Supporting Information

Text S1. Sodium chloride (NaCl), calcium chloride ($CaCl_2$), sodium hydroxide (NaOH), sodium diphosphate ($Na_4P_2O_7$), hydrochloride acid (HCl, 36~38 %), and hydrofluoric acid (HF, 40%) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Benzo[a]Pyrene (B[a]P, 98%), anthracene (ANT, 99%), phenanthrene (PHE, 98%), naphthalene (NAP, 99%), 5,5-Dimethyl-1-pyrrolidine N-oxide (DMPO, 97%), coumarin (98%), and *p*-benzoquinone (*p*-BQ, 99%) were purchased from Sigma-Aldrich (Shanghai, China). Dichloromethane, acetone, ethanol, and methanol are HPLC-grade, and these solvents were acquired from China National Medicines Corporation Ltd (Beijing, China). Peat soil, obtained from a peat moss in Jilin Changbai Mountain (Jilin Province, China), was air-dried at room temperature and sieved though a 48-mesh grid. The pH of the soil was ~ 6.6, determined in 0.01 M $CaCl_2$ solution at solid to solution ratio of 1:1.

Text S2. 20.0 g peat soil was added into a polyethylene bottles containing 200 mL 0.1 M $Na_2P_2O_7$, and the space was filled with N_2. After mixing, the bottle was shaken at 120 rpm for overnight. The treated sample was centrifuged at 6230 × g for 10 min, and then the precipitate was mixed with 200 L of 0.1 mol L^{-1} NaOH solutions. After shaken for 4 h and settled for 12 h, the supernatant was separated from solid residue by centrifuging at 6230 × g for 10 min and subsequently discarded. Sodium pyrophosphate/sodium hydroxide ($Na_2P_2O_7$/NaOH) extracting approaches, stated above, were repeated for six times. The residue was further suspended in 200 mL mixture solution of 0.10 M HCl and 0.30 M HF (v:v = 1:1) and shaken overnight to remove inorganic components. The dashed sample was washed with de-ionized water for several times

until the solution exhibited negative Cl^- ion test by adding silver nitrate. The obtained sample was freeze-dried and stored in a desiccator under air-flow condition for more than three months.

Text S3. The H_2O_2-treated samples were centrifuged for 10 min at 6230 × *g*, and then the supernatant was discharged. The precipitates were collected and added to approximately 20 mL of de-ionized water. The mixture was shaken at 150 rpm for 2 h and centrifuged for 6 min at 6230 × *g* to remove supernatant, and the residue was collected. The rinsing procedure was repeated for three times, and the final products were freeze-dried and stored in a desiccator. The oxidized HM samples were assigned as H_2O_2-HM. The reduced samples of HM were obtained by mixing 5 g of HM with 100 mL of L-ascorbic acid (Vitamin C, VC) at concentrations from 0.01 M to 0.10 M in *N,N*-dimethylacetamide, and stirred for 24 h under N_2 condition at room temperature. The reduced samples were centrifuged for 6 min at 6230 × *g* to remove supernatant, and the precipitate was washed for two times using N_2–purged Milli-Q deionized water to ensure the residual solute in the supernatant was undetectable. The final products were freeze-dried and stored in an anaerobic chamber before the characterization and following experiments.

Text S4. The spin densities of HM samples were collected as a function of aging time. The measurements of free radicals in HM samples were carried out by placing 0.2 g of solid samples in a high purity quartz tube and detected by the EPR technique at room temperature. EPR determination was conducted using a Bruker EMXmicro spectrometer (Karlsruhe, Germany). Instrument and operating parameters: X-band microwave frequency of 9.7 GHz, microwave power of 2.02 mW, and modulation amplitude of 4.00 G; center field, 3470 G; modulation amplitude, 4.0 G; sweep width, 200 G; receiver gain, 3.54×10^4; time constant, 41.0 ms; and sweep time, 167.7 s. Radical concentrations were calculated by comparing the signal peak area,

derived from $(\Delta H_{p\text{-}p})^2$ multiplied by the relative intensity, to a 2,2-diphenyl-1-picrylhydrazyl (DPPH) standard.

Text S5. Briefly, 1 g of the above prepared HM sample was mixed with 2 mL of individual PAH solution at a concentration 0.05 g mL^{-1} in acetone. This mixture was rapidly stirred for 5 min, and then stored in the dark until acetone was completely evaporated. The final concentration of PAHs in HM samples was 0.1 mg g^{-1}. Transformation of PAHs was monitored by aging the freshly prepared PAH-contaminated HM samples under dark condition. At pre-selected interval, ~ 0.50 g of reacted HM sample was sacrificed from Petri dish and mixed with extraction solvents (5.0 mL of acetone and 5.0 mL of dichloromethane) in an ultrasonic bath for 10.0 min to extract the residues of PAHs and their products.

Text S6. To quantify the concentration of ROS on modified HM, the spin-trap reagent such as DMPO in aqueous solvent was applied to capture the potentially produced ROS and subsequently detected by EPR. Specifically, 0.15 g of the solid samples was individually mixed with 0.45 mL of 150 mM freshly prepared DMPO in dimethyl sulfoxide or water, in order to trap superoxide radicals and hydroxyl radicals, respectively. The suspension was shaken on a vortex mixer (MX-S, DLAB, China) for 30 seconds in touch mode and then filtered using a 0.22 μm membrane syringe filter. After suspension, 20 μL of the extract was immediately (~ 60 seconds) transferred to an EPR capillary tube and sealed at one end by vacuum grease. The capillary was put into an EPR tube and fastened in the EPR resonator. The obtained EPR signal was fitted by SpinFit module of Xenon program in Bruker EMXmicro spectrometer. The exact spin densities were determined by comparison with the DPPH standard.

Table S1. The extraction efficiencies of PAHs in the newly prepared PAHs-spiked HM samples in the present study.

Type of HM	NAP[a]	PHE[a]	ANT[a]	B[a]P[a]
Original HM	95.9%	97.6%	97.0%	96.3%
0.02 M H_2O_2-HM	98.3%	98.0%	99.2%	97.2%
0.04 M H_2O_2-HM	96.7%	98.4%	97.4%	97.3%
0.08 M H_2O_2-HM	97.1%	96.9%	98.3%	99.0%
0.10 M H_2O_2-HM	97.3%	97.2%	97.6%	98.1%
0.02 M VC-HM	97.2%	96.2%	97.1%	96.7%
0.04 M VC-HM	96.4%	96.3%	95.3%	97.6%
0.08 M VC-HM	95.5%	95.5%	95.9%	97.2%
0.10 M VC-HM	96.1%	95.0%	96.5%	95.7%

[a] Naphthalene (NAP), anthracene (ANT), benzo[a]anthracene (B[a]A), pyrene (PYR), and benzo[a]pyrene (B[a]P).

Table S2. Elemental compositions, atomic ratios, and ash contents of original and treated humins.

Samples	Bulk elemental and ash composition (wt. %)					Atomic ratio		Surface C composition and functionalities (%)			
	C	H	N	O	Ash	C/H	O/C	Total	C—C	C—O	C=O
Humin	50.04	6.52	7.33	32.47	0.91	7.67	0.65	62.97	36.41	17.98	7.56
0.01 M H_2O_2-HM	53.02	9.67	2.61	29.07	0.89	7.69	0.65	63.02	36.97	18.15	7.90
0.04 M H_2O_2-HM	46.90	5.97	2.67	33.84	0.86	7.86	0.72	63.23	36.47	18.39	8.37
0.10 M H_2O_2-HM	43.85	5.26	2.87	34.25	0.77	8.34	0.78	66.62	36.38	20.98	9.26
0.01 M VC-HM	50.12	6.89	2.62	31.98	0.88	7.27	0.64	62.59	36.72	18.43	7.44
0.04 M VC-HM	50.03	7.85	2.62	31.46	0.90	6.37	0.63	62.94	36.76	19.97	6.21
0.10 M VC-HM	53.34	8.75	2.63	29.88	0.87	6.09	0.56	64.33	37.00	22.19	5.14

Table S3. Quantification of various ROS associated with original or treated HM samples.

Samples	Spin density (S) of HM samples, 10^{17} spin/g	Differences of S between original and treated HM, 10^{17} spin/g	Amount of various DMPO-ROS (spin/g)		
			Hydroxyl radical	Singlet oxygen	Superoxide radical
Original HM	5.57	0	—	—	—
0.01 H_2O_2-HM	6.53	0.95	0.36×10^{16}	0.21×10^{16}	0.14×10^{16}
0.02 H_2O_2-HM	8.83	3.25	1.18×10^{16}	0.74×10^{16}	0.22×10^{16}
0.04 H_2O_2-HM	10.14	4.57	1.48×10^{16}	0.95×10^{16}	0.24×10^{16}
0.08 H_2O_2-HM	10.94	5.37	1.51×10^{16}	1.37×10^{16}	0.35×10^{16}
0.01 VC-HM	7.96	2.36	0.23×10^{16}	0.67×10^{16}	0.31×10^{16}
0.02 VC-HM	10.84	5.23	1.50×10^{16}	1.19×10^{16}	0.34×10^{16}
0.04 VC-HM	14.29	8.69	1.98×10^{16}	1.64×10^{16}	0.50×10^{16}
0.08 VC-HM	18.54	12.94	2.32×10^{16}	1.71×10^{16}	0.56×10^{16}

Table S4. Transformation rate constants (K_{obs} , d^{-1}) of PAHs on the original and modified HM samples.

Samples	Type of PAHs	Scavenger type	Rate constants K_{obs} (d^{-1})	Normalized K_{obs} (d^{-1} g^{-1} C)
Original HM	ANT	None	0.0049	0.0097
0.01 VC-HM	B[a]P	None	0.0187	0.0373
0.01 VC-HM	ANT	None	0.0162	0.0323
0.01 VC-HM	PHE	None	0.0150	0.0299
0.01 VC-HM	NAP	None	0.0127	0.0253
0.02 VC-HM	ANT	None	0.0367	0.0732
0.04 VC-HM	ANT	None	0.0569	0.1137
0.08 VC-HM	ANT	None	0.0921	0.1748
0.10 VC-HM	ANT	None	0.0933	0.1749
0.02 H_2O_2-HM	ANT	None	0.0299	0.0616
0.04 H_2O_2-HM	ANT	None	0.0363	0.0774
0.08 H_2O_2-HM	ANT	None	0.0461	0.1023
0.10 H_2O_2-HM	ANT	None	0.0463	0.1056
0.10 VC-HM	ANT	Coumarin	0.0142	0.0493
0.10 VC-HM	ANT	*p*-BQ	0.0263	0.0266

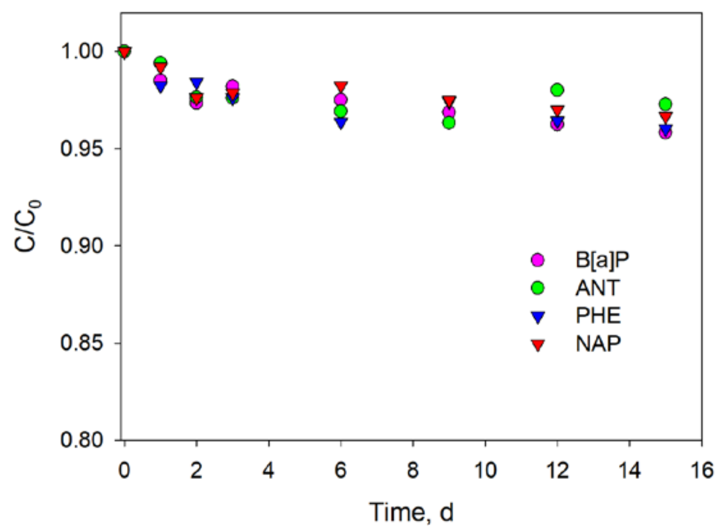

Fig.S1 Evolution of PAHs, including benzo[a]pyrene (B[a]P), anthracene (ANT), phenanthrene (PHE), and naphthalene (NAP), as a function of reaction time during the transformation process by 0.10 M L-ascorbic acid-HM sample under anoxic condition.

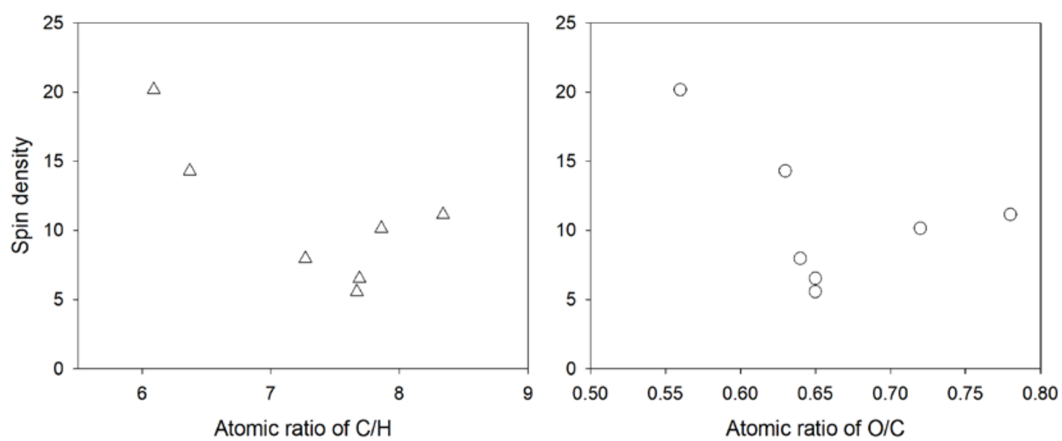

Fig. S2 Correlation between spin densities and atomic ratio of C/H (a) or O/C (b) in humin samples.

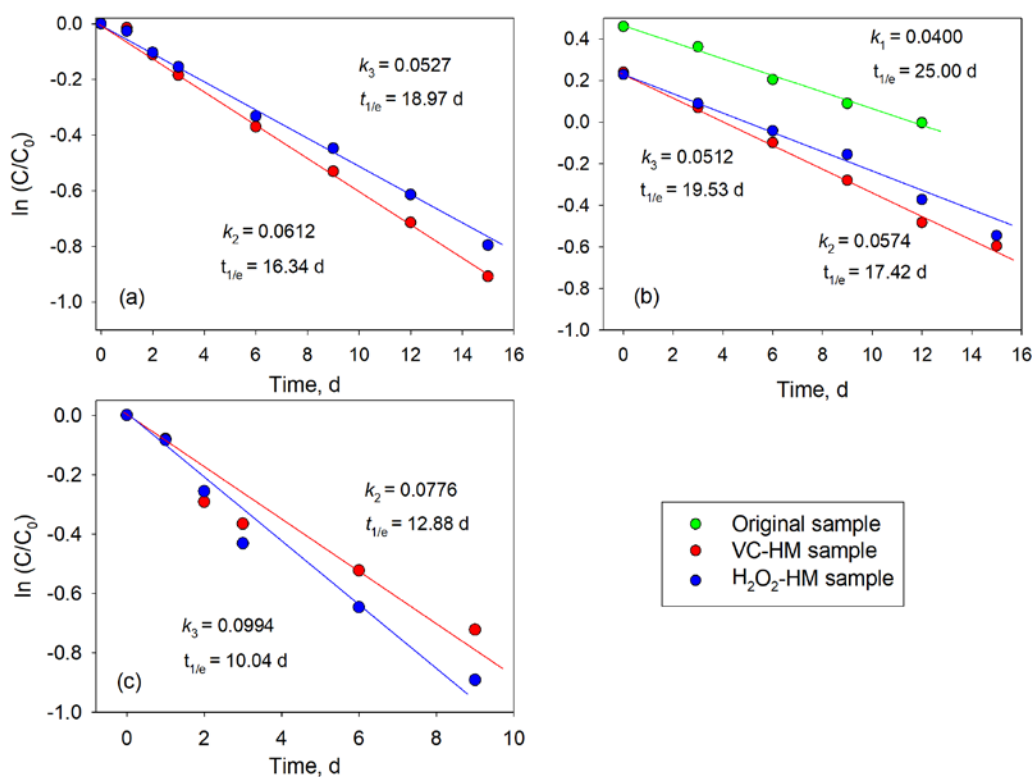

Fig. S3 Normalized pseudo-first-order decay kinetics of EPFRs derived from the reaction time at their highest yield for humin samples under various conditions, i.e., (a) Air, RH = 60%, (b) Air, RH = 7%, and (c) Air, RH = ~ 100%.

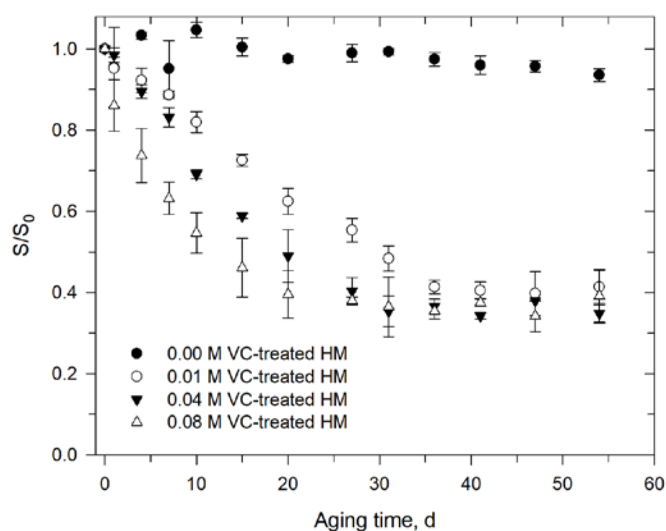

Fig. S4 Evolution of spin densities as a function of aging time for the L-ascorbic acid (VC)-treated HM samples under air with RH of 60%.

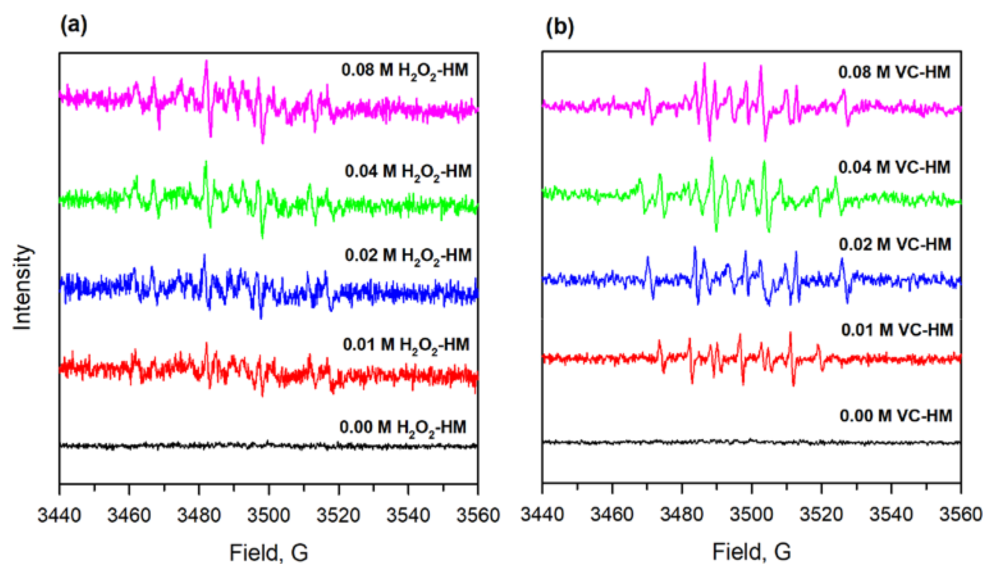

Fig. S5 Variation of DMPO spin-trapping EPR spectra in aqueous medium for the treated HM by H2O2 (a) and L-ascorbic acid (b) with concentrations of 0.00, 0.01, 0.02, 0.04, and 0.08 M.

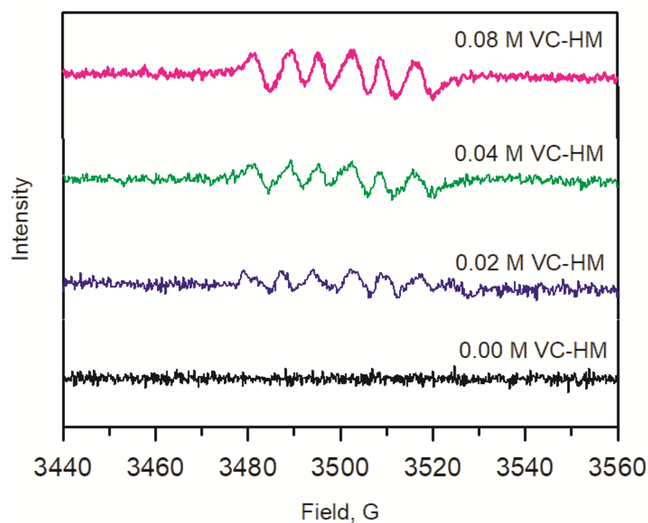

Fig. S6 Variation of DMPO spin-trapping EPR spectra in DMSO medium for the treated HM by L-ascorbic acid with concentrations of 0.00, 0.02, 0.04, and 0.08 M.