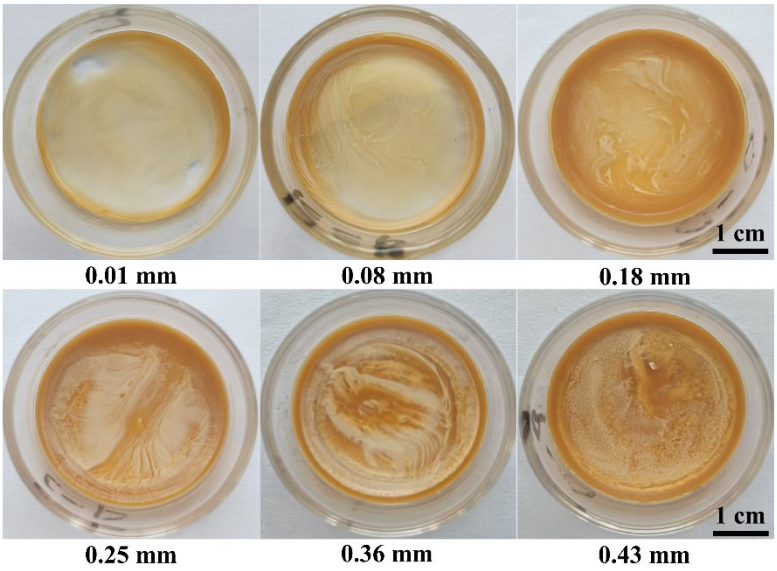


Fig. S8. Wax films of different thicknesses.

References

[1]S. Wang, J. Huang, Y. Yang, G. Yu, S. Deng and B. Wang, *J. Hazard. Mater.*, 2013, **260**, 16-23.