

Supplementary Information

Removal of 26 corticosteroids, potential COVID-19 remedies, at environmentally relevant concentrations in water by UV/free chlorine, UV/monochloramine, and UV/hydrogen peroxide

Ai Zhang¹, Yongqiang Ding¹, Ai Jia², Minkyu Park², Kevin D. Daniels², Xuhao Nie²,
Shimin Wu^{2,3,*}, Shane A. Snyder^{2,*}

¹ *College of Environmental Science and Engineering, Donghua University, 2999 North Renmin Road, Shanghai 201620, China.*

² *Department of Chemical and Environmental Engineering, University of Arizona, 1133 E. James E. Rogers Way, Harshbarger 108, Tucson, AZ 85721-0011, United States.*

³ *Jiangsu Shuangliang Environmental Technology Co., Ltd., Jiangyin, 214444, China.*

⁴ *Nanyang Technological University, Nanyang Environment & Water Research Institute, 1 Cleantech Loop, CleanTech One, #06-08, 637141, Singapore.*

*Corresponding author: Tel: +86 21 67792538; Fax: +86 21 67792522;

E-mail: wushimin@gmail.com (Shimin Wu), ssnyder@ntu.edu.sg (Shane A. Snyder)

14 Pages

4 Figures (S1-S4)

6 Tables (S1-S6)

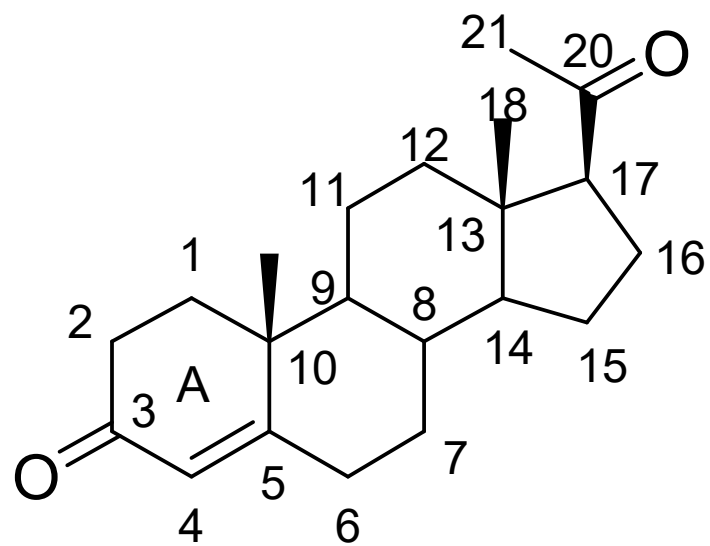


Fig. S1 The structure and nomenclature of corticosteroids.

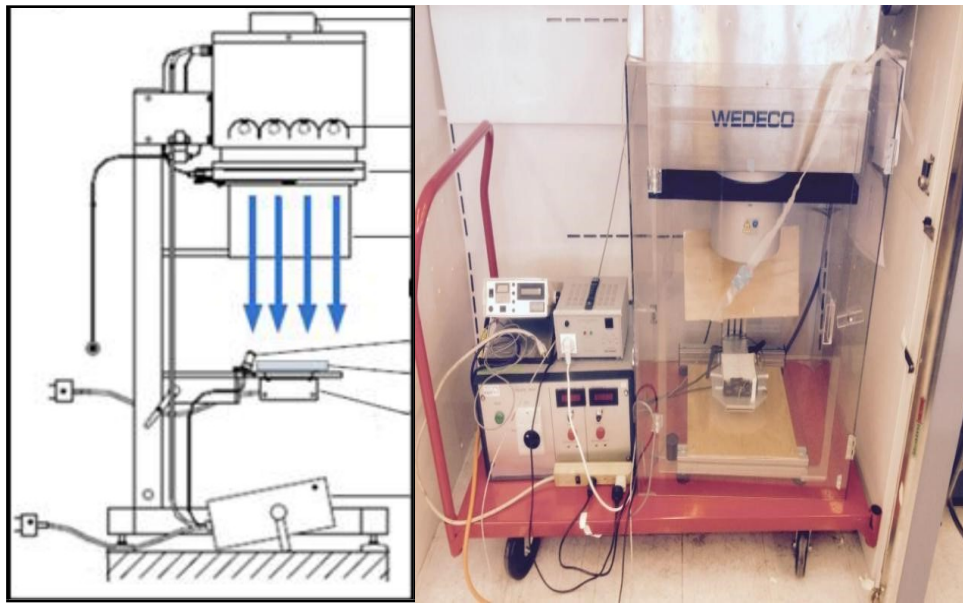


Fig. S2 Experimental scheme of the collimated beam device (Taken from Bolton et al. 2002) and the UV lamp equipment for the experiment

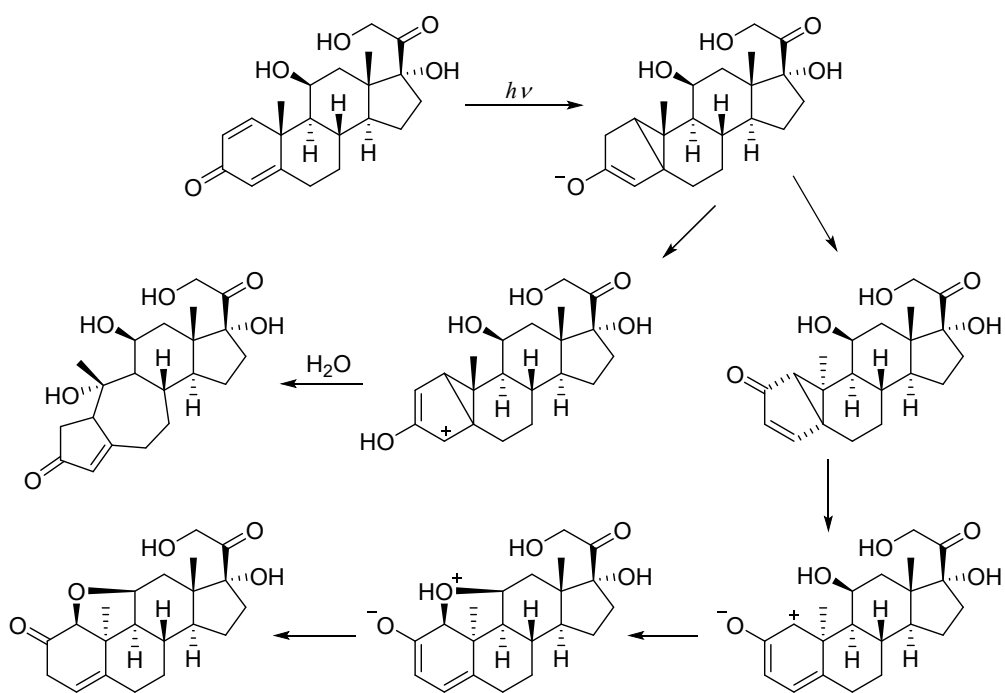


Fig. S3 Mechanism of phototransformation of PNL (Taken from DellaGreca et al.

2004)

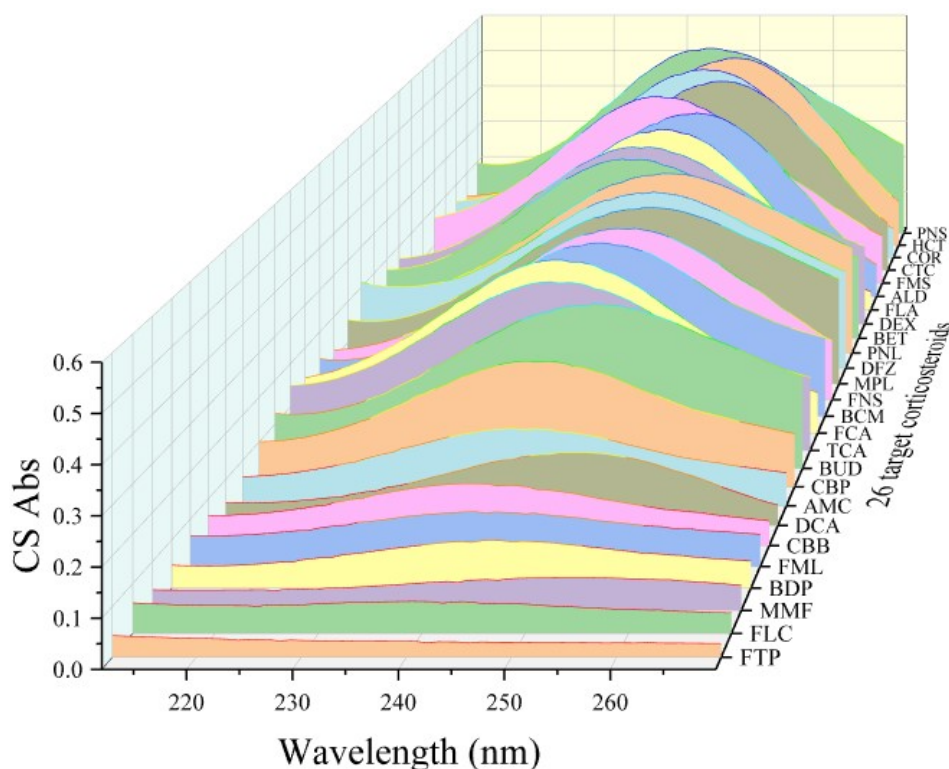


Fig. S4 UV absorption spectra at 210-270 nm of CS contaminated water samples
(initial CS concentration = 10 mg/L).

Table S1 Water quality parameters of tested WWTP secondary effluent

Parameters	pH	Conductivity ($\mu\text{s}/\text{cm}$)	TOC* (mg/L)	UV ₂₅₄ (cm^{-1})	NO ₃ ⁻ (mg/L)	NO ₂ ⁻ (mg/L)
Water quality	7.8	1108	4.4	0.14	5.4	<0.1

*Water was filtered with 0.7 μm glass microfiber filters (GF/F, Whatman) before TOC measurement.

Table S2 Optimized MRM conditions of target corticosteroids and surrogate standards

Compound	Abbr.	Ret Time (min)	Surrogate Assignment	Prec Ion	Prod Ion ^a	CE (V)	ESI Mode
				m/z (Formation)	m/z (RI, %) ^b		
Aldosterone	ALD	5.36	ALD-d ₇	359.2	331.2 (100)	12	Neg
				([M-H] ⁻)	189.1 (35)	16	
Prednisolone	PNL	6.24	HCT-d ₂	419.2	329.3 (100)	20	Neg
				([M+CH ₃ COO] ⁻)	295.1 (17)	36	
Prednisone	PNS	6.37	PNS-d ₈	417.2	327.2 (100)	12	Neg
				([M+CH ₃ COO] ⁻)	357.3 (36)	4	
Hydrocortisone	HCT	6.38	HCT-d ₂	421.2	331.3 (100)	16	Neg
				([M+CH ₃ COO] ⁻)	297.3 (22)	36	
Cortisone	COR	6.70	COR-d ₈	419.2	329.1 (100)	12	Neg
				([M+CH ₃ COO] ⁻)	359.2 (33)	4	
6 α -Methylprednisolone	MPL	8.87	MPL-d ₂	433.2	343.1 (100)	20	Neg
				([M+CH ₃ COO] ⁻)	309.1 (24)	36	
Betamethasone	BET	9.43	BET-d ₅	451.2	361.1 (100)	12	Neg
				([M+CH ₃ COO] ⁻)	307.1 (23)	36	
Dexamethasone	DEX	9.94	DEX-d ₄	451.2	361.1 (100)	16	Neg

Compound	Abbr.	Ret Time (min)	Surrogate Assignment	Prec Ion m/z (Formation)	Prod Ion ^a m/z (RI, %) ^b	CE (V)	ESI Mode
				([M+CH ₃ COO] ⁻)	307.1 (19)	36	
Flumethasone	FMS	10.42	BET-d ₅	469.2	379.1 (100)	12	Neg
				([M+CH ₃ COO] ⁻)	305.0 (17)	40	
Corticosterone	CTC	10.44	MPL-d ₂	347.2	329.2 (100)	12	Pos
				([M+H] ⁺)	120.9 (75)	24	
Beclomethasone	BCM	11.25	MPL-d ₂	467.2	377.1 (100)	8	Neg
				([M+CH ₃ COO] ⁻)	341.0 (50)	20	
Triamcinolone acetonide	TCA	12.52	TCA- ¹³ C ₃	493.2	413.2 (100)	20	Neg
				([M+CH ₃ COO] ⁻)	337.1 (51)	20	
Flunisolide	FNS	13.00	TCA- ¹³ C ₃	493.2	375.1 (100)	12	Neg
				([M+CH ₃ COO] ⁻)	59.2 (44)	32	
Fluocinolone acetonide	FCA	14.95	TCA- ¹³ C ₃	511.2	431.1 (100)	20	Neg
				([M+CH ₃ COO] ⁻)	355.1 (57)	28	
Fluorometholone	FML	15.85	TCA- ¹³ C ₃	435.2	58.9 (100)	16	Neg
				([M+CH ₃ COO] ⁻)	355.1 (55)	12	
Fludrocortisone acetate	FLA	15.95	MPL-d ₂	481.2	421.3 (100)	8	Neg

Compound	Abbr.	Ret Time (min)	Surrogate Assignment	Prec Ion m/z (Formation)	Prod Ion ^a m/z (RI, %) ^b	CE (V)	ESI Mode
				([M+CH ₃ COO] ⁻)	59.0 (28)	28	
Deflazacort	DFZ	16.21	BUD-d ₈	500.2	59.0 (100)	12	Neg
				([M+CH ₃ COO] ⁻)	440.2 (46)	8	
Budesonide	BUD	16.73	BUD-d ₈	489.2	357.2 (100)	12	Neg
				([M+CH ₃ COO] ⁻)	339.2 (26)	16	
Fluocinonide	FLC	17.35	BUD-d ₈	553.2	375.2 (100)	20	Neg
				([M+CH ₃ COO] ⁻)	355.1 (51)	24	
Deoxycorticosterone acetate	DCA	17.89	BUD-d ₈	373.2	97.1 (100)	28	Pos
				([M-H] ⁺)	108.9 (82)	20	
Amcinonide	AMC	18.09	FTP-d ₅	561.2	357.1 (100)	16	Neg
				([M+CH ₃ COO] ⁻)	481.2 (21)	16	
Clobetasol propionate	CBP	18.20	FTP-d ₅	525.2	429.2 (50)	12	Neg
				([M+CH ₃ COO] ⁻)	465.2 (100)	8	
Mometasone furoate	MMF	18.33	FTP-d ₅	519.1	35.2 (100)	8	Neg
				([M+CH ₃ COO] ⁻)	483 (28)	12	
Fluticasone propionate	FTP	18.37	FTP-d ₅	559.2	413.2 (100)	24	Neg

Compound	Abbr.	Ret Time (min)	Surrogate Assignment	Prec Ion m/z (Formation)	Prod Ion ^a m/z (RI, %) ^b	CE (V)	ESI Mode
				([M+CH ₃ COO] ⁻)	59.0 (80)	44	
Beclomethasone dipropionate	BDP	18.91	FTP-d ₅	579.2	34.8 (40)	16	Neg
				([M+CH ₃ COO] ⁻)	519.2 (100)	4	
Clobetasone butyrate	CBB	19.38	FTP-d ₅	479.2	71.1 (85)	24	Pos
				([M+H] ⁺)	42.9 (100)	56	
Aldosterone-d ₇	ALD-d ₇	4.91	–	366.2	338.1	16	Neg
Prednisone-d ₈	PNS-d ₈	6.30	–	425.2	333.2	16	Neg
Hydrocortisone-d ₂	HCT-d ₂	6.38	–	423.2	333	16	Neg
Cortisone-d ₈	COR-d ₈	6.62	–	427.2	335.2	8	Neg
Methylprednisolone-d ₂	MPL-d ₂	8.83	–	435.2	343.2	12	Neg
Betamethasone-d ₅	BET-d ₅	9.25	–	456.2	364.1	16	Neg
Dexamethasone-d ₄	DEX-d ₄	9.82	–	455.2	363.1	16	Neg
Triamcinolone acetonide- ¹³ C ₃	TCA- ¹³ C ₃	12.52	–	496.2	416.1	16	Neg
Budesonide-d ₈	BUD-d ₈	16.70	–	497.3	357.1	12	Neg
Fluticasone propionate-d ₅	FTP-d ₅	18.35	–	564.2	417.1	16	Neg

Table S3 IDLs and MDLs of target corticosteroids in direct injection LC-MS/MS analysis

Compounds	Surrogate Assignment	IDLs (pg/L)	MDLs (ng/L)
ALD	ALD-d ₇	0.5	5
AMC	FTD-d ₅	0.2	1
BCM	TCA- ¹³ C ₃	0.5	5
BDP	FTD-d ₅	1.0	5
BET	BET-d ₅	0.05	1
BUD	BUD-d ₈	0.2	1
CBP	FTD-d ₅	1.0	1
CBB	FTD-d ₅	0.2	2
CTC	DEX-d ₄	0.2	5
COR	COR-d ₈	1.0	2
DFZ	TCA- ¹³ C ₃	0.5	5
DCA	FTD-d ₅	0.1	2
DEX	DEX-d ₄	0.5	1
FLA	TCA- ¹³ C ₃	0.2	5
FMS	TCA- ¹³ C ₃	2.0	1
FNS	TCA- ¹³ C ₃	0.2	2
FCA	TCA- ¹³ C ₃	1.0	5
FLC	BUD-d ₈	0.2	1
FML	TCA- ¹³ C ₃	2.5	5
FTD	FTD-d ₅	0.2	1
HCT	HCT-d ₂	0.05	1
MPL	MPL-d ₂	2.0	1
MMF	FTD-d ₅	0.05	10
PNL	PNS-d ₈	0.1	1
PNS	PNS-d ₈	0.1	2
TCA	TCA- ¹³ C ₃	0.5	2

Table S4 The k_{obs} and corresponding R^2 for CS degradation during UV/ Cl_2 treatmentunder various doses of Cl_2

CS compound	$\text{Cl}_2 = 0 \text{ mg/L}$		$\text{Cl}_2 = 2.5 \text{ mg/L}$		$\text{Cl}_2 = 5 \text{ mg/L}$	
	k_{obs}	R^2	k_{obs}	R^2	k_{obs}	R^2
ALD	0.0012	0.9919	0.0016	0.9908	0.0018	0.991
AMC	0.0190	0.8742	0.0316	1	0.0313	1
BCM	0.0017	0.9884	0.0013	0.8714	0.0016	0.9679
BDP	0.0011	0.9566	0.0013	0.9001	0.0016	0.9679
BET	0.0267	1	0.0269	1	0.0313	1
BUD	-	-	-	-	-	-
CBP	0.0254	1	0.0243	1	0.0256	1
CBB	0.0193	1	0.0205	1	0.0268	1
CTC	0.0024	0.9849	0.0030	0.9795	0.0034	0.9944
COR	0.0007	0.9598	0.0010	0.9944	0.0012	0.9903
DFZ	-	-	-	-	-	-
DCA	0.0021	0.9672	0.0023	0.9914	0.0023	0.9951
DEX	0.0238	0.987	0.0309	1	0.0302	1
FLA	0.0012	0.9782	0.0010	0.9511	0.0012	0.985
FMS	0.0153	0.9866	0.0159	0.9876	0.0169	0.995
FNS	-	-	-	-	-	-
FCA	0.0158	0.991	0.0172	0.9968	0.0175	0.9974
FLC	0.0156	0.9859	0.0164	0.9914	0.0163	0.9902
FML	0.0174	0.9967	0.0192	1	0.0198	1
FTP	0.0150	0.9746	0.0169	0.9902	0.0174	0.994
HCT	0.0027	0.9927	0.0030	0.9963	0.0032	0.9975
MPL	-	-	-	-	-	-
MMF	0.0092	0.9686	0.0092	0.8902	0.0099	0.8984
PNL	-	-	-	-	-	-
PNS	-	-	-	-	-	-
TCA	0.0250	1	0.0265	1	0.0266	1

Table S5 The k_{obs} and corresponding R^2 for CS degradation during UV/ NH_2Cl treatment under various doses of NH_2Cl

CS compound	$\text{NH}_2\text{Cl} = 0 \text{ mg/L}$		$\text{NH}_2\text{Cl} = 2.5 \text{ mg/L}$		$\text{NH}_2\text{Cl} = 5 \text{ mg/L}$	
	k	R^2	k	R^2	k	R^2
ALD	0.0012	0.9919	0.0017	0.9969	0.0019	0.9979
AMC	0.0190	0.8742	0.0283	0.9993	0.0292	0.9989
BCM	0.0017	0.9884	0.0016	0.9959	0.0018	0.9979
BDP	0.0011	0.9566	0.0013	0.9703	0.0015	0.9216
BET	0.0267	1	0.0266	0.9998	0.0311	0.9997
BUD	-	-	-	-	-	-
CBP	0.0254	1	0.0254	1	0.027	0.9992
CBB	0.0193	1	0.022	0.9995	0.0299	0.9902
CTC	0.0024	0.9849	0.0033	0.9912	0.0038	0.9911
COR	0.0007	0.9598	0.0009	0.9932	0.001	0.993
DFZ	-	-	-	-	-	-
DCA	0.0021	0.9672	0.0021	0.9959	0.0025	0.9929
DEX	0.0238	0.987	0.028	0.9957	0.028	0.9841
FLA	0.0012	0.9782	0.0013	0.9754	0.0016	0.9729
FMS	0.0153	0.9866	0.0147	0.9978	0.0161	0.9978
FNS	-	-	-	-	-	-
FCA	0.0158	0.991	0.0167	0.9994	0.017	0.9978
FLC	0.0156	0.9859	0.0161	0.9993	0.0173	0.9988
FML	0.0174	0.9967	0.0174	0.9955	0.0215	0.9851
FTP	0.0150	0.9746	0.0161	0.9944	0.0167	0.9959
HCT	0.0027	0.9927	0.0032	0.9979	0.0037	0.9973
MPL	-	-	-	-	-	-
MMF	0.0092	0.9686	0.0115	0.9997	0.013	0.9984
PNL	-	-	-	-	-	-
PNS	-	-	-	-	-	-
TCA	0.0250	1	0.0267	0.9993	0.0281	0.9981

Table S6 The k_{obs} and corresponding R^2 for CS degradation during UV/H₂O₂ treatment under various doses of H₂O₂

CS compound	H ₂ O ₂ = 0 mg/L		H ₂ O ₂ = 3 mg/L		H ₂ O ₂ = 7 mg/L	
	k	R ²	k	R ²	k	R ²
ALD	0.0012	0.9919	0.0016	0.9905	0.0019	0.9968
AMC	0.0190	0.8742	0.0306	0.9988	0.0334	0.9966
BCM	0.0017	0.9884	0.0022	0.9959	0.0025	0.9847
BDP	0.0011	0.9566	0.0018	0.9545	0.0021	0.9214
BET	0.0267	1	0.0260	1	0.0269	0.9991
BUD	-	-	-	-	-	-
CBP	0.0254	1	0.0304	0.9986	0.0321	0.9977
CBB	0.0193	1	0.0191	0.9998	0.0208	0.9887
CTC	0.0024	0.9849	0.0034	0.9917	0.0041	0.9893
COR	0.0007	0.9598	0.0009	0.9904	0.0012	0.9866
DFZ	-	-	-	-	-	-
DCA	0.0021	0.9672	0.0026	0.9922	0.0028	0.9740
DEX	0.0238	0.987	0.0306	0.9975	0.0344	0.9977
FLA	0.0012	0.9782	0.0017	0.9460	0.0020	0.9267
FMS	0.0153	0.9866	0.0179	0.9953	0.0188	0.9947
FNS	-	-	-	-	-	-
FCA	0.0158	0.991	0.0173	0.9979	0.0180	0.9969
FLC	0.0156	0.9859	0.0170	0.9914	0.0185	0.9904
FML	0.0174	0.9967	0.0221	0.9999	0.0238	0.9994
FTP	0.0150	0.9746	0.0176	0.9960	0.0186	0.9948
HCT	0.0027	0.9927	0.0033	0.9972	0.0034	0.9941
MPL	-	-	-	-	-	-
MMF	0.0092	0.9686	0.010	0.9726	0.0119	0.9521
PNL	-	-	-	-	-	-
PNS	-	-	-	-	-	-
TCA	0.0250	1	0.0291	0.9998	0.0315	0.9994