Supporting information

A sustainable method for oxidizing phenanthrene in tropical soil using natural iron as a catalyst in a slurry phase reactor with persulfate assistance

Mohammad Qutob[1], Mohd Rafatullah[1,*] Syahidah Akmal Muhammad[1], Masoom Raza Siddiqui[2], Mahboob Alam[3]

[1]Environmental Technology Division, School of Industrial Technology, Universiti Sains Malaysia, Penang 11800, Malaysia

[2]Chemistry Department, College of Science, King Saud University, Riyadh 11451, Saudi Arabia

[3]Division of Chemistry and Biotechnology, Dongguk University, 123, Dongdaero, Gyeongju-si 780714, Republic of Korea

Corresponding author*:

E-mail address: mohd_rafatullah@yahoo.co.in; mrafatullah@usm.my (MR)

Tel: +6046532111; Fax: +604656375

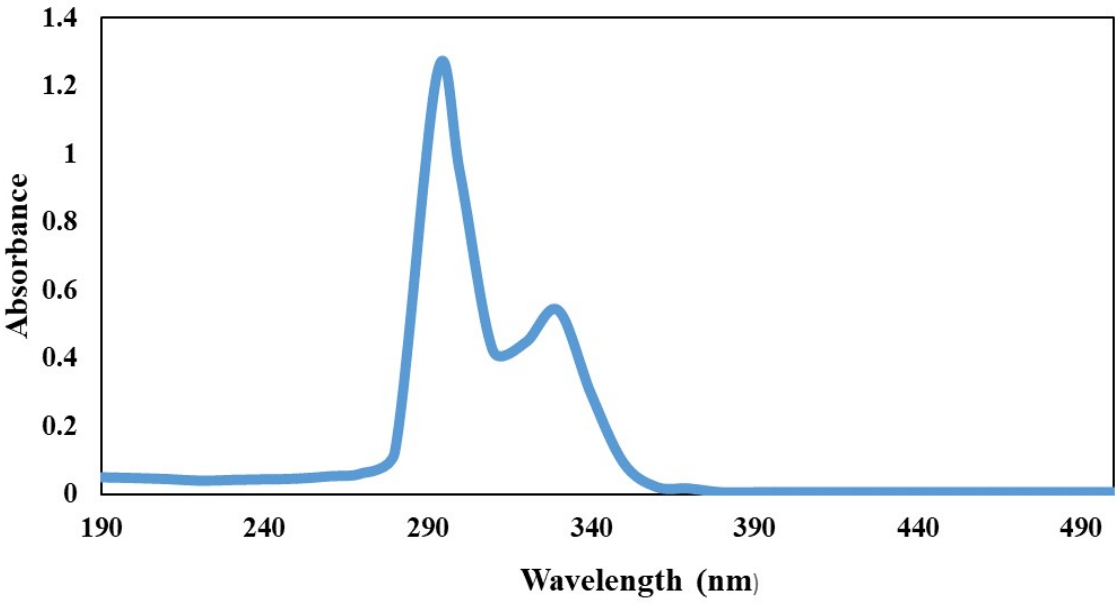


Fig. S1. The spectrum of the phenanthrene absorbance by UV-spectrophotometer.

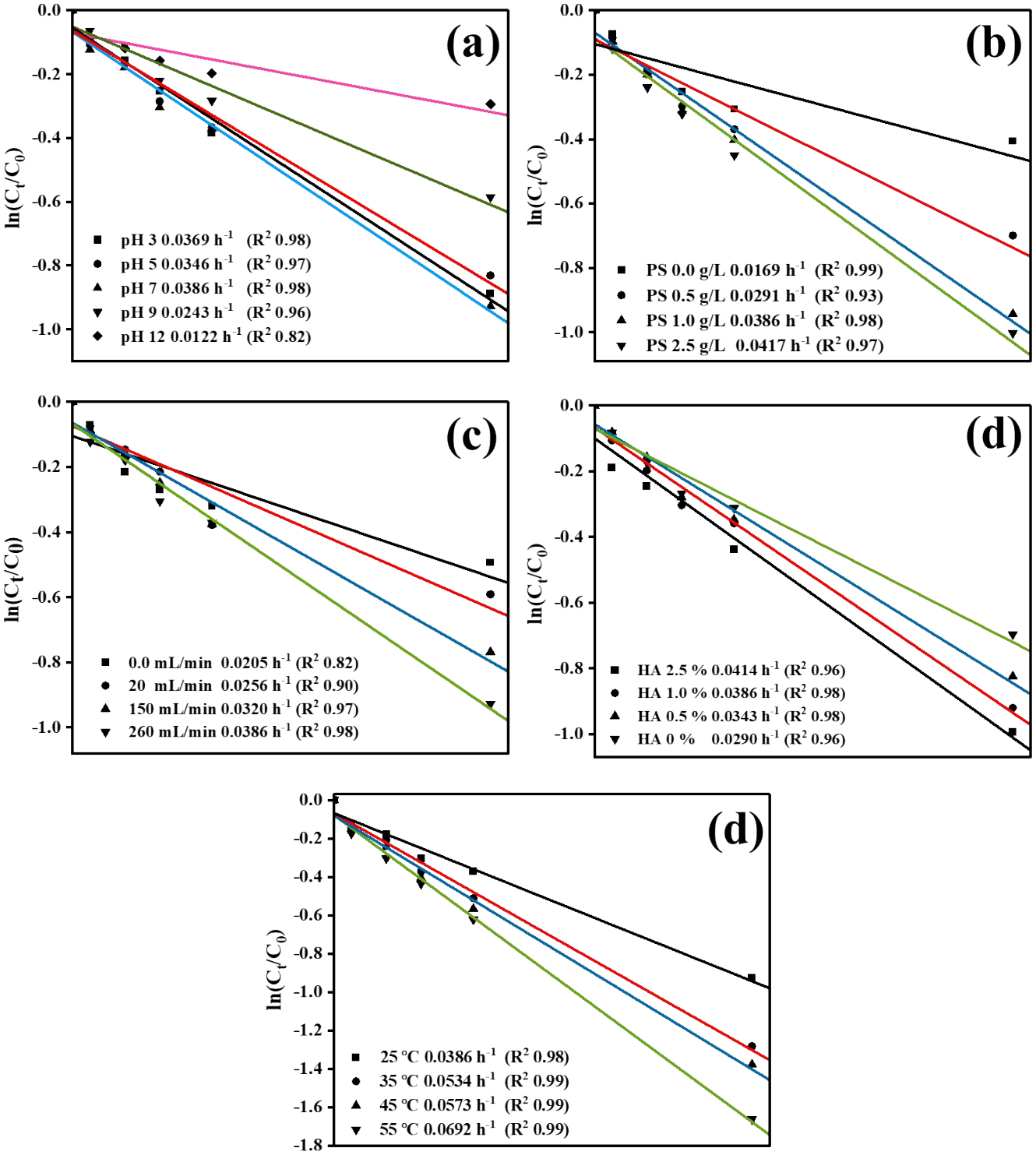
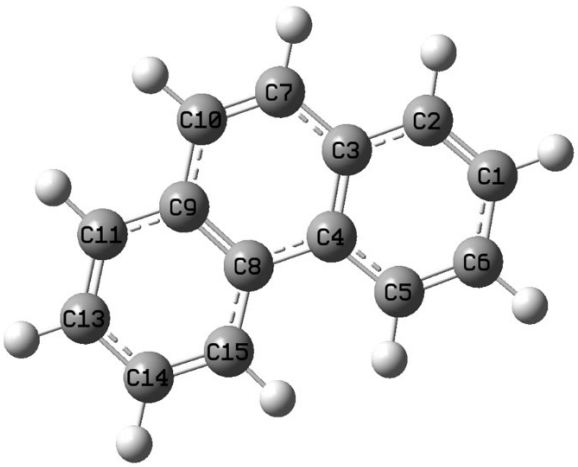


Fig. S2. ln (C_t/C_0) of PHE removal under different experimental conditions (a) pH, (b) PS, (c) airflow, (d) HA%, and (e) Temperature.



Atom	$q_i(N)$	$q_i(N+1)$	$q_i(N-1)$	f^+	f^-	f°
C1	-0.139	-0.083	0.176	0.056	-0.316	0.130
C2	0.060	0.192	-0.051	0.131	0.112	-0.122
C3	0.385	0.359	0.377	-0.025	0.008	0.008
C4	-0.261	-0.293	-0.249	-0.031	-0.011	0.021
C5	0.036	0.157	-0.017	0.121	0.053	-0.087
C6	-0.159	-0.062	-0.317	0.097	0.158	-0.127
C7	0.078	0.229	-0.064	0.151	0.142	-0.147
C8	-0.261	-0.293	-0.249	-0.031	-0.011	0.021
C9	0.385	0.360	0.377	-0.025	0.008	0.008
C10	0.077	0.229	-0.064	0.151	0.142	-0.147
C11	0.060	0.192	-0.051	0.131	0.112	-0.121
C13	-0.139	-0.083	-0.176	0.056	0.036	-0.046
C14	-0.159	-0.062	-0.317	0.097	0.158	-0.127
C15	0.036	0.157	-0.017	0.121	0.053	-0.087

Fig. S3. the values of nucleophilic attack, electrophilic attack, and radical attack.

Table S1: The studies that investigated the degradation of PHE via different AOP systems

Pollutant	System	Experimental conditions	Degradation efficiency	Time	Reference
PHE	Bacterial community in the combined system of photocatalysis	[PHE] = 10 mg/L, T = 25℃	88.6%	6 h	[1]
PHE	Clay-based catalyst/PS/H_2O_2	[PHE] = 200 mg/kg, T = 28℃ pH = 5.7, [H_2O_2] = 2.4g/L, [PS] = 41 g/L	83%	3 days	[2]
PHE	Fenton	[PHE] = 90 mg/kg, T = 20℃, pH = 3, [H_2O_2] = 882 mmol/L, [Fe] = 1 mmol/L	80%	5 days	[3]
PHE	UVB activation of hydrogen peroxide and peroxydisulfate	[PHE] = 10 mg/L, T = 25℃ [TW80] = 0.5 g/L, [PDS] = [H_2O_2] = 5 mM, pH 3.	85%	6 h	[4]
PHE	Microwave-activated persulfate	[PHE] = 1000 mg/kg, T = 60 ℃, [PS] = 50 g/L.	100%	1 h	[5]
PHE	Oxidation by PS and Fe-Modified Diatomite (Ex-situ)	[PHE] =200 mg/kg.	77%	7 days	[6]
PHE	Electrokinetically -delivered persulfate (Ex-situ)	[PHE] =299 mg/kg.	88%	7 days	[7]
ΣPAHs	Electro-Fenton	[ΣPAHs] = 3605 mg/kg,	28%	2 days	[8]
PHE	UV/PS	[PHE] =10 mg/L, [TW 80] =10 g/L, [H_2O_2] = [PS] = 10 mM, pH 6.4, UV power = 6 W.	90%	1 day	[9]
PHE	Soil naturally containing hematite as a catalyst of PS and O_2	[PHE] =300 mg/50g, [PS] = 1 g/L, pH 7, HA = 0.5%, Airflow 260 mL/min, T = 55 ℃	81%	1 day	This study

Table S2: Soil physiochemical characteristics

Soil texture	Sandy clay loam, Sand = 50%, Silt = 23%, Clay = 22%
Soil pH	2.9
Soil zero-point charge	3.5
Bulk density	1.006 g/cm^3
Soil organic matter	2.4%
Soil taxonomy	ultisols
CEC	9 cmolc/kg
Soil salinity	15.2 µS

Table S3. XRD analysis for the soil sample presented the minerals and their lattice planes.

2θ	lattice planes	Mineral	Card number	Reference
12.3°	(0 0 1)	Kaolinite	PDF card: 14-0164	[39]
20°	(1 1 0)	Kaolinite	PDF card: 14-0164	[39]
20.8°	(1 0 0)	Quartz	PDF card: 85-1054	[40]
24.9	(0 0 2)	Kaolinite	PDF card: 14-0164	[39]
26.6°	(1 0 1)	Quartz	PDF card: 85-1054	[40]
35°	(1 0 4)	Hematite	PDF card: 89-8103	[41]
36.5°	(1 1 0)	Hematite	PDF card: 89-8103	[41]
38.4°	(- 2 0 2)	Kaolinite	PDF card: 14-0164	[39]
50.2°	(1 1 2)	Quartz	PDF card: 85-1054	[40]
60°	(1 2 1)	Quartz	PDF card: 85-1054	[40]
62.3°	(6 0 6)	Kaolinite	PDF card: 14-0164	[39]
68.2°	(0 3 1)	Quartz	PDF card: 85-1054	[40]

Table S4: The removal rate and removal efficiency of [PHE] = 300 mg/50 g, [Fe^{2+}] = g/L soil under different experimental conditions

pH	HA (w/w %)	Temperature (°C)	Air flow (mL/min)	PS (g/L)	Pseudo- second order reaction model		Pseudo-first order reaction model		Removal efficiency
					Removal rate ($M^{-1}. h^{-1}$)	R^2	Removal rate (h^{-1})	R^2	
3	0.5	25	260	1	3.877	0.724	0.0369	0.98	58 %
5	0.5	25	260	1	3.699	0.758	0.0346	0.97	56 %
7	0.5	25	260	1	3.903	0.711	0.0386	0.98	60 %
9	0.5	25	260	1	2.953	0.818	0.0243	0.96	44 %
12	0.5	25	260	1	1.493	0.961	0.0122	0.82	25 %
7	0.5	25	260	0	2.126	0.991	0.0169	0.99	33 %
7	0.5	25	260	0.5	3.423	0.854	0.0291	0.93	50 %
7	0.5	25	260	2.5	4.335	0.735	0.0417	0.97	63 %
7	0.5	35	260	1	4.107	0.735	0.0534	0.99	73 %
7	0.5	45	260	1	3.972	0.745	0.0573	0.99	75 %
7	0.5	55	260	1	3.459	0.791	0.0692	0.99	81 %
7	0	25	260	1	5.324	0.664	0.0414	0.96	59 %
7	1	25	260	1	5.459	0.665	0.0343	0.98	56 %
7	2.5	25	260	1	5.848	0.611	0.0290	0.96	53 %
7	0.5	25	0	1	2.419	0.962	0.0205	0.81	39 %
7	0.5	25	20	1	2.999	0.888	0.0246	0.90	45 %
7	0.5	25	150	1	3.613	0.785	0.032	0.97	54 %

Table S5: PHE by-products

Index	Name	R. Time	R. Index	Chemical formula	SmilesRan
P1	Phenanthrene	12.678	1782	$C_{14}H_{10}$	C=1C=CC2=C(C1)C=CC=3C=CC=CC32
P2	9-methylidene-9H-fluorene	12.678	1560	$C_{14}H_{10}$	C=C1C=2C=CC=CC2C=3C=CC=CC13
P3	1,2-ditridecyl benzene-1,2 dicarboxylate	22.905	3826	$C_{34}H_{58}O_4$	O=C(OCCCCCCCCCCCCCC)C=1C=CC=CC1C(=O)OCCCCCCCCCCCCCC
P4	Phthalic acid, bis(7-methyloctyl) ester	9.013	2902	$C_{26}H_{42}O_4$	O=C(OCCCCCCC(C)C)C=1C=CC=CC1C(=O)OCCCCCCC(C)C
P5	1,2-Benzenedicarboxylic acid, diisooctyl ester	9.013	2704	$C_{24}H_{38}O_4$	O=C(OCCCCCC(C)C)C=1C=CC=CC1C(=O)OCCCCCC(C)C
P6	19-methyl-3,6,9,12,15-pentaoxabicyclo[15.3.1]henicosa-1(21),17,19-trien-21-ol	31.082	2764	$C_{17}H_{26}O_6$	OC=1C2=CC(=CC1COCCOCCOCCOCCOC2)C
P7	3,6,9,12,15-pentaoxabicyclo[15.3.1]henicosa-1(21),17,19-trien-21-ol	31.082	2651	$C_{16}H_{24}O_6$	OC=1C2=CC=CC1COCCOCCOCCOCCOC2
P8	3,6,9,12,15,18,21,24,27,30-decaoxadotriacontane-1,32-diol	35.202	2628	$C_{22}H_{26}O_{12}$	OCCOCCOCCOCCOCCOCCOCCOCCOCCOCCOCCOCCO
P9	2-[2-[2-[2-[2-[2-[2-[2-[2-(2-Hydroxyethoxy) ethoxy]ethoxy]ethoxy]ethoxy]ethoxy] ethoxy]ethoxy]ethoxy]ethanol	35.202	2903	$C_{20}H_{46}O_{12}$	OCCOCCOCCOCCOCCOCCOCCOCCOCCOCCOCCO
P10	3,6,9,12,15,18,21,24-octaoxahexacosane-1,26-diol	35.202	2903	$C_{18}H_{38}O_{10}$	OCCOCCOCCOCCOCCOCCOCCOCCOCCO
P11	3,6,9,12,15,18-hexaoxaicosane-1,20-diol	39.242	2354	$C_{14}H_{30}O_8$	OCCOCCOCCOCCOCCOCCOCCO
P12	3,6,9,12,15-pentaoxaheptadecane-1,17-diol	39.242	2079	$C_{12}H_{26}O_7$	OCCOCCOCCOCCOCCOCCO
P13	3,6,9,12-tetraoxatetradecane-1,14-diol	32.915	1804	$C_{10}H_{22}O_6$	OCCOCCOCCOCCOCCO
P14	Ethyl 2-ethoxy-2-hydroxyacetate	29.062	1023	$C_6H_{12}O_4$	O=C(OCC)C(O)OCC

P15	Dihydroxypropanedioic acid	28.958	1300	$C_3H_4O_6$	O=C(O)C(O)(O)C(=O)O
P16	methyl 2-methoxy-3-(4-methoxy-2-methyl-4-oxobutanoyl)-6-methylbenzoate	35.732	2212	$C_{16}H_{20}O_6$	O=C(OC)C1=C(OC)C(=CC=C1C)C(=O)C(C)CC(=O)OC
P17	(4-tert-butylphenoxy)methyl acetate	35.732	1563	$C_{13}H_{18}O_3$	O=C(OCOC1=CC=C(C=C1)C(C)(C)C)C
P18	Methyl 2-(4-tert-butylphenoxy)acetate	35.732	1563	$C_{13}H_{18}O_3$	O=C(OC)COC1=CC=C(C=C1)C(C)(C)C
P19	4-(methoxymethoxy)benzaldehyde	20.727	1346	$C_9H_{10}O_3$	O=CC1=CC=C(OCOC)C=C1
P20	Methoxyacetic acid, 4-hexadecyl ester	8.525	2089	$C_{19}H_{38}O_3$	O=C(OC(CCC)CCCCCCCCCCCCC)COC
P21	Methoxyacetic acid, 6-ethyl-3-octyl ester	8.525	1428	$C_{13}H_{26}O_3$	O=C(OC(CC)CCC(CC)CC)COC
P22	Oxalic acid, 6-ethyloct-3-yl propyl ester	8.615	1719	$C_{15}H_{28}O_4$	O=C(OCCC)C(=O)OC(CC)CCC(CC)CC
P23	3,7-dimethylnona-1,6-dien-3-ol	8.615	1183	$C_{11}H_{20}O$	OC(C=C)(C)CCC=C(C)CC
P24	Hept-6-ene-2,4-diol	39.242	1032	$C_7H_{14}O_2$	OC(C)CC(O)CC=C
P25	1-(propan-2-yloxy)propan-2-ol	22.797	792	$C_6H_{14}O_2$	OC(C)COC(C)C
P26	2,4,6-trimethyl-1,3,5-trioxane	39.242	870	$C_6H_{12}O_3$	O1C(OC(OC1C)C)C
P27	2-ethoxypropane	18.828	616	$C_5H_{12}O$	O(CC)C(C)C
P28	Propan-2-yl formate	22.797	619	$C_4H_8O_2$	O=COC(C)C

Table S6: The results of toxicity tests for PHE and its by-products

Compound index	Oral rat LD_{50}			Ames mutagenicity test		Developmental toxicity test	
	Prediction value (mg/kg)	GHS toxicity Category	GHS Hazard statement	Prediction results	Prediction value	Prediction results	Prediction value
PHE	2451.64	5	Harmful if swallowed	Positive	0.59	Developmental toxicant	0.97
P1	3093.92	5	Harmful if swallowed	N/A	N/A	Developmental toxicant	1.00
P2	22531.82	5	Harmful if swallowed	Negative	-0.01	Developmental toxicant	0.89
P3	30743.30	5	Harmful if swallowed	Negative	-0.03	Developmental toxicant	0.62
P4	26460.18	5	Harmful if swallowed	Negative	0.20	Developmental toxicant	0.65
P5	2482.20	5	Harmful if swallowed	Negative	0.04	Developmental NON-toxicant	0.36
P6	2868.75	5	Harmful if swallowed	Negative	0.02	Developmental NON-toxicant	0.25
P7	9005.15	5	Harmful if swallowed	Negative	0.38	Developmental NON-toxicant	-0.02
P8	8614.13	5	Harmful if swallowed	Negative	0.38	Developmental NON-toxicant	-0.02
P9	8156.67	5	Harmful if swallowed	Negative	0.38	Developmental NON-toxicant	-0.29
P10	19680.47	5	Harmful if swallowed	Negative	0.37	Developmental NON-toxicant	-0.20
P11	21685.78	5	Harmful if swallowed	Positive	0.58	Developmental NON-toxicant	-0.21
P12	24142.26	5	Harmful if	Positive	0.61	Developmental	0.12

			swallowed			NON-toxicant	
P13	6904.30	5	Harmful if swallowed	Negative	0.12	Developmental toxicant	0.62
P14	3953.36	5	Harmful if swallowed	Negative	0.06	Developmental NON-toxicant	0.33
P15	2617.45	5	Harmful if swallowed	Negative	0.44	Developmental toxicant	0.84
P16	1916.26	4	Harmful if swallowed	Negative	0.28	Developmental toxicant	0.69
P17	1924.71	4	Harmful if swallowed	Negative	0.32	Developmental toxicant	0.77
P18	N/A	N/A	N/A	Negative	0.03	Developmental toxicant	0.94
P19	10020.22	5	Harmful if swallowed	Negative	0.24	Developmental NON-toxicant	0.12
P20	4114.74	5	Harmful if swallowed	Negative	0.27	Developmental NON-toxicant	0.24
P21	10304.43	5	Harmful if swallowed	Negative	0.44	Developmental NON-toxicant	0.32
P22	2572.82	5	Harmful if swallowed	Negative	-0.09	Developmental toxicant	0.99
P23	752.68	4	Harmful if swallowed	Negative	0.49	Developmental toxicant	0.70
P24	4322.54	5	Harmful if swallowed	Negative	0.12	Developmental toxicant	0.54
P25	2698.31	5	Harmful if swallowed	Negative	0.30	Developmental toxicant	0.80
P26	1028.91	4	Harmful if swallowed	Negative	0.03	Developmental NON-toxicant	0.45
P27	N/A	N/A	N/A	Negative	0.28	Developmental toxicant	0.80

References

1 Z. Qin, Z. Zhao, W. Jiao, Z. Han, L. Xia, Y. Fang, S. Wang, L. Ji and Y. Jiang, Phenanthrene removal and response of bacterial community in the combined system of photocatalysis and PAH-degrading microbial consortium in laboratory system, *Bioresour Technol*, 2020, **301**, 122736, doi: 10.1016/j.biortech.2020.122736.

2 V. M. A. Magalhães, G. P. Mendes, J. D. B. Costa-Filho, R. Cohen, C. S. M. Partiti, M. M. G. R. Vianna and O. Chiavone-Filho, Clay-based catalyst synthesized for chemical oxidation of phenanthrene contaminated soil using hydrogen peroxide and persulfate, *J Environ Chem Eng*, 2020, 8, 103568. doi: 10.1016/j.jece.2019.103568.

3 F. Pardo, M. Peluffo, A. Santos and A. Romero, Optimization of the application of the Fenton chemistry for the remediation of a contaminated soil with polycyclic aromatic hydrocarbons, *J Chem Technol Biotechnol*, 2016, **91**, 1763–1772. doi: 10.1002/jctb.4767.

4 Y. Tao, O. Monfort, M. Brigante, H. Zhang and G. Mailhot, Phenanthrene decomposition in soil washing effluents using UVB activation of hydrogen peroxide and peroxydisulfate, *Chemosphere*, 2021, **263**, 127996. doi: 10.1016/j.chemosphere.2020.127996.

5 L. Peng, D. Deng and F. Ye, Efficient oxidation of high levels of soil-sorbed phenanthrene by microwave-activated persulfate: implication for in situ subsurface remediation engineering, *J Soils Sediments*, 2016, **16**, 28–37. doi: 10.1007/s11368-015-1176-5.

6 C. K. O. Da Silva, M. M. G. R. Vianna, E. L. Foletto, O. Chiavone-Filho and C. A. O. Do Nascimento, Optimizing phenanthrene and anthracene oxidation by sodium persulfate and Fe-modified diatomite using the response surface method, *Water Air Soil Pollut*, 2015,266, 88. doi: 10.1007/s11270-015-2362-1.

7 D. Wen, X. Guo, Q. Li and R. Fu, Enhanced electrokinetically-delivered persulfate and alternating electric field induced thermal effect activated persulfate in situ for remediation of phenanthrene contaminated clay, *J Hazard Mater*, 2022, **423**, 127199. doi: 10.1016/j.jhazmat.2021.127199.

8 Z. Liu, Z. Gao and X. Lu, An Integrated Approach to Remove PAHs from Highly Contaminated Soil: Electro-Fenton Process and Bioslurry Treatment, *Water Air Soil Pollut*, 2020, **231**, 314. doi: 10.1007/s11270-020-04696-7.

9 X. Bai, Y. Wang, X. Zheng, K. Zhu, A. Long, X. Wu and H. Zhang, Remediation of phenanthrene contaminated soil by coupling soil washing with Tween 80, oxidation using the UV/$S_2O_8^{2-}$ process and recycling of the surfactant, *Chem Eng J*, 2019, **369**, 1014–1023. doi: 10.1016/j.cej.2019.03.116.