Supplementary information

for

Heterogeneous degradation of carbamazepine by Prussian blue analogues in the interlayer of layered double hydroxides: performance, mechanism and toxicity evaluation

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Text S1. Materials and Reagents

Carbamazepine (CBZ, ≥98.0%), Oxcarbazepine (OXC, ≥98.0%), Atrazine (ATZ, ≥99.0%), Bisphenol A (BPA, ≥99.0%), and tetracycline (TC, ≥98.0%), were supplied by Aladdin Industrial Co. (China). 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), methanol (MeOH, HPLC grade, ≥99.9%) and acetonitrile (HPLC grade, ≥99.9%) were purchased from Sigma–Aldrich Chemical Co. Ltd. (USA). Aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$), magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$), cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$), trisodium citrate dihydrate ($Na_3C_6H_5O_7 \cdot 5H_2O$), potassium ferricyanide ($K_3[Fe(CN)_6$), PMS ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$), and tertiary butanol (TBA, ≥98.0%) were obtained from Sinopharm Chemical Reagent Co. (China). All the chemicals and reagents were of at least analytical grade and used as received.

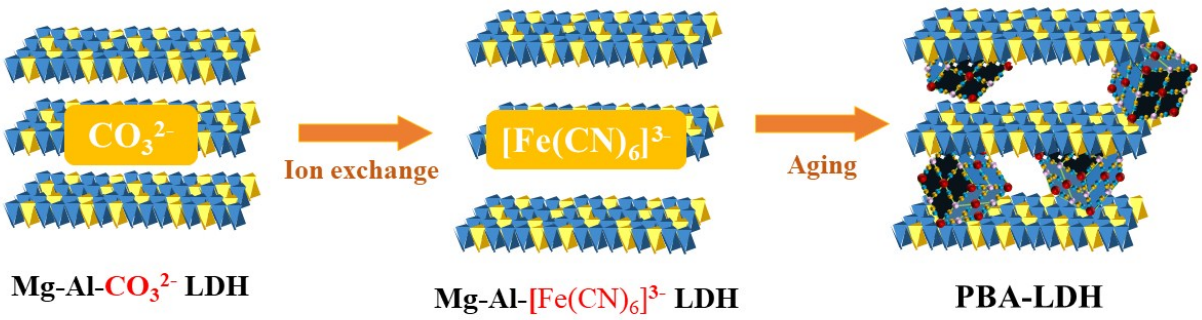


Fig. S1. Schematic Illustration for synthesis of PBA-LDH.

Text S2. The detailed test conditions.

1. High performance liquid chromatography-electrospray ionization-tandem mass spectrometry (HPLC-ESI-MS/MS)

The flow rate was set at 0.24 mL/min, being eluent A deionized water (containing 0.1% formic acid) and eluent B acetonitrile. The initial conditions of the elution gradient programmed were 90%A:10%B. From 5 to 30 min the eluent B was increased to 70%, held for 10 min and returned to initial conditions in 10 min. The injection volume of sample was set at 10 μL.

Table S1. Chemical Formula and Detailed Information for HPLC Analyses.

Compounds	Formula	HPLC analytical condition				
		Mobile phase				Wave-length (nm)
		ultrapure water	ultrapure water with 0.1% formic acid	Methanol	Acetonitrile	
Carbamazepine	$C_{15}H_{12}N_2O$	40			60	286
Oxcarbazepine	$C_{15}H_{12}N_2O_2$	45		55		254
Atrazine	$C_8H_{14}ClN_5$	30		60	10	230
Bisphenol A	$C_{15}H_{16}O_2$	60			40	280
Tetracycline	$C_{22}H_{24}N_2O_8$		80		20	355

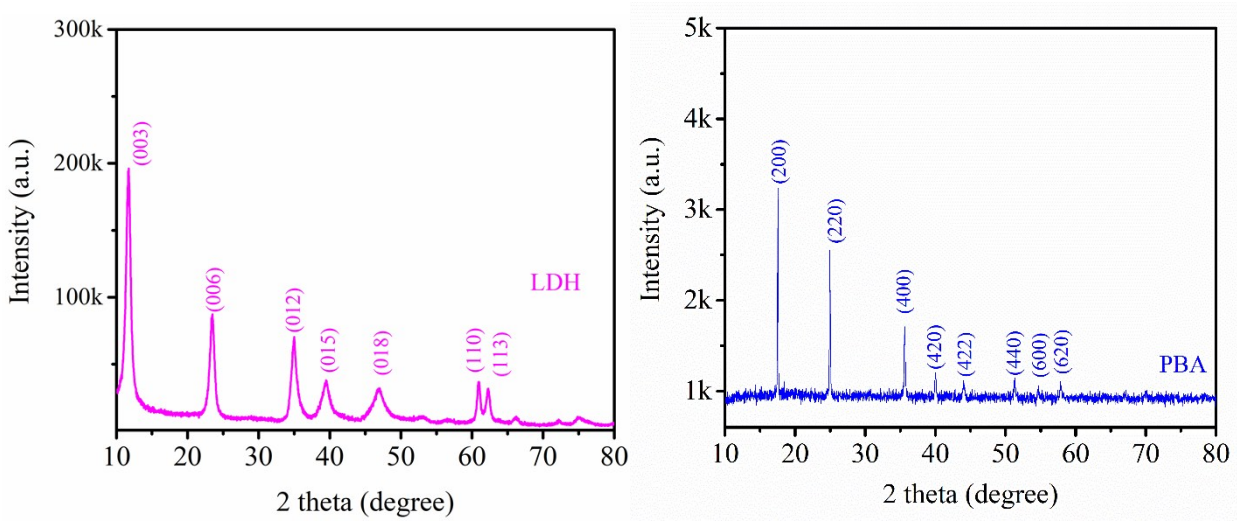


Fig. S2. XRD diffraction patterns of LDH and PBA.

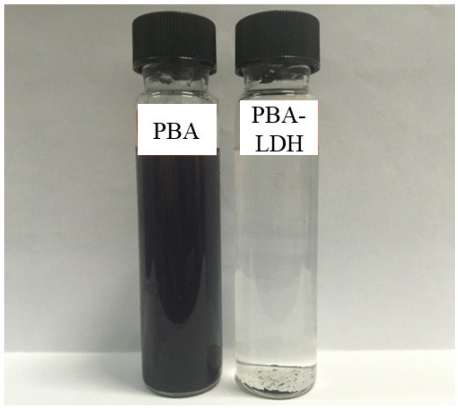


Fig. S3. Dispersion of PBA and PBA-LDH in CBZ solution.

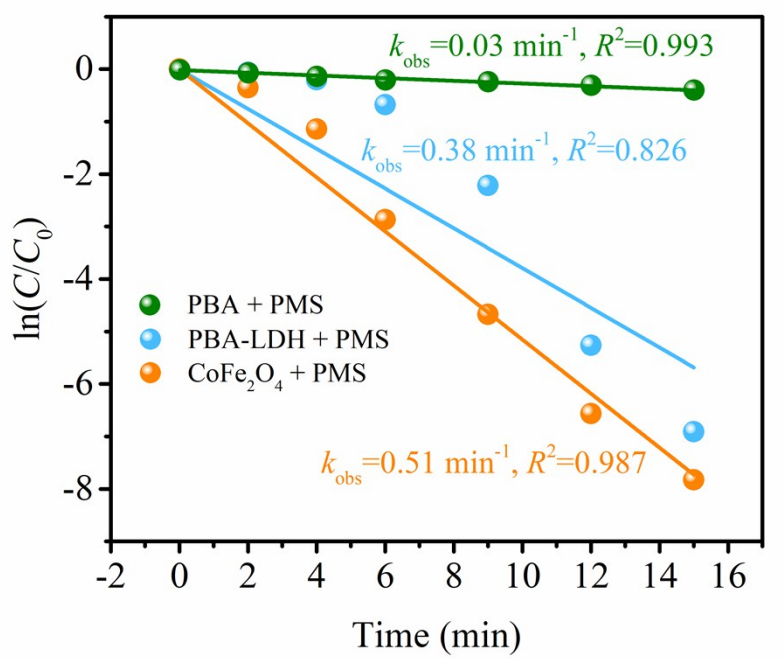


Fig. S4. Plots of ln(C/C_0) *versus* reaction time.

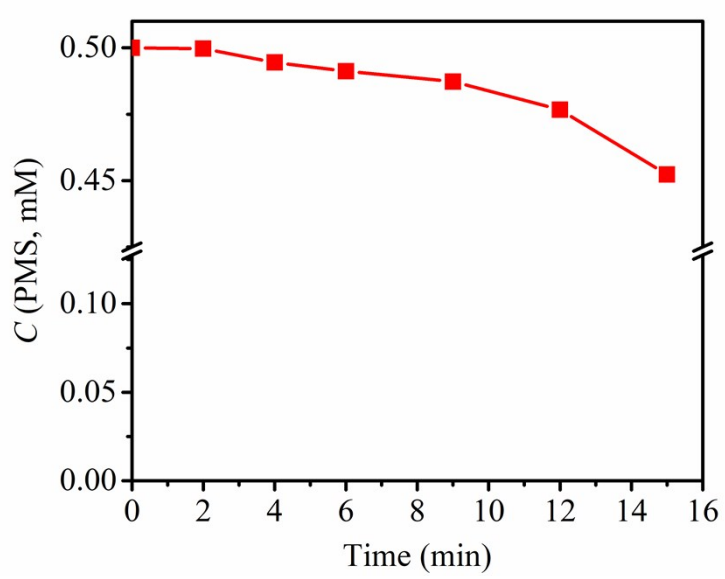


Fig. S5. PMS concentration variation in PBA-LDH activated PMS system.

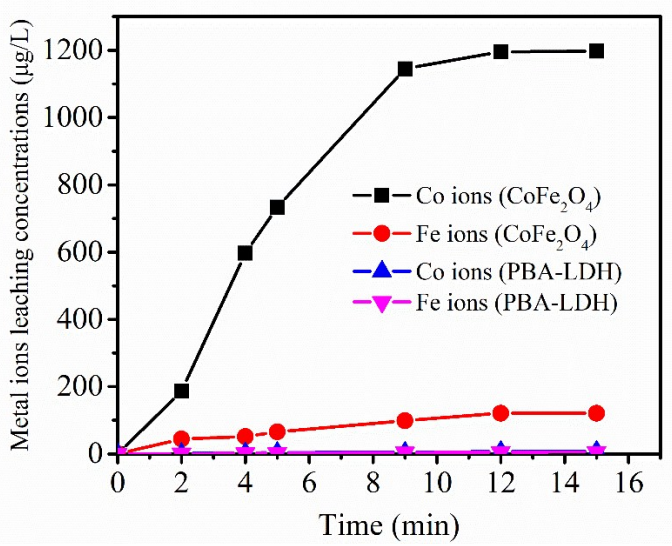


Fig. S6. Metal ions leaching concentrations in $CoFe_2O_4$ and PBA-LDH activated PMS systems.

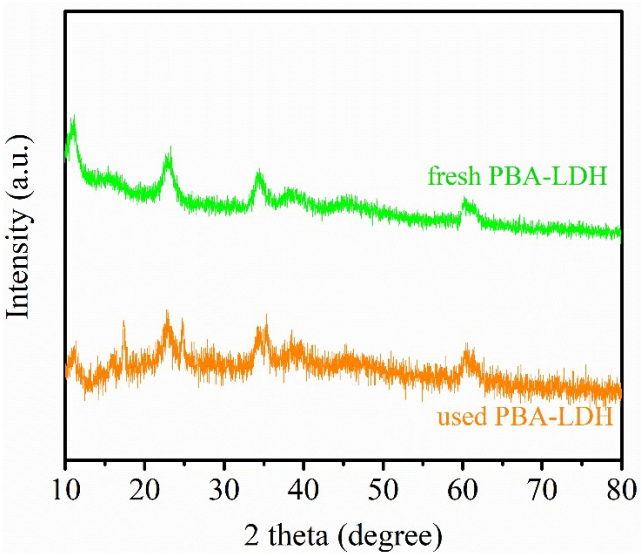


Fig. S7. XRD diffraction patterns of PBA-LDH before and after reaction.

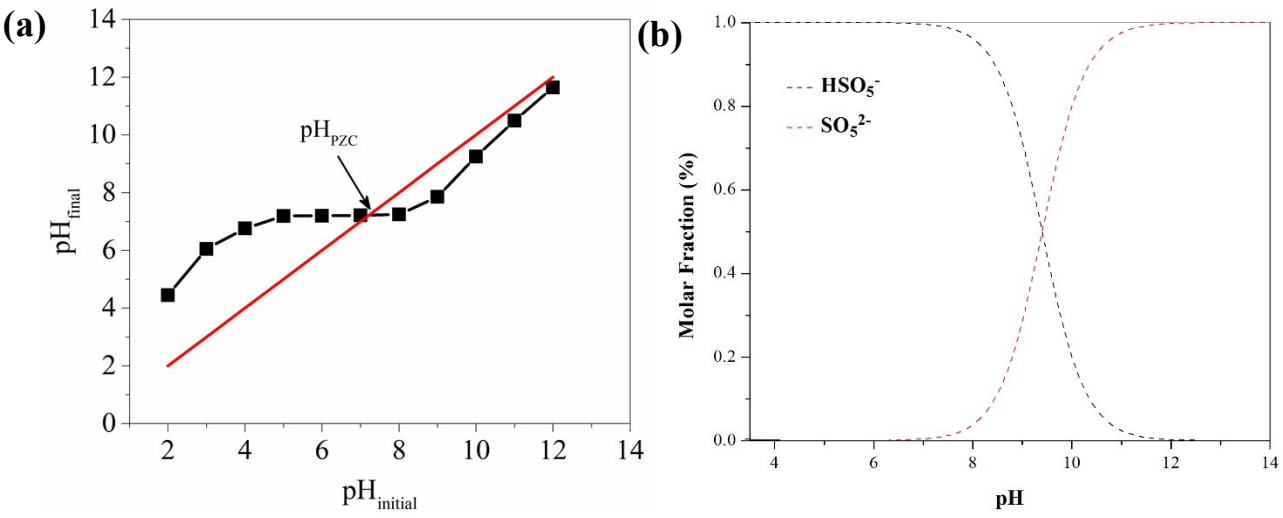


Fig. S8. (a) illustration of pH_{PZC} of PBA-LDH, (b) Species distribution of PMS at different pH values.

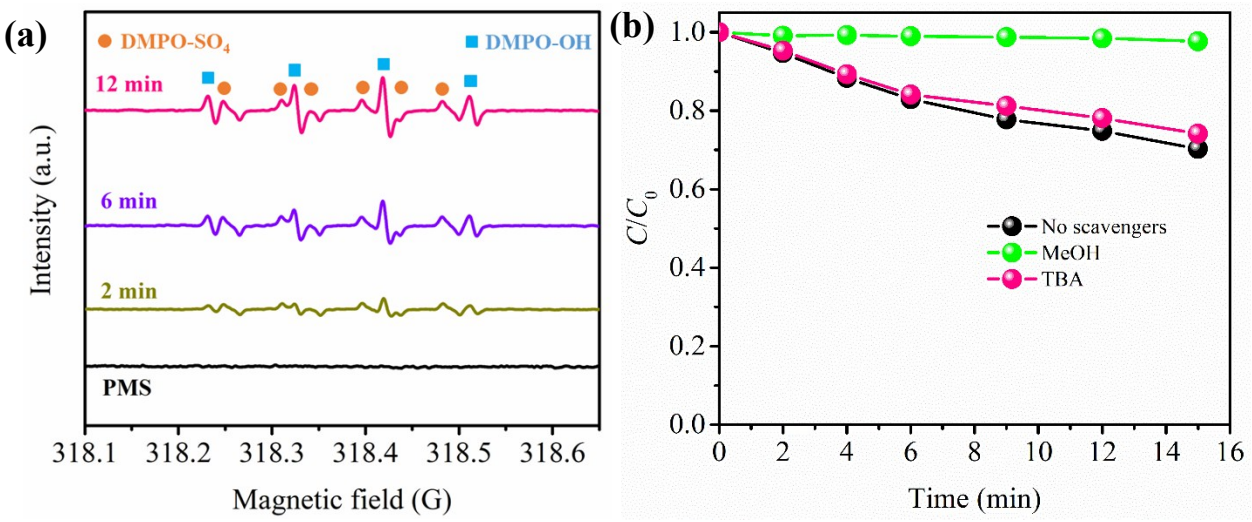


Fig. S9. (a) ESR spectra using DMPO as a spin-trapping agent at different time intervals; (b) Effect of MeOH and TBA on CBZ degradation (PBA dose 0.2 g/L, PMS dose 0.5 mM, CBZ concentration 20 mg/L, DMPO dose 100 mM, pH 7.0).

Table S2. The chemical composition of PBA-LDH before and after reaction (%).

	Co	Fe	Mg	Al	C	N	O
Before reaction	0.94	0.67	15.39	6.22	23.45	5.58	47.75
After reaction	0.95	0.68	14.82	7.35	22.06	5.52	48.62

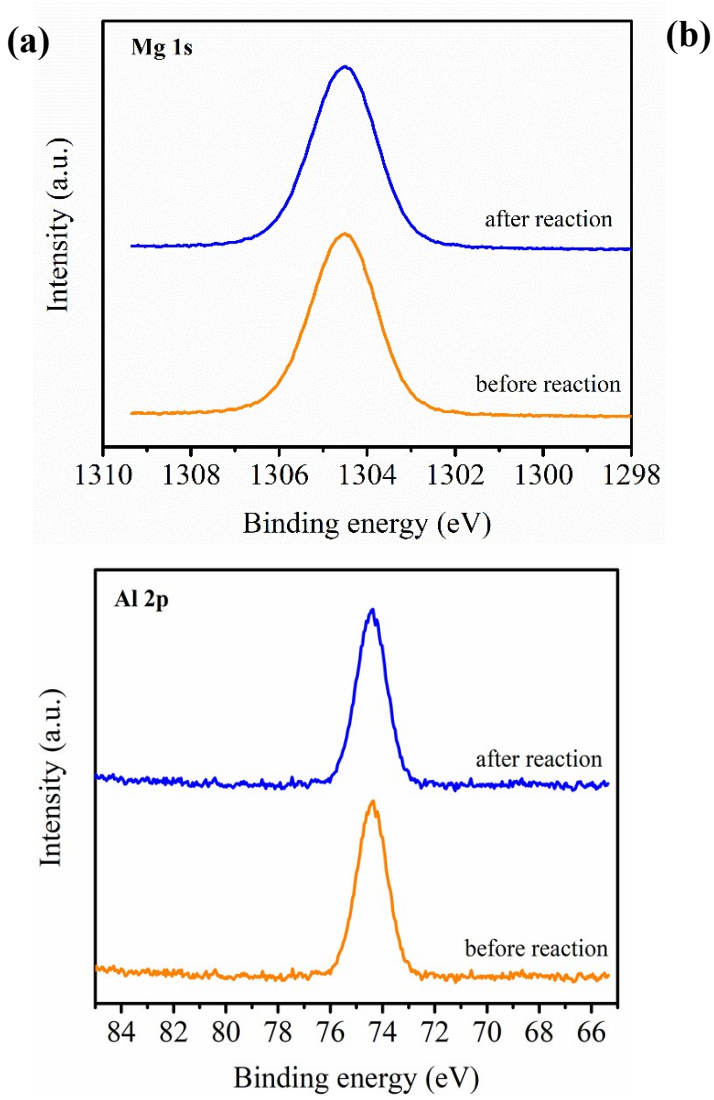
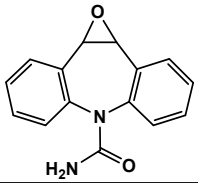
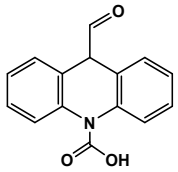
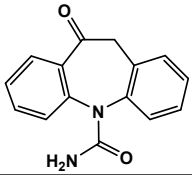
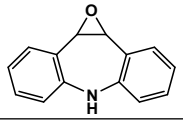
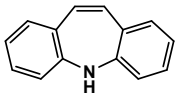
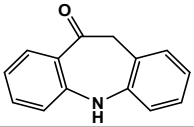
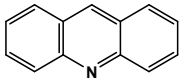
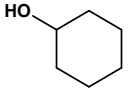
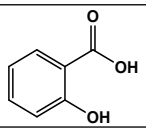


Fig. S10. High-resolution XPS spectra of (a) Mg 1s and (b) Al 2p before and after reaction.

Table S3. Peaks information of Co $2p_{3/2}$, Co $2p_{1/2}$, Fe $2p_{3/2}$ and Fe $2p_{1/2}$.

Co 2p		Binding energy (eV)	Relative ratio (%)	
			Before reaction	After reaction
Co $2p_{3/2}$	Co^{3+}	781.6	58%	58%
	Co^{2+}	783.5	42%	42%
Co $2p_{1/2}$	Co^{3+}	797.5	57%	50%
	Co^{2+}	798.5	43%	50%
Fe $2p_{3/2}$	Fe^{2+}	708.6	89%	80%
	Fe^{3+}	715.3	11%	20%
Fe $2p_{1/2}$	Fe^{2+}	721.5	92%	79%
	Fe^{3+}	723.9	8%	21%

Table S4. Oxidative intermediates of CBZ degradation by PBA-LDH activated PMS system.

Product ID and structural formula	Retention time (min)	Proposed structure	Measured accurate m/z
A $C_{15}H_{12}N_2O_2$	3.74		252.9000
B $C_{15}H_{12}N_2O_2$	3.74		252.9000
C $C_{15}H_{10}N_2O_2$	7.54		251.1000
D $C_{14}H_{11}NO$	7.54		210.2000
E $C_{14}H_{11}N$	3.74		193.1000
F $C_{14}H_{11}NO$	7.54		210.2000
G $C_{13}H_9N$	7.54		180.1000
H $C_6H_{12}O$	6.96		99.0000
I $C_7H_6O_3$	6.96		137.0000

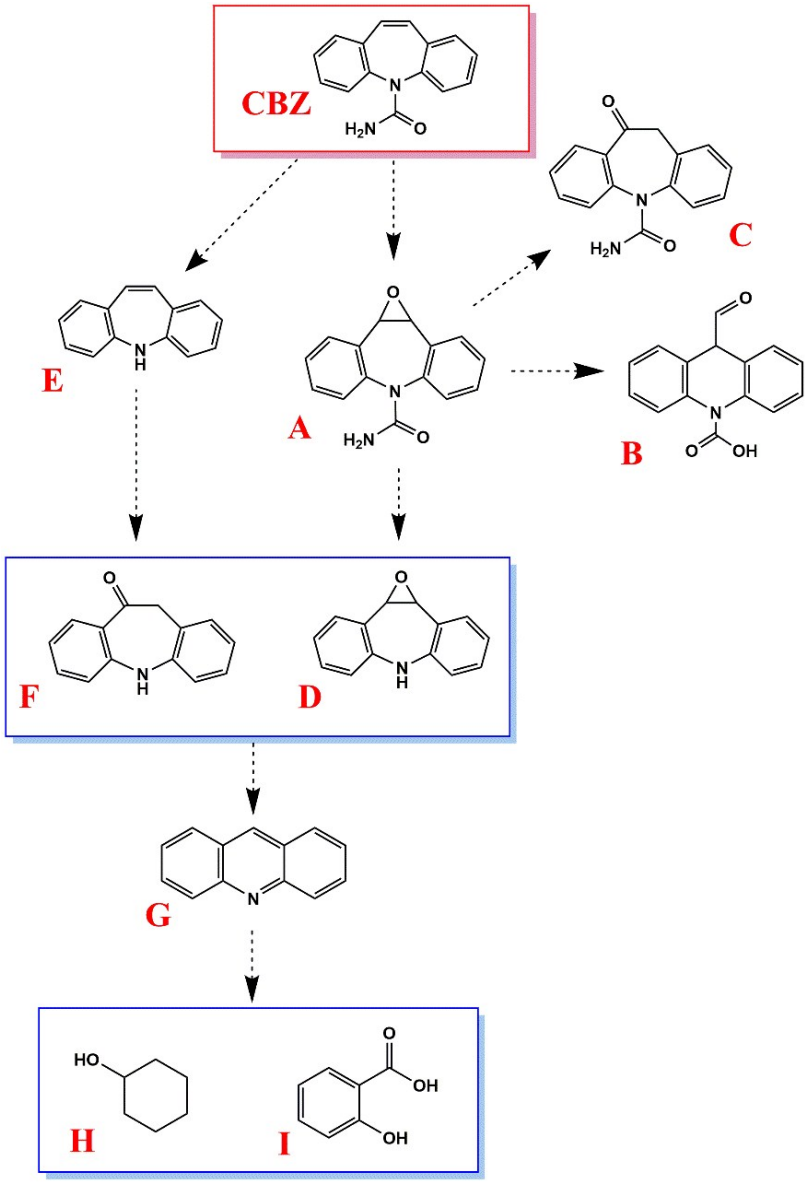


Fig. S11. Proposed pathways for CBZ degradation in PBA-LDH activated PMS system.

Table S5. Toxicity classification according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) (**United Nations, 2011**)

Toxicity range (mg/L)	Class
LC50/EC50/ChC ≤ 1	Very toxic
1 < LC50/EC50/ChC ≤ 10	Toxic
10 < LC50/EC50/ChC ≤ 100	Harmful
LC50/EC50/ChC > 100	Not harmful

Table S6. Basic characteristics of lake water, river water and well water.

Sample	pH	TOC (mg/L)	Ca (mmol/L)	K (mmol/L)	Mg (mmol/L)	Na (mmol/L)
Lake water	7.42	3.36	0.42	0.11	0.18	0.21
River water	7.83	4.27	0.91	0.07	0.34	0.35
Well water	6.67	0.63	0.05	0.02	0.03	0.01

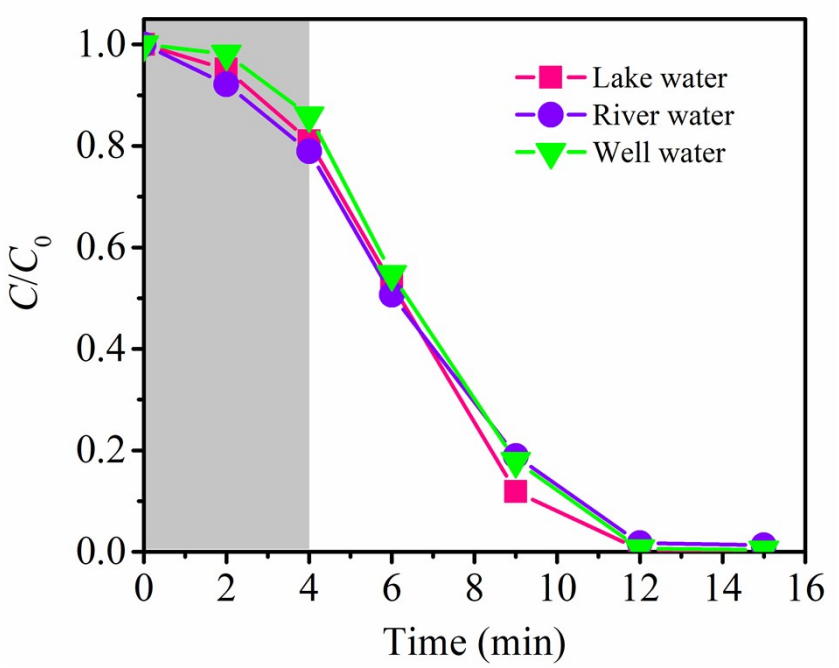


Fig. S12. PBA-LDH activated PMS system in treating lake water, river water and well water.