New Evidence for High Sorption Capacity of Hydrochar for Hydrophobic Organic Pollutants

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Supplementary Information

Figure numbers: 4

Table numbers: 9

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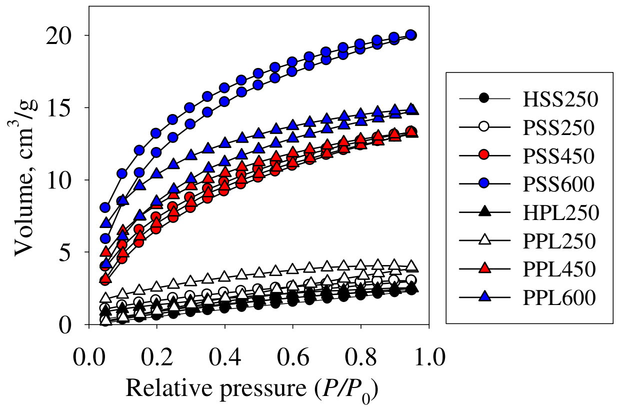


Figure S1. Carbon dioxide (CO_2) adsorption isotherm on the swine solid- and poultry litter-derived hydrochars and pyrochars. Note that H and P represent hydrochars and pyrochars, respectively; SS and PL refer to the biochars obtained from swine solids and poultry litter, respectively; 250, 450 and 600 mean the heating treatment temperature (^{o}C).

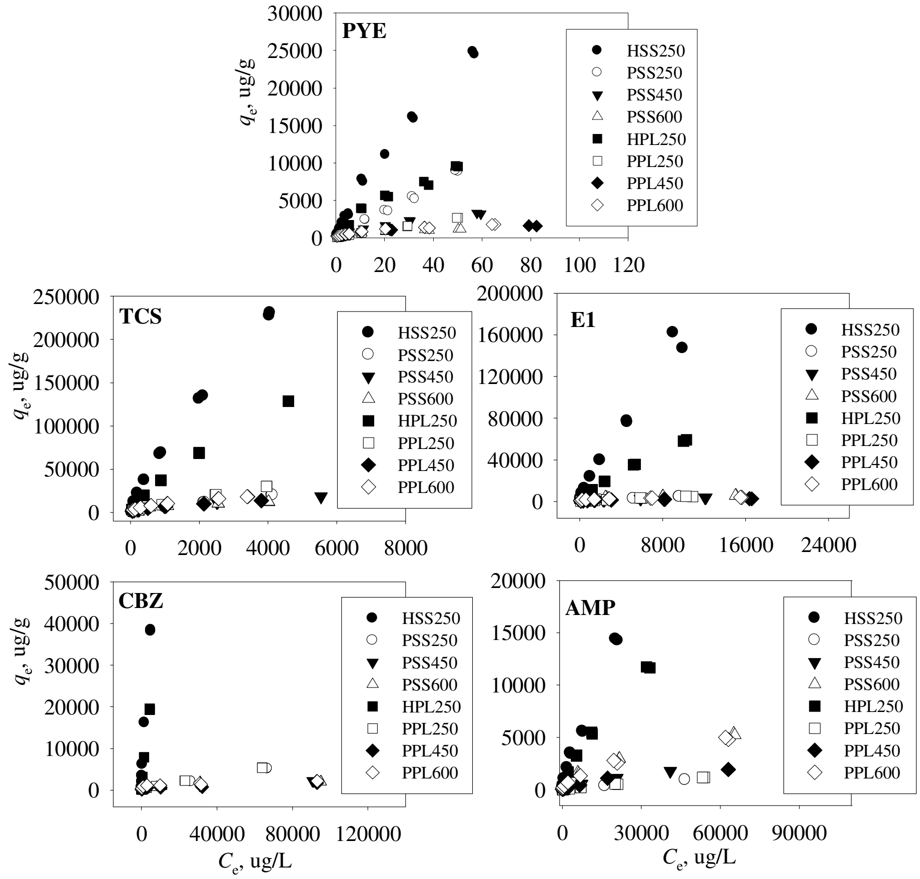


Figure S2. Sorption isotherms of pyrene (PYE) and four pharmaceuticals and personal care products (PPCPs) including triclosan (TCS), estrone (E1), carbamazepine (CBZ), acetaminophen (AMP) by swine solid and poultry litter-derived hydrochars and pyrochars. Note that H and P represent hydrochars and pyrochars, respectively; SS and PL refer to the biochars obtained from swine solids and poultry litter, respectively; 250, 450 and 600 mean the heating treatment temperature (^{o}C).

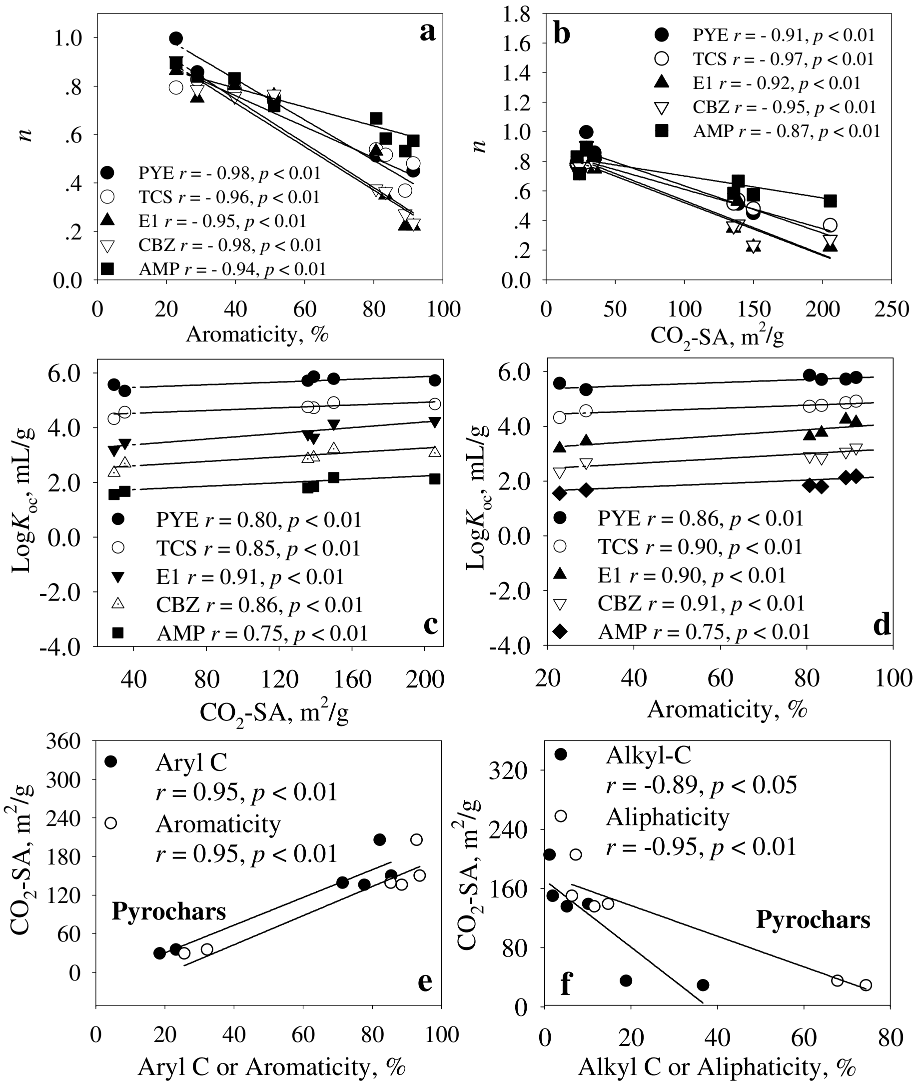


Figure S3. Relationships between the Freundlich nonlinearity coefficients (*n*) of sorption isotherms of pyrene (PYE) and four pharmaceuticals and personal care products (PPCPs) including triclosan (TCS), estrone (E1), carbamazepine (CBZ), acetaminophen (AMP) by all tested biochars and their aromaticity (a) and CO_2-surface area (CO_2-SA, determined using CO_2 adsorption) (b); between logK_{oc} values (mL/g) of five sorbates by pyrochars and their CO_2-SA (c) and aromaticity (d); between CO_2-SA of pyrochars and aryl C or aromaticity (e) and alkyl C or aliphaticity (f), respectively.

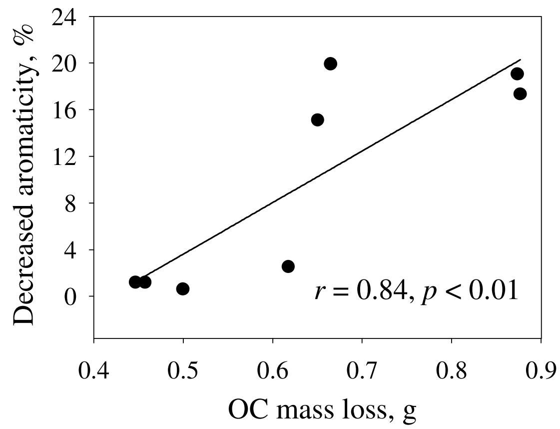
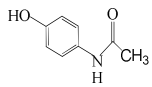
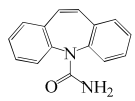
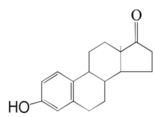
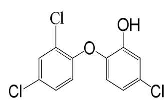
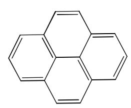


Figure S4. Relationships between the organic carbon (OC) mass loss and the dereased aromaticity by bleaching of hydrochars and pyrochars.

Table S1. The properties and chemical structure of tested sorbates

Compound (Formula) [ID]	Structure	MW	LogK_{ow}	pK_a	S_w	MV
Acetaminophen $C_8H_9NO_2$ AMP		152.2	0.46	9.38	12.9	138.1
Carbamazepine $C_{15}H_{12}N_2O$ CBZ		236.3	2.45	13.96	0.121	210.3
Estrone $C_{18}H_{22}O_2$ E1		270.4	3.13	10.40	0.03	263.2
Triclosan $C_{12}H_7C_{13}O_2$ TCS		287.5	4.76	8.14	0.01	212.1
Pyrene $C_{16}H_{10}$ PYE		202.0	5.18		0.000135	184.1

MW: molecular weight (g/mol); K_{ow}: octanol-water partition coefficient; pKa: negatively-transformed acid dissociation constant; S_w: aqueous solubility (g/L); MV: molecular volume (Å^3), it was obtained from chemicalize.org by ChemAxon (http://www.chemicalize.org).

Table S2. Yields by bleaching treatment, elemental compositions and surface area analysis of hydrochars and pyrochars

			Bulk elemental composition (elemental analysis)								Surface area	
Samples	Mass Recovery (%)[a]	OC Recovery (%)[b]	C (%)	H (%)	N (%)	O (%)	H/C	(O+N) /C	Ash (%)	N_2-SA (m^2/g)	CO_2-SA (m^2/g)
HSS250			54.02	5.69	2.67	12.51	1.26	0.22	25.11	1.9	22.4
PSS250			50.92	5.55	3.3	20.22	1.31	0.35	20.01	1.2	29.1
PSS450			42.29	2.38	3.25	10.58	0.68	0.25	41.5	14.3	139
PSS600			44.62	1.37	2.82	7.92	0.37	0.19	43.29	5.5	205.6
HPL250			39.13	3.06	3.09	8.95	0.94	0.24	45.77	2.8	24.2
PPL250			40.81	3.93	3.4	25.6	1.15	0.54	26.26	3	35.1
PPL450			37.44	1.79	2.86	10.44	0.58	0.27	47.46	4.8	135.7
PPL600			38.8	1.1	2.26	8.36	0.34	0.21	49.49	4.2	150
HSS250-BL	48.86	34.99	38.69	4.56	1.86	24.12	1.41	0.51	30.77	nd	nd
PSS250-BL	25.56	12.66	25.23	4.56	2.21	38.54	2.17	1.22	29.46	nd	nd
PSS450-BL	53.36	50.03	39.65	2.02	2.45	21.12	0.61	0.45	34.76	nd	nd
PSS600-BL	68.91	54.27	35.14	1.16	2.15	12.56	0.40	0.32	48.99	nd	nd
HPL250-BL	44.25	33.53	29.65	2.48	2.19	18.54	1.00	0.53	47.14	nd	nd
PPL250-BL	22.41	12.34	22.47	3.03	2.84	42.23	1.62	1.52	29.43	nd	nd
PPL450-BL	59.1	38.25	24.23	1.54	2.01	19.56	0.76	0.68	52.66	nd	nd
PPL600-BL	69.23	55.33	31.01	0.94	1.84	14.21	0.36	0.39	52.00	nd	nd

[a]Mass Recovery (%) = $M_{(BL)}/M_{(OR)} \times 100$, [b]OC Recovery (%) = $OC_{(BL)} \times M_{(BL)}/[\ OC_{(OR)} \times M_{(OR)}] \times 100$, where M is the weight of original (OR) or bleached (BL) sample; N_2-SA of samples was calculated using the Brunaer-Emmett-Teller (BET) equation for data in the range from 0.05 to 0.25 of relative pressure; CO_2-SA of samples was calculated from nonlocal density functional theory (NLDFT) using CO_2 adsorption; nd: not detected; Note that H and P represent hydrochars and pyrochars, respectively; SS and PL refer to the biochars obtained from swine solids and poultry litter, respectively; 250, 450 and 600 mean the heating treatment temperature (°C); BL: bleached samples.

Table S3. Surface elemental compositions and surface area analysis of hydrochars and pyrochars.

	Total C (%)	C-C (%)	C-O (%)	C=O (%)	COOH (%)	O (%)	N (%)	Si (%)	(O+N)/C
HSS250	79.08	87.78	7.42	2.18	2.62	17.04	3.11	0.78	0.21
PSS250	77.74	83.79	10.81	1.80	3.60	19.08	2.69	0.49	0.22
PSS450	64.47	87.57	4.52	4.52	3.39	30.74	3.37	1.42	0.42
PSS600	71.66	83.09	10.33	2.82	3.76	24.46	3.40	0.48	0.31
HPL250	57.26	88.57	5.24	4.29	1.90	30.08	4.77	7.88	0.49
PPL250	54.01	76.71	9.66	11.93	1.70	36.36	7.84	1.80	0.67
PPL450	64.56	81.88	8.77	5.26	4.09	28.99	3.68	2.77	0.40
PPL600	62.42	79.14	9.82	6.13	4.91	31.01	2.27	4.30	0.42

The polarity index ((O+N)/C) of individual samples was calculated from the atomic ratio of (O+N) and C. Note that H and P represent hydrochars and pyrochars, respectively; SS and PL refer to the biochars obtained from swine solids and poultry litter, respectively; 250, 450 and 600 mean the heating treatment temperature (^{o}C).

Table S4. Functional groups from the ^{13}C NMR spectra of hydrochars and pyrochars

Sample	Alkyl 0-45 ppm	Methoxyl 45-63 ppm	Carbohydrate 63-108 ppm	Aryl 108-148 ppm	O-Aryl 148-165 ppm	Carboxyl 165-190 ppm	Carbonyl 190-220 ppm	Aromatic C (%)	Aliphatic C (%)	Aromaticity (%)[a]	Aliphaticity (%)[b]	Aromatic $C_{(BL/OR)}$ (%)[c]
HSS250	48.3	2.9	2.3	34.4	5.3	4.4	2.4	39.7	53.5	42.6	57.4	78.4
PSS250	36.6	7.5	22.1	18.5	4.3	8.4	2.5	22.8	66.3	25.6	74.4	96.9
PSS450	10.1	1.0	2.7	71.4	9.3	4.0	1.4	80.7	13.9	85.3	14.7	54.6
PSS600	1.1	0.6	5.1	82.2	6.9	3.1	0.9	89.1	6.9	92.8	7.2	49.0
HPL250	35.5	3.9	2.4	43.7	7.5	4.6	2.5	51.1	41.8	55.0	45.0	79.1
PPL250	18.9	8.0	34.0	23.2	5.7	7.7	2.5	28.9	60.9	32.2	67.8	98.4
PPL450	5.1	1.1	4.7	77.7	5.7	3.6	2.1	83.4	10.9	88.5	11.5	64.5
PPL600	1.9	0.0	4.2	85.4	6.0	2.2	0.2	91.4	6.1	93.7	6.3	47.5
HSS250-BL	47.2	3.0	14.4	19.5	5.0	6.7	4.2	24.5	64.6	27.5	72.5	
PSS250-BL	36.1	7.8	36.0	4.0	1.6	9.9	4.6	5.6	79.9	6.5	93.5	
PSS450-BL	9.5	1.3	2.5	58.4	14.8	9.2	4.4	73.2	13.2	84.7	15.3	
PSS600-BL	1.0	2.4	4.2	72.2	11.6	6.9	1.7	83.8	7.6	91.7	8.3	
HPL250-BL	34.2	4.0	20.8	19.7	12.3	5.6	3.5	31.9	59.0	35.1	64.9	
PPL250-BL	19.8	8.9	44.8	5.2	7.6	10.4	3.3	12.8	73.5	14.9	85.1	
PPL450-BL	4.6	1.6	6.5	61.7	15.8	6.2	3.6	77.5	12.7	86.0	14.0	
PPL600-BL	1.8	1.2	4.0	79.4	7.4	4.6	1.6	86.8	7.0	92.5	7.5	

[a] Aromaticity (%) = 100 × aromatic C (108-165 ppm)/[aromatic C (108-165 ppm) + aliphatic C (0-108 ppm)]; [b] Aliphaticity (%) = 100 × aliphatic C (0-108 ppm)/[aromatic C (108-165 ppm) + aliphatic C (0-108 ppm)]; [c] Aromatic $C_{(BL/OR)}$ (%) = 100 – 100 × aromatic C (108-165 $ppm)_{(BL)}$ × [$OC\%_{(BL)}$ × $M_{(BL)}$]/[aromatic C (108-165 ppm) $_{(OR)}$ × OC% $_{(OR)}$ × M $_{(OR)}$], it represents the percentage of aromatic C removed by bleaching technique to the total aromatic C of original samples, where M is the weight of original (OR) or bleached (BL) samples (hydrochar or pyrochar). Note that H and P represent hydrochars and pyrochars, respectively; SS and PL refer to the biochars obtained from swine solids and poultry litter, respectively; 250, 450 and 600 mean the heating treatment temperature (^{o}C); BL: bleached sample.

Table S5. Freundlich isotherm parameters and calculated concentration-dependent distribution coefficients (logK_d and logK_{oc}) of pyrene (PYE)

Samples	K_F	logK_F	logK_{FOC}	n	N^a	R^2	logK_d	logK_{oc}^b		
							$C_e = 0.01S_w$	$C_e = 0.01S_w$	$C_e = 0.1S_w$	$C_e = 1S_w$
HSS250	905.60	2.96	3.22	0.77	20	0.972	5.93	6.19	5.97	5.74
PSS250	185.62	2.27	2.56	1.00	20	0.978	5.27	5.56	5.56	5.55
PSS450	346.06	2.54	2.91	0.51	20	0.976	5.48	5.85	5.36	4.87
PSS600	278.59	2.44	2.80	0.37	18	0.962	5.36	5.71	5.08	4.44
HPL250	511.49	2.71	3.12	0.74	20	0.972	5.67	6.08	5.82	5.56
PPL250	91.07	1.96	2.35	0.86	20	0.992	4.94	5.33	5.19	5.04
PPL450	219.37	2.34	2.77	0.52	20	0.971	5.28	5.70	5.22	4.74
PPL600	274.84	2.44	2.85	0.45	20	0.940	5.37	5.78	5.23	4.68

[a] Number of data; K_{oc}^b is the organic carbon (OC) normalized sorption distributed coefficient (K_d); S_w: aqueous solubility of pyrene (PYE). Note that H and P represent hydrochars and pyrochars, respectively; SS and PL refer to the biochars obtained from swine solids and poultry litter, respectively; 250, 450 and 600 mean the heating treatment temperature (^oC).

Table S6. Freundlich isotherm parameters and calculated concentration-dependent distribution coefficients (logK_d and logK_{oc}) of triclosan (TCS)

Samples	K_F	logK_F	logK_{FOC}	n	N^a	R^2	logK_d	log$K_{oc}{}^b$		
							$C_e = 0.01S_w$	$C_e = 0.01S_w$	$C_e = 0.1S_w$	$C_e = 1S_w$
HSS250	329.50	2.52	2.79	0.79	12	1.000	5.09	5.36	5.15	4.94
PSS250	27.10	1.43	1.73	0.79	12	0.995	4.02	4.31	4.10	3.90
PSS450	185.17	2.27	2.64	0.54	14	0.913	4.34	4.72	4.25	3.79
PSS600	584.40	2.77	3.12	0.37	14	0.798	4.50	4.85	4.22	3.59
HPL250	220.86	2.34	2.75	0.75	14	1.000	4.85	5.26	5.01	4.76
PPL250	32.36	1.51	1.90	0.83	14	1.000	4.16	4.55	4.38	4.20
PPL450	195.21	2.29	2.72	0.52	14	0.878	4.32	4.75	4.26	3.78
PPL600	340.25	2.53	2.94	0.48	14	0.840	4.49	4.90	4.38	3.86

[a] Number of data; $K_{oc}{}^b$ is the organic carbon (OC) normalized sorption distributed coefficient (K_d); S_w: aqueous solubility of triclosan (TCS). Note that "H and P" represent hydrochars and pyrochars, respectively; SS and PL refer to the biochars obtained from swine solids and poultry litter, respectively; 250, 450 and 600 mean the heating treatment temperature (^oC).

Table S7. Freundlich isotherm parameters and calculated concentration-dependent distribution coefficients (logK_d and logK_{oc}) of estrone (E1)

amples	K_F	logK_F	logK_{FOC}	n	N^a	R^2	logK_d	log$K_{oc}{}^b$		
							$C_e = 0.01S_w$	$C_e = 0.01S_w$	$C_e = 0.1S_w$	$C_e = 1S_w$
HSS250	100.48	2.00	2.27	0.80	13	0.984	4.51	4.78	4.58	4.38
PSS250	1.71	0.23	0.53	0.86	14	0.999	2.90	3.19	3.05	2.92
PSS450	26.38	1.42	1.80	0.53	14	0.999	3.26	3.63	3.16	2.69
PSS600	665.18	2.82	3.17	0.22	14	0.992	3.89	4.24	3.46	2.68
HPL250	51.88	1.71	2.12	0.76	13	1.000	4.13	4.53	4.29	4.06
PPL250	4.77	0.68	1.07	0.75	14	0.996	3.06	3.45	3.20	2.95
PPL450	88.95	1.95	2.38	0.35	14	0.994	3.34	3.76	3.11	2.46
PPL600	460.47	2.66	3.07	0.22	14	0.989	3.74	4.15	3.37	2.59

[a] Number of data; $K_{oc}{}^b$ is the organic carbon (OC) normalized sorption distributed coefficient (K_d); S_w: aqueous solubility of estrone (E1). Note that H and P represent hydrochars and pyrochars, respectively; SS and PL refer to the biochars obtained from swine solids and poultry litter, respectively; 250, 450 and 600 mean the heating treatment temperature (^{o}C).

Table S8. Freundlich isotherm parameters and calculated concentration-dependent distribution coefficients (logK_d and logK_{oc}) of carbamazepine (CBZ)

Samples	K_F	logK_F	logK_{FOC}	n	N^a	R^2	logK_d	logK_{oc}[b]		
							$C_e = 0.01S_w$	$C_e = 0.01S_w$	$C_e = 0.1S_w$	$C_e = 1S_w$
HSS250	61.48	1.79	2.06	0.76	14	1.000	4.04	4.31	4.06	3.82
PSS250	0.22	-0.66	-0.37	0.91	12	0.995	2.05	2.34	2.25	2.15
PSS450	28.74	1.46	1.83	0.38	14	0.957	2.53	2.91	2.28	1.66
PSS600	91.30	1.96	2.31	0.27	12	0.917	2.72	3.07	2.34	1.61
HPL250	31.60	1.50	1.91	0.77	14	1.000	3.78	4.19	3.95	3.72
PPL250	0.90	-0.04	0.35	0.79	10	0.997	2.29	2.68	2.47	2.25
PPL450	24.34	1.39	1.81	0.36	14	0.909	2.42	2.85	2.21	1.57
PPL600	145.61	2.16	2.57	0.23	14	0.942	2.80	3.21	2.45	1.68

[a] Number of data; K_{oc}[b] is the organic carbon (OC) normalized sorption distributed coefficient (K_d); S_w: aqueous solubility of carbamazepine (CBZ). Note that H and P represent hydrochars and pyrochars, respectively; SS and PL refer to the biochars obtained from swine solids and poultry litter, respectively; 250, 450 and 600 mean the heating treatment temperature (^oC).

Table S9. Freundlich isotherm parameters and calculated concentration-dependent distribution coefficients (logK_d and logK_{oc}) of acetaminophen (AMP)

Samples	K_F	logK_F	logK_{FOC}	n	N^a	R^2	logK_d	logK_{oc}[b]		
							$C_e = 0.01S_w$	$C_e = 0.01S_w$	$C_e = 0.1S_w$	$C_e = 1S_w$
HSS250	3.68	0.57	0.83	0.83	14	0.993	2.70	2.97	2.80	2.63
PSS250	0.06	-1.20	-0.91	0.89	12	1.000	1.26	1.55	1.45	1.34
PSS450	1.50	0.18	0.55	0.67	12	1.000	1.47	1.85	1.51	1.18
PSS600	14.70	1.17	1.52	0.53	14	0.999	1.77	2.12	1.65	1.18
HPL250	6.75	0.83	1.24	0.72	13	0.999	2.39	2.79	2.51	2.23
PPL250	0.13	-0.90	-0.51	0.84	14	0.999	1.28	1.67	1.51	1.35
PPL450	3.13	0.50	0.92	0.58	14	0.983	1.37	1.79	1.38	0.96
PPL600	8.68	0.94	1.35	0.57	14	0.997	1.76	2.17	1.75	1.32

[a] Number of data; K_{oc}[b] is the organic carbon (OC) normalized sorption distributed coefficient (K_d); S_w: aqueous solubility of acetaminophen (AMP). Note that H and P represent hydrochars and pyrochars, respectively; SS and PL refer to the biochars obtained from swine solids and poultry litter, respectively; 250, 450 and 600 mean the heating treatment temperature (^{o}C).

Description of the surface area (SA) of hydrochars and pyrochars:

N_2-SA values of hydrochars and pyrochars ranged from 1.9 to 2.8 m^2/g and 1.2 to 14.3 m^2/g, respectively (Table S2). Except for PSS450, N_2-SA value generally tended to be high when the ash content of the sample was high (Table S2) and low for the samples high in OC content, such as HSS250 and PSS250, which was consistent with other reports.[1] The CO_2-SA of all investigated biochars was much higher than their respective N_2-SA values (Table S2). In line with our previous research,[2] CO_2-SA values of pyrochars were positively linked with their aryl C and aromaticity (Figure S3e), but negatively related to alkyl C and aliphaticity (Figure S3f), validating that the micropores within pyrochars were probably derived from their aromatic matrix.

Reference:

1. Ran, Y.; Yang, Y.; Xing, B.; Pignatello, J. J.; Kwon, S.; Su, W.; Zhou, L., Evidence of micropore filling for sorption of nonpolar organic contaminants by condensed organic matter. *J. Environ. Qual.* **2013,** *42*, (3), 806-814.

2. Han, L.; Sun, K.; Jin, J.; Wei, X.; Xia, X.; Wu, F.; Gao, B.; Xing, B., Role of structure and microporosity in phenanthrene sorption by natural and engineered organic matter. *Environ. Sci. Technol.* **2014,** *48*, 11227-11234.