Supporting information:

Text S1

2.1 Reagents

Hydrogen peroxide (H_2O_2, 30 wt%), and dichloromethane (CH_2Cl_2, chromatographically pure) were achieved from Zhengzhou Paini chemical reagent factory (Zhengzhou, China). Ferrous sulfate ($FeSO_4 \cdot 7H_2O$, analytically pure), Aluminum sulfate ($Al_2(SO_4)_3$, analytically pure), Tryptophan ($C_{11}H_{12}N_2O_2$, 99%) and anhydrous sodium sulfate (Na_2SO_4, analytically pure) were obtained from Tianjin Kemiou chemical reagent co., LTD (Tianjin, China).

Text S2

2.2 Soil sample preparation method

The specific treatment steps are as follows:

Step 1. Calcination of soil: weigh 500 g of soil sample S, wrap it in aluminum foil, and place it in a muffle furnace at 550°C for 5 hours to remove organic matter components. After cooling, retrieve the sample and label it as soil S1.

Step 2. Preparation of simulated protein-like organic matter soil: dissolve 1 g of tryptophan in 100 mL of deionized water and stir thoroughly to prepare a 1% (w/v) tryptophan solution. Take 100 g of calcined soil (S1) and place it in a 250 mL conical flask. Add a small amount of distilled water to moisten the soil, followed by the addition of 10 mL of the tryptophan solution. Mix thoroughly to ensure homogeneity. Transfer the mixed sample to a freeze dryer for drying. The final product is soil with a 1% (w/w) simulated protein-like organic matter, labeled as soil S2.

Step 3. Passivation of soil organic matter: take 100 g of S2 soil sample and place it in a 250 mL beaker. Dissolve 20 g of aluminum sulfate in 100 mL of deionized water to prepare an aluminum sulfate solution, ensuring a passivator-to-soil mass ratio of 20 g/kg. Subsequently, accurately weigh 10 g of the passivated S2 soil sample into a 150 mL beaker and add a small amount of deionized water to uniformly disperse the soil.

Step 4. Soil oil contamination: add an appropriate amount of crude oil to the prepared soil, adjusting the petroleum contamination concentration to 21538 mg/kg.

Step 5. Fenton oxidation experiment: add freshly prepared ferrous sulfate solution and hydrogen peroxide solution to the reaction system, adjusting the total volume to 30 mL. Ensure that the final concentrations of ferrous sulfate and hydrogen peroxide in the system reach 0.0058 mol/L and 0.45 mol/L, respectively.

Text S3

2.3 Extraction methods, characterization and testing methods of soil petroleum hydrocarbons

Extraction methods: the extraction of petroleum hydrocarbons was conducted in accordance with the U.S. Environmental Protection Agency (EPA) test method 3550B. After the reaction was completed, 20 mL of dichloromethane (DCM) was added to the conical flask, and the mixture was shaken on a shaker at 180 r/min for 12 hours. Subsequently, the mixture was subjected to ultrasonic treatment for 1 hour, and the soil-solution mixture was transferred to a separatory funnel for phase separation. During the extraction process, the lower oil phase was filtered through a common funnel with anhydrous sodium sulfate to remove moisture. Finally, the extract was collected in a 50 mL volumetric flask, and the anhydrous sodium sulfate was rinsed multiple times with dichloromethane to ensure that all extracts were combined to the 50 mL volume mark.

Characterization and testing methods: the concentration of TPH was determined using gas chromatography (GC, Agilent 6890N, USA). The specific operational parameters were as follows: the initial temperature of the GC was set at 70°C and held for 1 minute, then increased to 300°C at a rate of 4°C/min, and maintained at 300°C for 5 minutes. Changes in organic matter in the supernatant before and after the oxidation reaction were characterized using a fluorescence spectrophotometer (3DEEM, Hitachi F-7000, Japan)(Chow, 2013). Fourier-transform infrared spectroscopy (FT-IR, Nicolet iS50, Thermo Fisher, USA) was employed to analyze functional groups in the soil samples(Alvarez-Puebla and Garrido, 2005). The changes in free radicals during the reaction process were monitored using an electron paramagnetic resonance spectrometer (EPR, A300, Bruker, Germany) (Fang et al., 2015). The decomposition process of hydrogen peroxide was characterized using ultraviolet-visible spectrophotometry (U-3900, Japan). The decomposition rate was determined using the titanium sulfate colorimetric method by measuring the absorbance at a wavelength of 412 nm. In the specific procedure, 2 mL of supernatant samples were collected at different time points, filtered through a 0.45 μm cellulose acetate membrane, and transferred to a 5 mL colorimetric tube. Subsequently, 1.0 mL of 0.3 mol/L H_2SO_4 and 0.2 mL of 0.003 mol/L titanium sulfate solution were added for further analysis.

Text S4

2.4 Statistical analysis

To investigate the passivation mechanisms of soil organic matter and achieve targeted oxidation of TPH in petroleum contaminated soil, the following parameters were calculated(Xu et al., 2020): 1) The targeted oxidation amount of TPH. 2) the amount of free radicals consumed to oxidize the same quantity of TPHs before and after passivation treatment; 3) the total instantaneous intensity of • OH; 4) the relative reactivity coefficient, $K_{TPH/SOM}$; 5) the • OH allocation proportion of SOM; 6) the • OH transferred percentage; 7) the number of targeted-oxidation reactions of n-alkanes; and 8) changes in the extent of SOM oxidation.

1) The targeted oxidation amount of TPH = $C_{AR} - C_{BR}$

Where the CBR and CAR (mg/kg) are the oxidation amount of TPH before and after regulation, respectively, under the same condition of relative reactivity coefficient K.

2) The amount of free radicals consumed to oxidize the same quantity of TPHs before and after passivation treatment

After passivation adjustment, a fixed oxidation value is selected, and its fixed value is the same as the unpassivation adjustment value, and the amount of free radicals consumed is calculated by proportion.

3) The total instantaneous intensity of • OH

The instantaneous intensity of • OH is the peak height of the complete peak shape of • OH, and the total intensity of • OH is the integral area of the instant intensity of • OH over time in each period.

4) The relative reactivity coefficient, $K_{TPH/SOM} = \frac{T/T_0}{S/S_0}$

Where the T and S (mg/kg) are the oxidation amount of TPH and SOM after oxidation, the T_0 and S_0 (mg/kg) are the initial concentration of TPH and SOM, respectively, under the same condition of relative reactivity coefficient K.

5) The • OH allocation proportion of SOM $= \frac{\eta_{SOM}}{\eta_{SOM} + \eta_{TPH}} \times 100\%$

Where the ηSOM and ηTPH (%) are the oxidation efficiency of SOM and TPH, respectively, under the same condition of relative reactivity coefficient K.

6) The • OH transferred percentage = $P_B - P_A$

Where the PA and PB (%) are the proportion of • OH for SOM allocation before and after regulation, respectively, under the same condition of relative reactivity coefficient K.

7) The number of targeted-oxidation reactions of n-alkanes

When the targeted oxidation amount of the alkane is greater than 60mg/kg, it is considered that the alkane has reached targeted oxidation.

8) Changes in the extent of SOM oxidation = $S_A - S_B$

Where the SA and SB are the absorbance of blank soil before and after regulation, respectively, under the same condition of relative reactivity coefficient K.

Table S1 Distribution of petroleum chain hydrocarbon in oil-stained soil.

Alkane	Concentration（mg/kg）	Alkane	Concentration（mg/kg）
C_{11}	48.54	C_{21}	1328.44
C_{12}	644.23	C_{22}	1288.77
C_{13}	794.00	C_{23}	1164.86
C_{14}	395.69	C_{24}	1080.72
C_{15}	1199.66	C_{25}	1231.76
C_{16}	1372.85	C_{26}	1330.76
C_{17}	1294.37	C_{27}	1393.52
C_{18}	1307.38	C_{28}	1235.90
C_{19}	1264.18	C_{29}	1047.08
C_{20}	1225.88	C_{30}	870.03

Table S2 The total radical intensity.

Process mode	Relative reactivity coefficient ($K_{TPH/SOM}$)	• OH total intensity (a.u.·h)	SOM oxidation (mg/kg)	SOM distribution ratio (%)	TPH oxidation (mg/kg)	Targeted oxidation (mg/kg)	• OH transfer ratio (%)
Untreated soil	0.54	2.73	12478.29	64.83	6770.56	-	-
Calcine	5.77	1.87	1741.06	14.77	10050.49	3279.93	50.06
Unpassivated	0.84	2.40	9647.15	54.49	8058.01	1278.45	10.34
Passivation	2.78	2.81	4326.00	26.44	12036.24	5265.44	28.05

Table S3 Changes in absorbance of organic functional groups under four treatment methods.

Process mode	State of oxidation	C-O-C	C-H	C=O	$-CH_2$	O-H
Untreated soil	Pre-oxidation	0.327	0.215	0.223	0.214	0.256
	Post-oxidation	0.304	0.194	0.178	0.173	0.174
Calcine	Pre-oxidation	0.178	0.152	0.151	0.163	0.161
	Post-oxidation	0.172	0.149	0.146	0.16	0.147
Unpassivated	Pre-oxidation	0.252	0.189	0.163	0.123	0.147
	Post-oxidation	0.115	0.105	0.117	0.115	0.121
Passivation	Pre-oxidation	0.168	0.137	0.142	0.121	0.114
	Post-oxidation	0.152	0.121	0.135	0.105	0.110

Table S4 Surface area distribution data of Glutamic acid in different electrostatic potential regions.

Electrostatic potential (kcal/mol)	Percentage of area (%)
-55-(-50)	6.2316
-50-(-45)	6.7816
-45-(-40)	10.5417
-40-(-35)	12.1461
-35-(-30)	10.7922
-30-(-25)	8.3259
-25-(-20)	7.1235
-20-(-15)	6.5583
-15-(-10)	7.1738
-10-(-5)	7.3784
-5-(0)	6.6111
0-5	6.2514
5-10	6.6625
10-15	8.1088
15-20	8.3101
20-25	5.29
25-30	3.6681
30-35	2.7231

35-40	2.4201
40-45	2.1014
45-50	1.9894
50-55	1.9879
55-60	2.0611
60-65	2.3493
65-70	2.3786
70-75	2.8727
75-80	3.3651
80-85	4.2672
85-90	6.9428
90-95	2.0969

Table S5 Surface area distribution data of Glutamic acid and aluminum ion complex in different electrostatic potential regions.

Electrostatic potential (kcal/mol)	Percentage of area (%)
-65-(-60)	0.2509
-60-(-55)	1.5074
-55-(-50)	2.1199
-50-(-45)	2.4183
-45-(-40)	4.9696
-40-(-35)	5.1254
-35-(-30)	5.5255
-30-(-25)	7.1322
-25-(-20)	7.4266
-20-(-15)	7.7056
-15-(-10)	8.1702
-10-(-5)	9.9849
-5-(0)	14.4845
0-5	23.7797
5-10	37.6582
10-15	18.9453
15-20	12.1497
20-25	8.4546

25-30	7.9487
30-35	10.33
35-40	9.2831
40-45	0.6922

Table S6 Surface area distribution data of fulvic acid in different electrostatic potential regions.

Electrostatic potential (kcal/mol)	Percentage of area (%)
-80-(-75)	0.0059
-75-(-70)	1.6103
-70-(-65)	1.5498
-65-(-60)	1.9046
-60-(-55)	2.194
-55-(-50)	2.503
-50-(-45)	2.9334
-45-(-40)	3.5592
-40-(-35)	7.1448
-35-(-30)	16.2147
-30-(-25)	12.5188
-25-(-20)	11.9775
-20-(-15)	12.9365
-15-(-10)	12.2417
-10-(-5)	12.8521
-5-(0)	16.0055
0-5	19.1747
5-10	23.159
10-15	20.1398

15-20	13.6744
20-25	12.4074
25-30	12.4666
30-35	10.8358
35-40	5.2291
40-45	2.4484
45-50	2.1471
50-55	1.8468
55-60	1.3981
60-65	0.6547
65-70	0.693
70-75	0

Table S7 Surface area distribution data of Fulvic acid and aluminum ionic complexes in different electrostatic potential regions.

Electrostatic potential (kcal/mol)	Percentage of area (%)
-50-(-45)	3.0225
-45-(-40)	9.1259
-40-(-35)	11.5378
-35-(-30)	11.3466
-30-(-25)	9.7168
-25-(-20)	11.0801
-20-(-15)	11.0061
-15-(-10)	13.8383
-10-(-5)	23.9875
-5-(0)	36.2137
0-5	39.4325
5-10	28.625
10-15	24.998
15-20	15.8696
20-25	6.7832
25-30	13.6945
30-35	12.1077
35-40	8.2667

40-45	5.817
45-50	3.8046
50-55	1.9563
55-60	0.2753

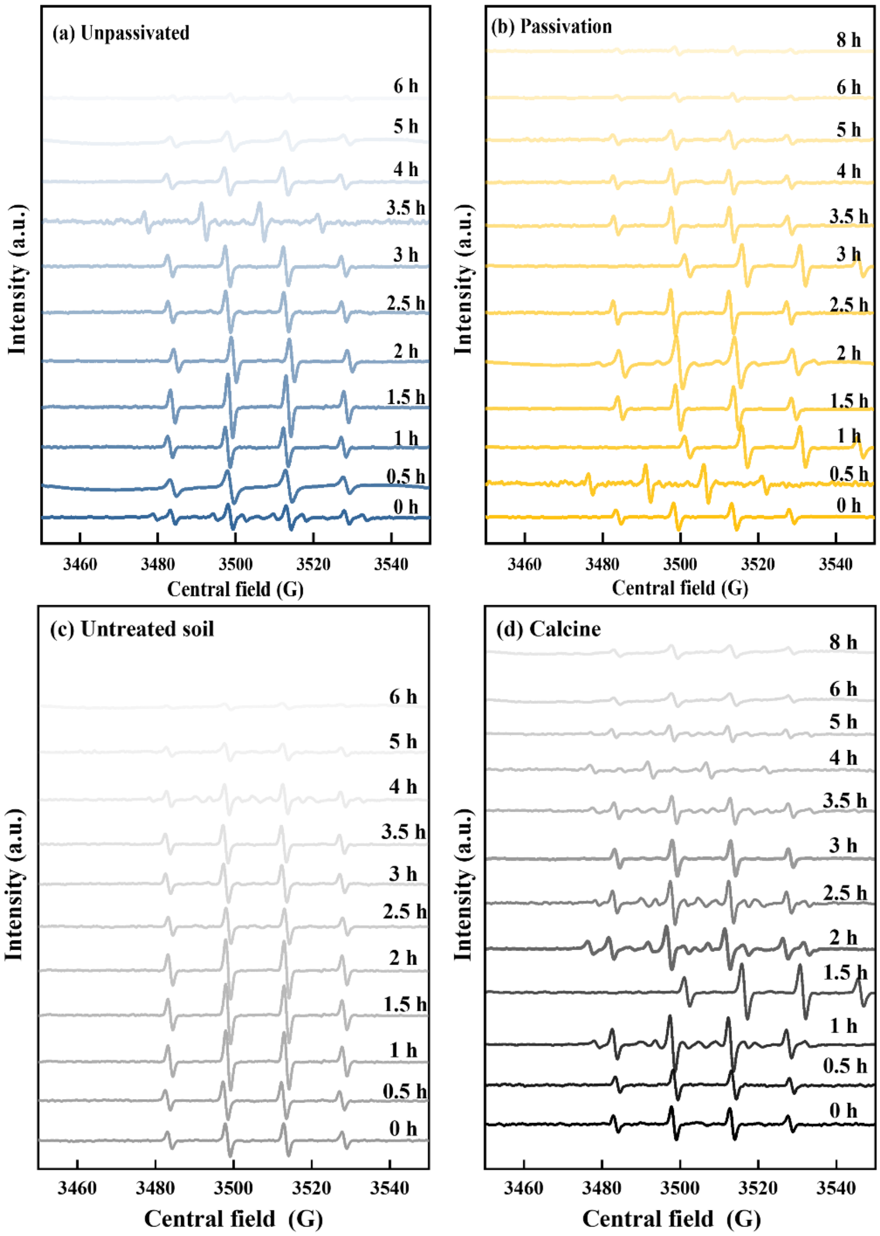

Fig. S1 (a) Measured instantaneous intensity of • OH in the unpassivated treatment group. (b) Measured instantaneous intensity of • OH in the passivated treatment group. (c) Measured instantaneous intensity of hydroxyl radicals (• OH) in the untreated soil group. (d) Measured instantaneous intensity of hydroxyl radicals (• OH) in the calcined group.

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