Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Material

Sustainable hierarchically porous carbons from bio-oil to remove emerging contaminant

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1. Additional information: Materials and methods

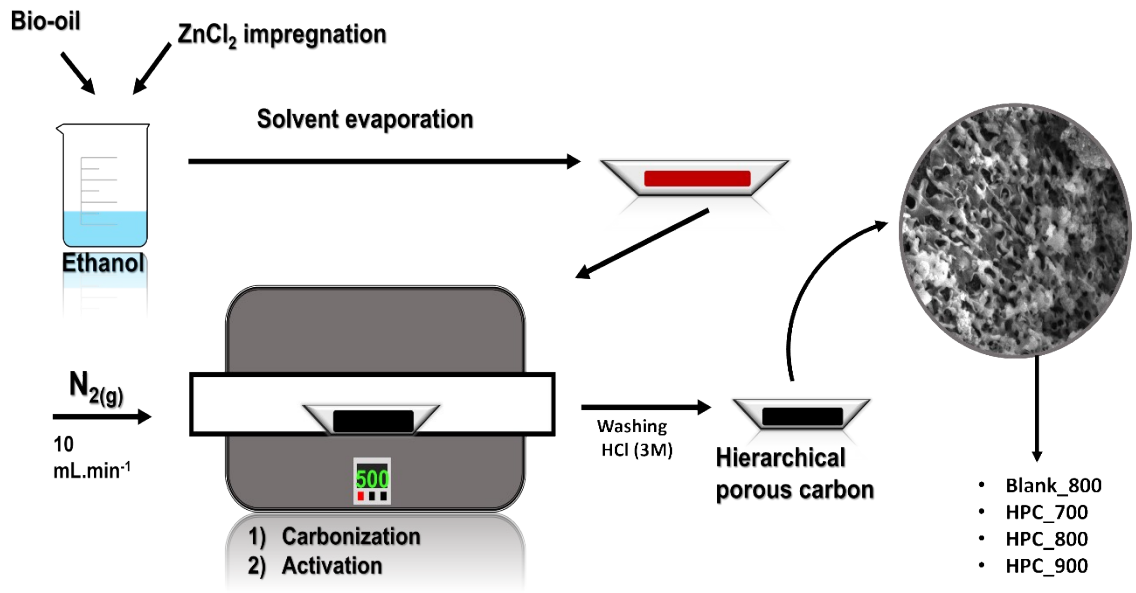

Figure S1 - Schematic representation of the hierarchical porous carbon synthesis from bio-oil as biomass.

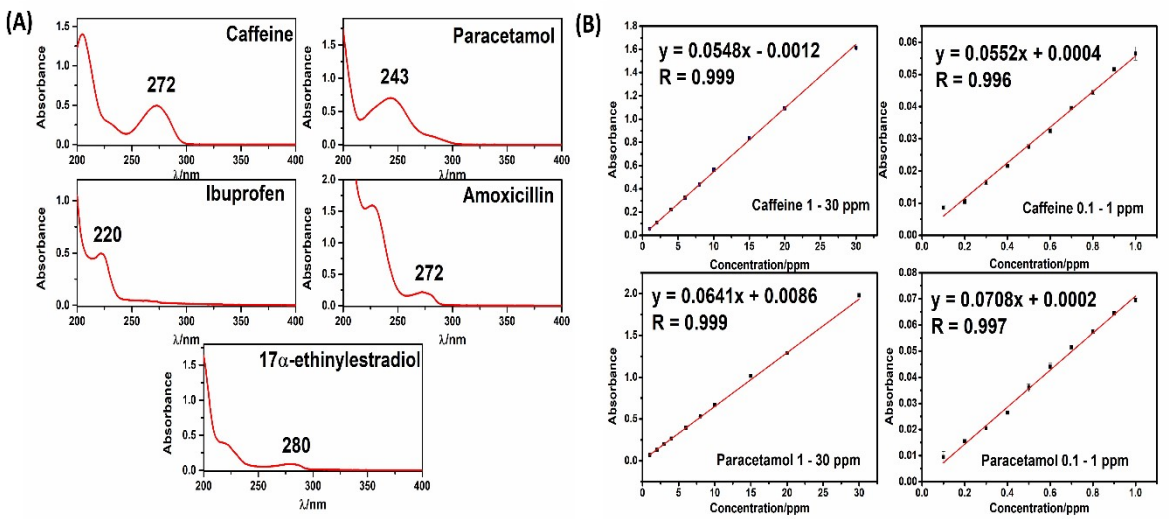

Figure S2 UV-Vis spectra of emerging contaminants (a) and analytical curve for the contaminants caffeine and paracetamol (b).

2. Experimental Section

2.1. Kinectis and Isotherms studies

The kinetic study was performed to PAR and CAF under same conditions of mass, volume and concentration as the contact test, between 1 minute and 24 hours. The pseudo-first-order, pseudo-second-order and Elovich models were applied to understand adsorption kinetics (Equations 1, 2 and 3 respectively)[1–6].

$$q_t = q_e\left(1 - e^{-K1t}\right) \quad (1)$$

$$q_t = \frac{q_e^2 K_2 t}{1 + q_e K_2 t} \quad (2)$$

$$q_t = \frac{1}{\beta}\ln\left(1 + \alpha\beta t\right) \quad (3)$$

where t is time (min), K_1 is the pseudo-first order adsorption rate constant (min^{-1}), K_2 is the pseudo-second model adsorption rate constant ($g.mg^{-1}.min^{-1}$), q_e is the amount adsorbed at equilibrium ($mg.g^{-1}$), q_t is the amount adsorbed at time t (min). α and β are Elovich constants ($mg.g^{-1}.min^{-1}$) ($g.mg^{-1}$) respectively.

The isotherm study was performed under same conditions of mass, volume, stirring, with the variation of concentration from 10 ppm to 1000 ppm of CAF and PAR. The system was stirred for 3 h at 21 ºC. The experimental data were fitted using Langmuir, Freundlich and Sips isotherms models (Equations 5, 6 and 7 respectively). [7–9]

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

$$q_e = K_F C_e^{1/n_F} \quad (5)$$

$$q_e = \frac{q_m K_s C_e^{1/ns}}{1 + K_s C_e^{1/ns}} \quad (6)$$

where q_e is the amount of contaminant adsorbed (mg.g^{-1}) at equilibrium, Q_m is the maximum adsorption capacity of a monolayer (mg.g^{-1}), K_L is the Langmuir constant (L.mg^{-1}), C_e is the concentration of contaminant at equilibrium (mg.L^{-1}), K_F (mg$^{1-(1/n_F)}$.L$^{1/n_F}$.g^{-1}) is the Freundlich constant relating to the relative capacity of adsorption (mg.g^{-1}), n_F is a constant relating to the intensity of adsorption, K_S is the Sips adsorption constant (L.mg^{-1})$^{1/nS}$, and $1/n_S$ is the Sips exponent (non-dimensional).

3. Supplementary Figures and Tables from the characterization

Tables

Table S1. Adjustment results from the BET method for all materials. Selecting range: 0.05 to 0.25 $p.p_0^{-1}$.

	S_{BET}/m^2. g^{-1}	Intercept/g^{-1}	Slope/g^{-1}	R	C constant
Blank_800	0.993	4.45x10^{-2}	3062.597	0.998	7.881
HPC_700	831.754	9.896x10^{-3}	4.177	0.999	423.091
HPC_800	835.779	1.22x10^{-2}	4.155	0.999	341.565
HPC_900	764.455	1.33x10^{-2}	4.542	0.999	341.474

Table S2. Adjustment results from the t-plot method for all materials. Selecting range: 0.07 to 0.30 $p.p_0^{-1}$.

	Slope	Intercept	R	Micropore Area/$m^2.g^{-1}$	External Area/$m^2.g^{-1}$	Micropore Volume/$cm^3.g^{-1}$
Blank_800	0.102	-0.257	0.999	0	0.993	0
HPC_700	40.939	58.188	0.999	198.508	633.247	0.090
HPC_800	42.54	52.310	0.999	179.092	656.687	0.081
HPC_900	38.157	50.497	0.999	174.240	590.216	0.078

Table S3. Elemental analysis obtained by EDS of the synthesized materials.

Sample	%C	%O	%Fe	%Si	%K	%Zn	%Cl	%S	%Ca	%Al
Blank_800	72.60	18.00	3.20	1.52	1.78	0.30	1.14	0.12	1.02	0.32
HPC_700	84.03	7.47	-	1.50	0.14	2.28	3.70	0.44	0.18	-
HPC_800	84.88	13.02	-	0.32	-	0.58	0.88	0.23	-	0.09
HPC_900	86.58	10.79	-	0.30	-	0.54	1.40	0.28	-	0.12

By %w:w

Table S4. Carbon, Nitrogen, Hydrogen and sulfur contents obtained by elemental analysis.

Sample	%C	%N	%H	%S
Bio-oil	58.34 ± 0.34	1.10 ± 0,01	6.72 ± 0.04	0.16 ± 0,01

Table S5. Band D, G and I_D/I_G ratio values for all materials obtained.

Sample	D band/cm^{-1}	G band/cm^{-1}	I_D/I_G
Blank_800	1351	1585	0.94
HPC_700	1328	1586	1.21
HPC_800	1328	1585	1.26
HPC_900	1327	1586	1.32

Table S6 D and G Band values, ID/IG ratio, and statistical parameters by Lorentz adjustment of HPCs synthesized from bio-oil.

Sample	D Band /cm^{-1}	G Band/cm^{-1}	I_D/I_G	R^2	X^2
Blank_800	1337	1573	1.64	0.999	237.900
HPC_700	1327	1571	2.75	0.999	46.850
HPC_800	1326	1570	3.04	0.999	46.005
HPC_900	1324	1572	3.54	0.999	15.091

Table S7 Results of mathematical adjustments obtained from the adsorption kinetics of contaminants.

Sample	Contaminant	Pseudo-First-Order (PFO)	PseudoSecond-Order (PSO)	Elovich
HPC_700	Caffeine	R^2 = 0.991 X^2 = 0.051 q_e = 8.638 k_1 = 2.095	R^2 = 0.993 X^2 = 0.039 q_e = 8.694 k_2 = 0.752	R^2 = 0.984 X^2 = 0.087 α = 3.492x10^{28} β = 8.395
	Paracetamol	R^2 = 0.984 X^2 = 0.126 q_e = 10.248 k_1 = 1.538	R^2 = 0.995 X^2 = 0.033 q_e = 10.394 k_2 = 0.300	R^2 = 0.983 X^2 = 0.138 α = 8.48x10^{11} β = 3.229
HPC_800	Caffeine	R^2 = 0.972 X^2 =0.051 q_e = 8.304 k_1 = 0.242	R^2 = 0.992 X^2 = 0.0051 q_e = 8.576 k_2 = 0.054	R^2 = 0.885 X^2 = 0.800 α = 573.11 β = 1.409
	Paracetamol	R^2 = 0.927 X^2 = 0.732 q_e = 9.923 k_1 = 0.185	R^2 = 0.975 X^2 = 0.251 q_e = 10.265 k_2 = 0.034	R^2 = 0.913 X^2 = 0.868 α = 238.76 β = 1.068
HPC_900	Caffeine	R^2 = 0.983 X^2 = 0.101 q_e = 8.291 k_1 = 0.584	R^2 = 0.992 X^2 = 0.048 q_e = 8.538 k_2 = 0.113	R^2 = 0.898 X^2 = 0.636 α = 7.81x10^4 β = 2.016
	Paracetamol	R^2 = 0.974 X^2 = 0.276 q_e = 10.339 k_1 = 0.248	R^2 = 0.987 X^2 = 0.145 q_e = 10.649 k_2 = 0.046	R^2 = 0.869 X^2 = 1.404 α = 1139.1 β =1.183

R^2: correlation coefficient. X^2: Nonlinear Chi Square Test. k_1: pseudo first-order constant (min^{-1}). k_2: pseudo second-order constant (g mg^{-1} min^{-1}); q_e: amount adsorved at equilibrium (mg.g^{-1}). α: Elovich constant (mg g^{-1} min^{-1}). β: Elovich constant (g.mg^{-1}).

Table S8 Results of mathematical adjustments obtained from the adsorption isotherms of contaminants.

Sample	Contaminant	Langmuir	Freundlich	Sips
HPC_700	Paracetamol	R^2 = 0.945 X^2 = 134.70 q_m = 140.25 K_L = 0.067	R^2 = 0.931 X^2 = 167.79 $1/n_F$ = 0.225 K_F = 34.956	R^2 = 0.987 X^2 = 30.02 **q_m = 173.74** K_S = 0.153 $1/n_S$ = 0.538
	Caffeine	R^2 = 0.957 X^2 = 128.02 q_m = 150.09 K_L = 0.051	R^2 = 0.929 X^2 = 211.32 $1/n_F$ = 0.246 K_F = 31.699	R^2 = 0.980 X^2 = 59.04 **q_m = 176.31** K_S = 0.111 $1/n_S$ = 0.617
HPC_800	Paracetamol	R^2 = 0.946 X^2 = 258.84 q_m = 168.02 K_L = 0.046	R^2 = 0.984 X^2 = 73.02 $1/n_F$ = 0.252 K_F = 37.526	R^2 = 0.995 X^2 = 24.20 **q_m = 309.82** K_S = 0.106 $1/n_S$ = 0.417
	Caffeine	R^2 = 0.962 X^2 = 112.44 q_m = 154.16 K_L = 0.075	R^2 = 0.903 X^2 = 286.18 $1/n_F$ = 0.225 K_F = 37.785	R^2 = 0.975 X^2 = 79.76 **q_m = 169.14** K_S = 0.127 $1/n_S$ = 0.695
HPC_900	Paracetamol	R^2 = 0.903 X^2 = 537.181 q_m = 187.66 K_L = 0.086	R^2 = 0.956 X^2 = 240.50 $1/n_F$ = 5.054 K_F = 51.847	R^2 = 0.977 X^2 = 132.14 **q_m = 279.96** K_S =0.183 $1/n_S$ = 2.660
	Caffeine	R^2 = 0.975 X^2 = 82.18 q_m = 170.88 K_L = 0.152	R^2 = 0.902 X^2 = 322.95 $1/n_F$ = 0.188 K_F = 53.879	R^2 = 0.984 X^2 = 51.80 **q_m =183.31** K_S = 0.206 $1/n_S$ = 0.700

R^2: correlation coefficient. X^2: Nonlinear Chi Square Test. q_m: maximum adsorption capacity ($mg.g^{-1}$). K_L: Langmuir constant ($L.mg^{-1}$). K_F: Freundlich constant($mg^{(1-1/n)}$ $L^{1/n}$ g^{-1}) e $1/n_F$: constant related to surface heterogeneity. 1/ns : Sips constant (dimensionless). e K_s: Sips adsorption constant $(L.mg^{-1})^{1/ns}$.

Figures

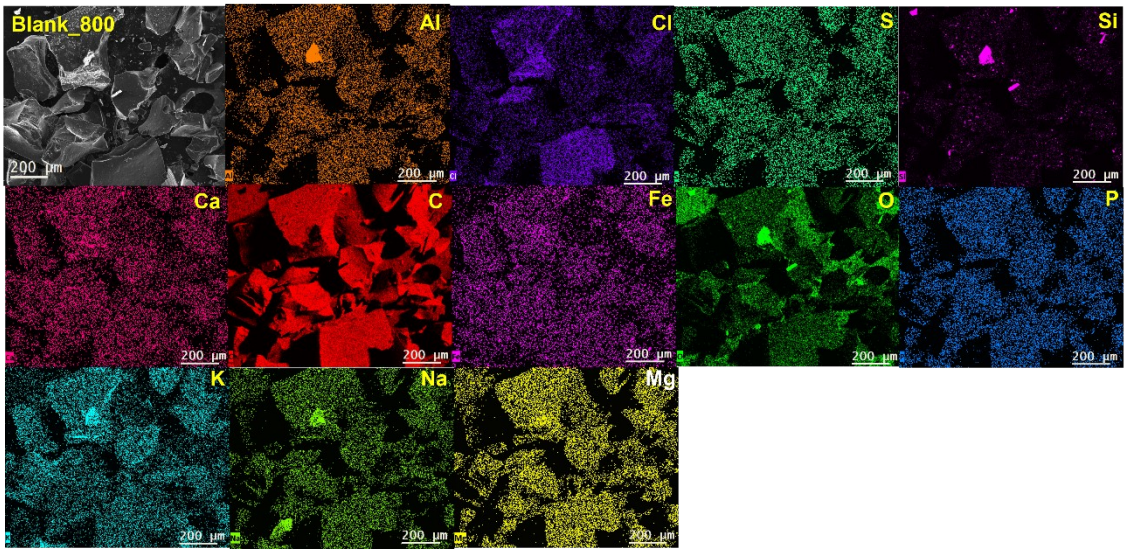

Figure S3 SEM-EDS elemental mapping of Blank_800.

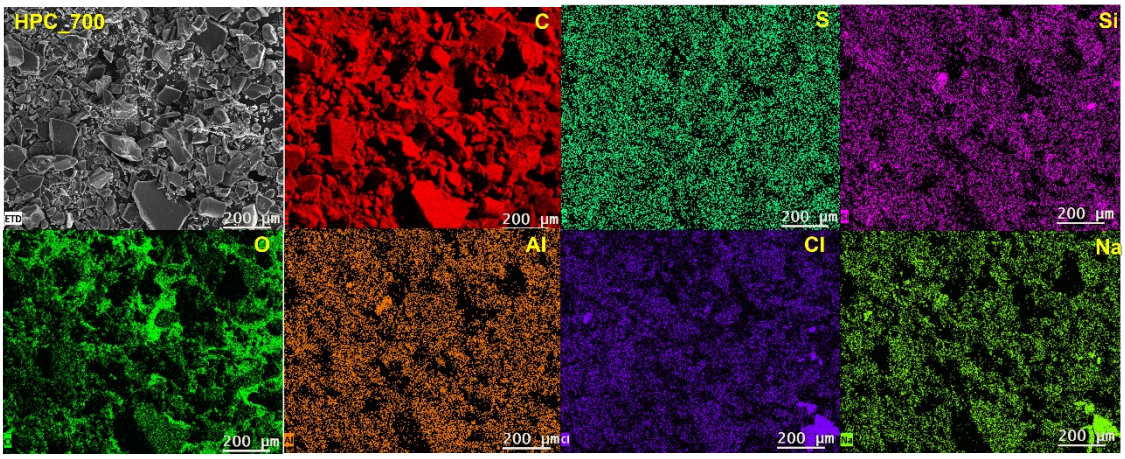

Figure S4 SEM-EDS elemental mapping of HPC_700.

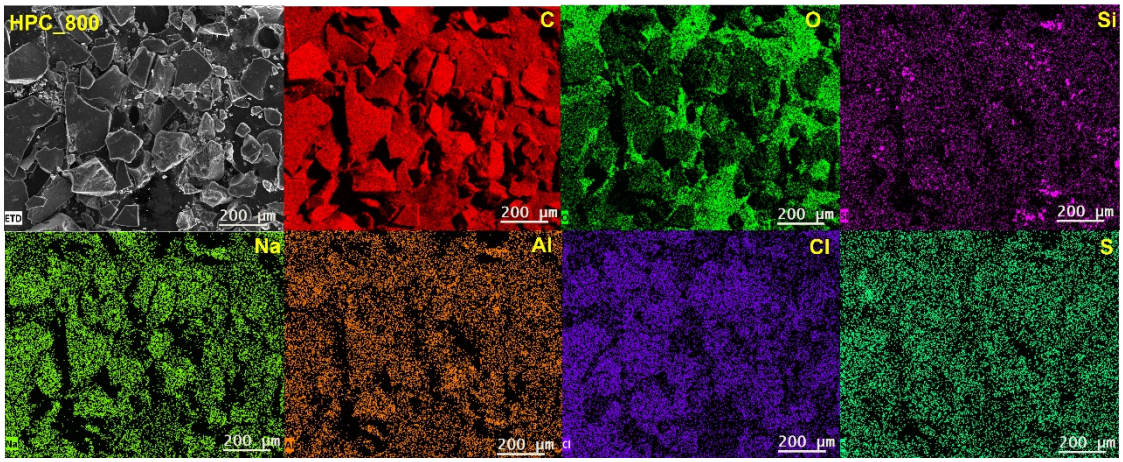

Figure S5 SEM-EDS elemental mapping of HPC_800.

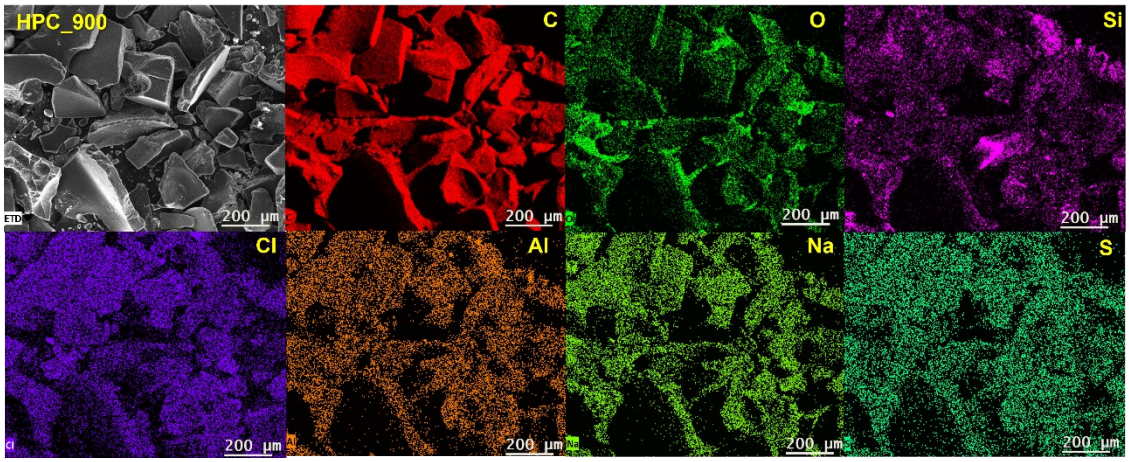

Figure S6 SEM-EDS elemental mapping of HPC_900.

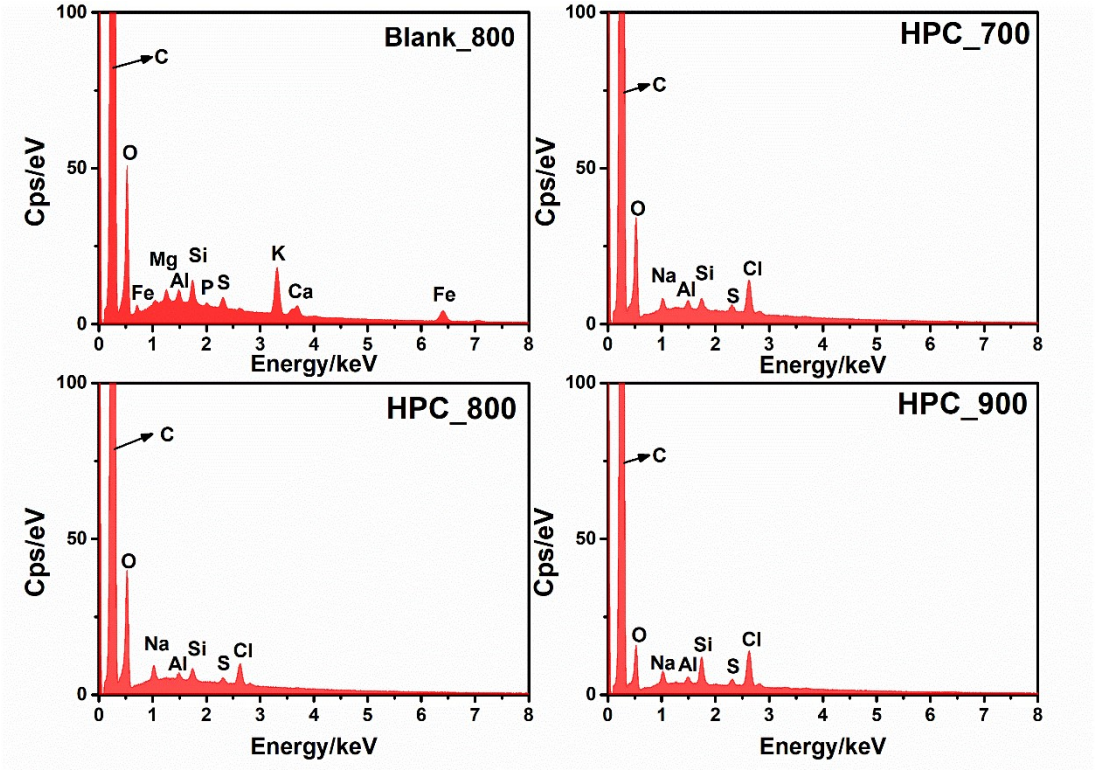

Figure S7 EDS spectra of synthesized materials.

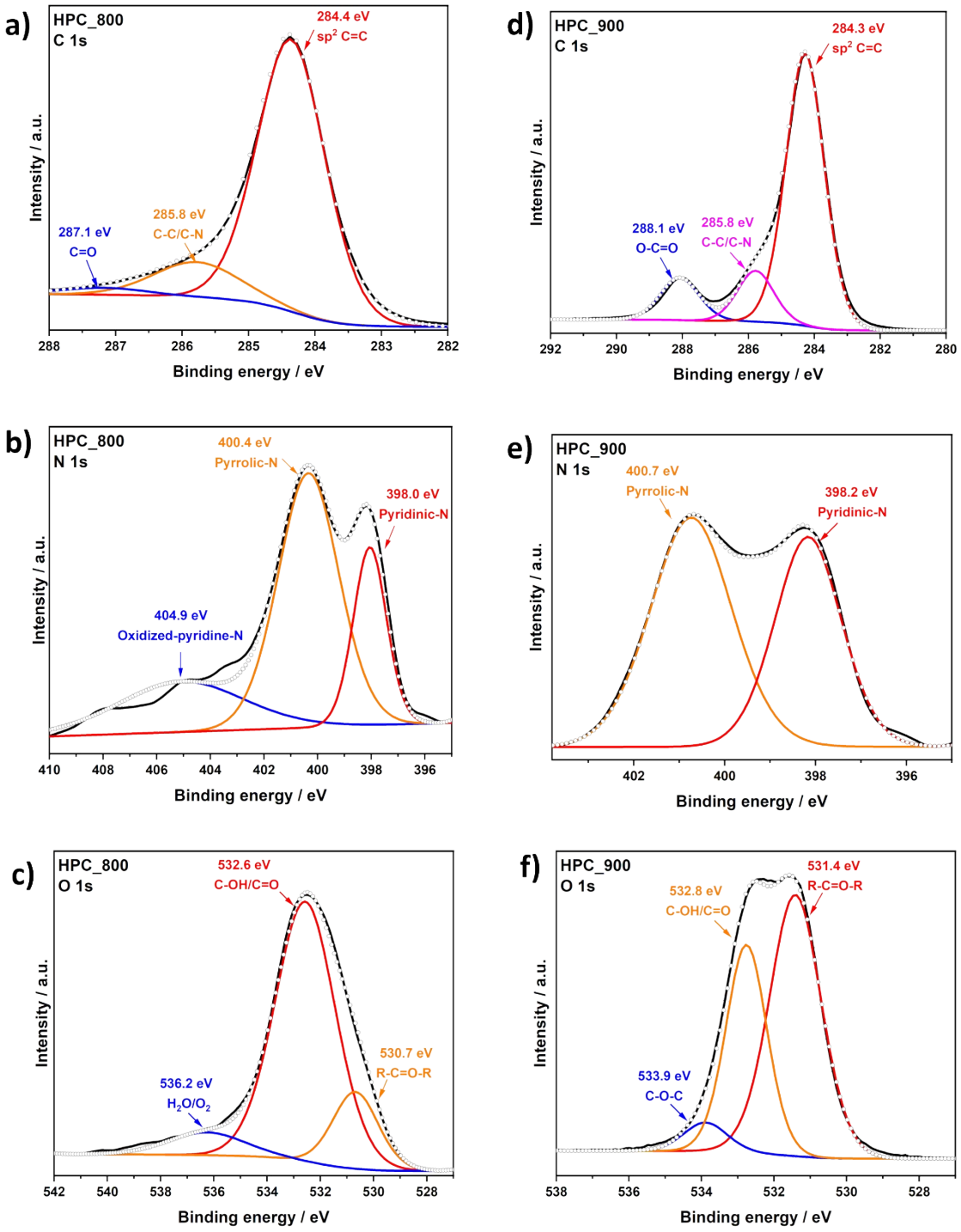

Figure S8 XPS spectra of synthesized materials (a-c) HPC_800 and (d-f) HPC_900.

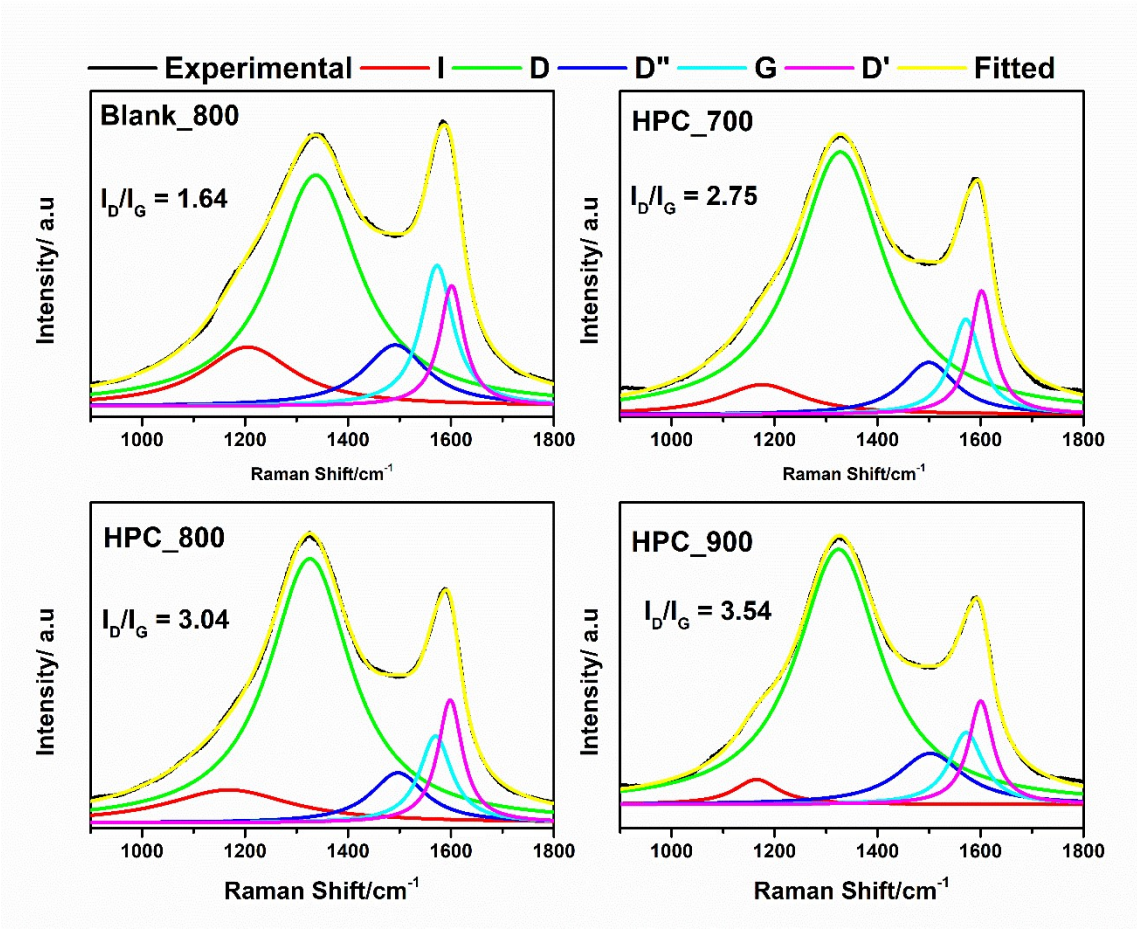

Figure S9 Raman spectra after deconvolution performed by Lorentz fit for HPC materials produced from bio-oil.

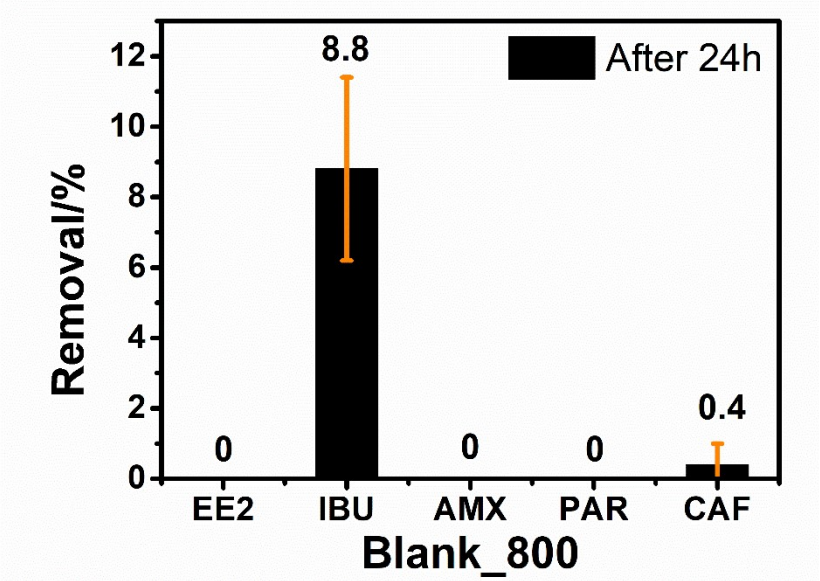

Figure S10 Evaluation of removals using Blank_800 as adsorbent in contact tests with contaminants: paracetamol (PAR). caffeine (CAF). ibuprofen (IBU). amoxicillin (AMX) and 17α-ethinylestradiol (EE2).

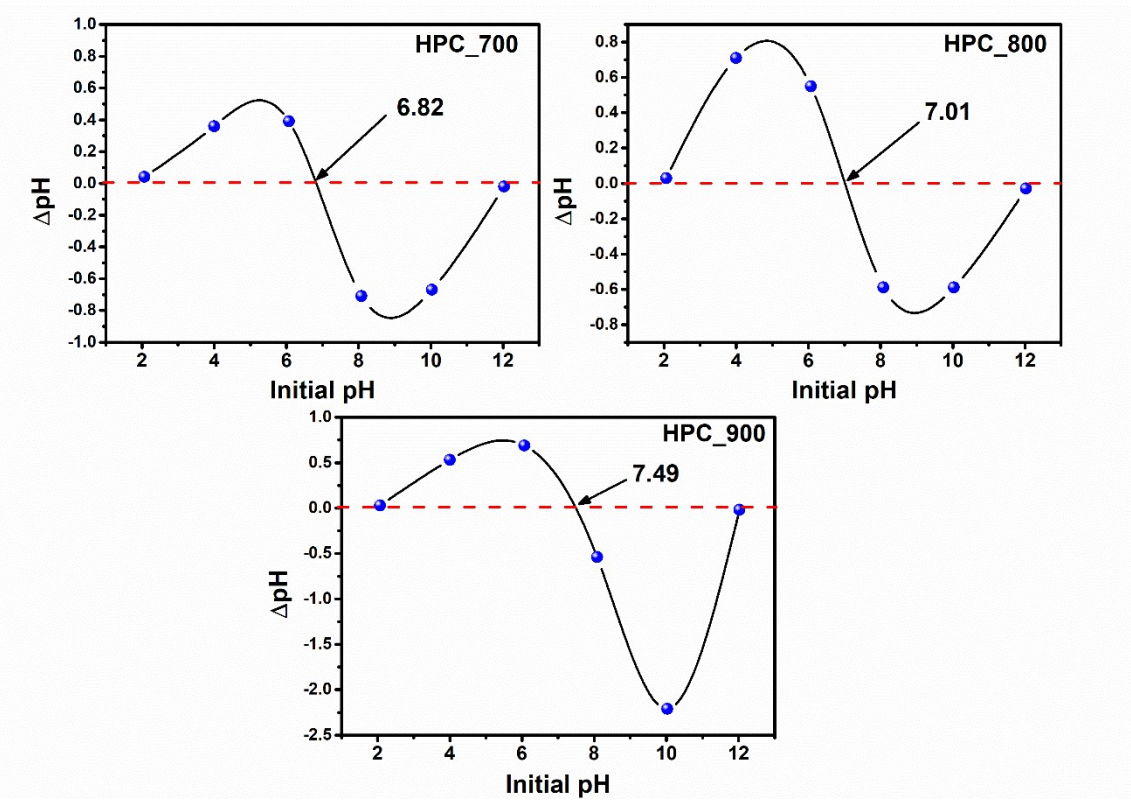

Figure S11 PCZ experiments performed on the synthesized HPC_T.

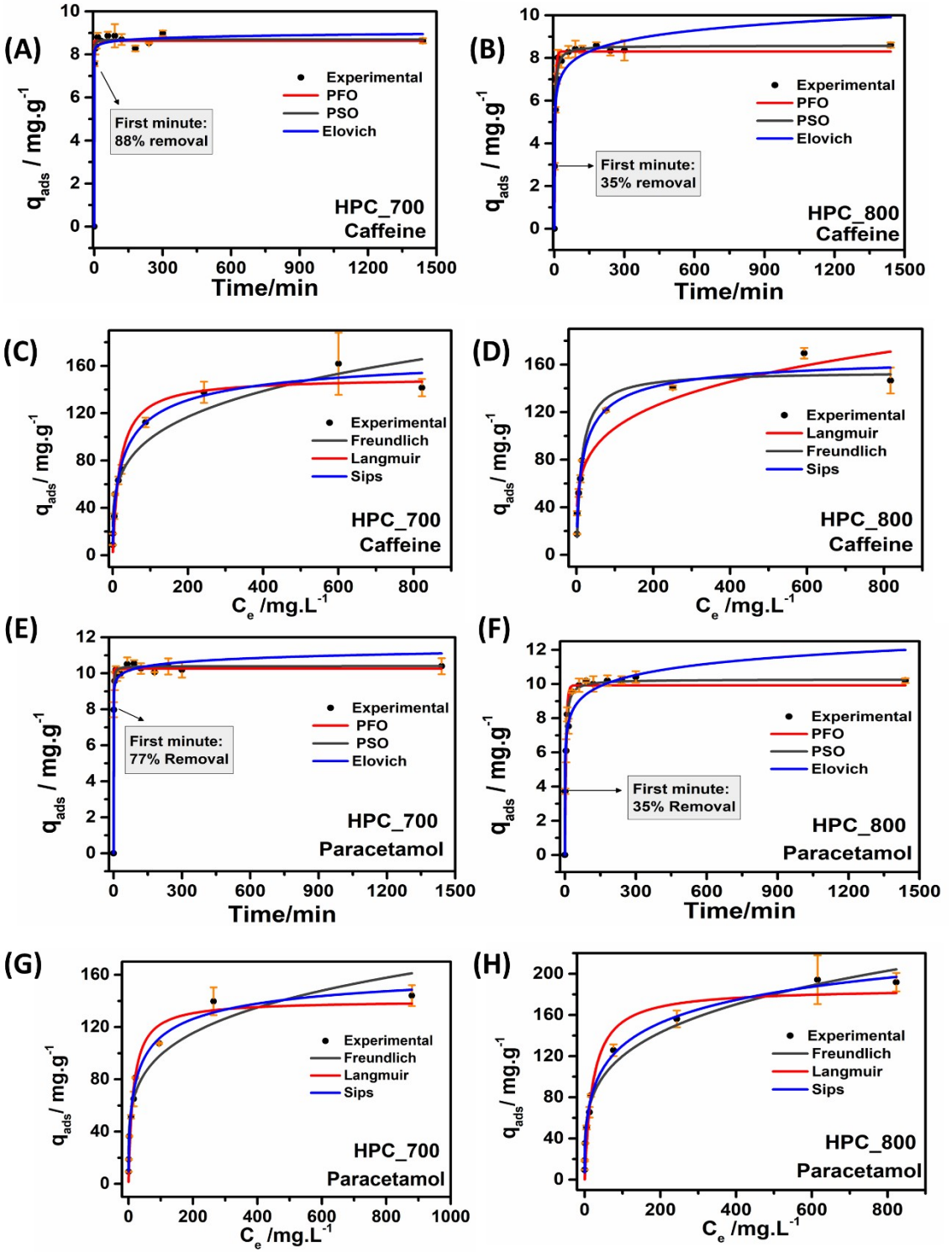

Figure S12 Caffeine adsorption kinetic curve using as adsorbent: HPC_700. HPC_800 (a-b) respectively. Caffeine adsorption isotherms using as adsorbent: HPC_700. HPC_800 (c-d) respectively. Paracetamol adsorption kinetic curve using as adsorbent: HPC_700. HPC_800 (e-f) respectively. Paracetamol adsorption isotherms using as adsorbent: HPC_700 and HPC_800 (g-h) respectively.

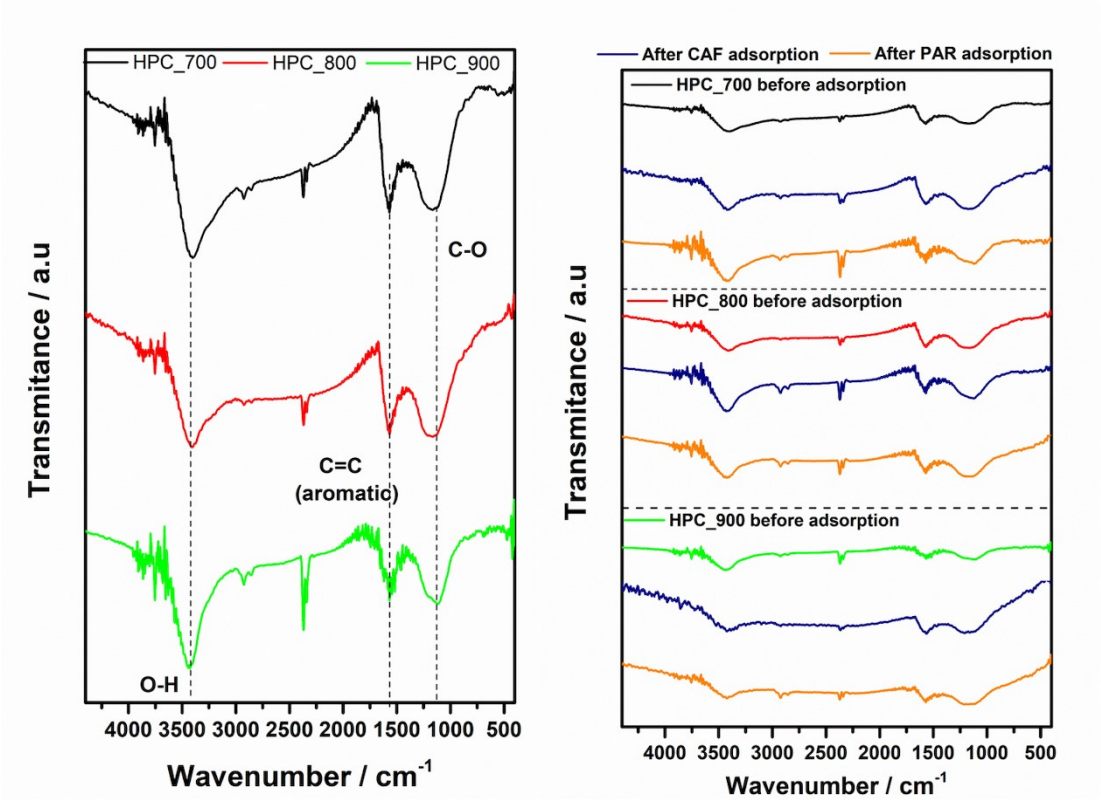

Figure S13. FTIR spectra of HPC_T synthetized (a) and HPC_T before and after adsorption of contaminants (PAR and CAF).

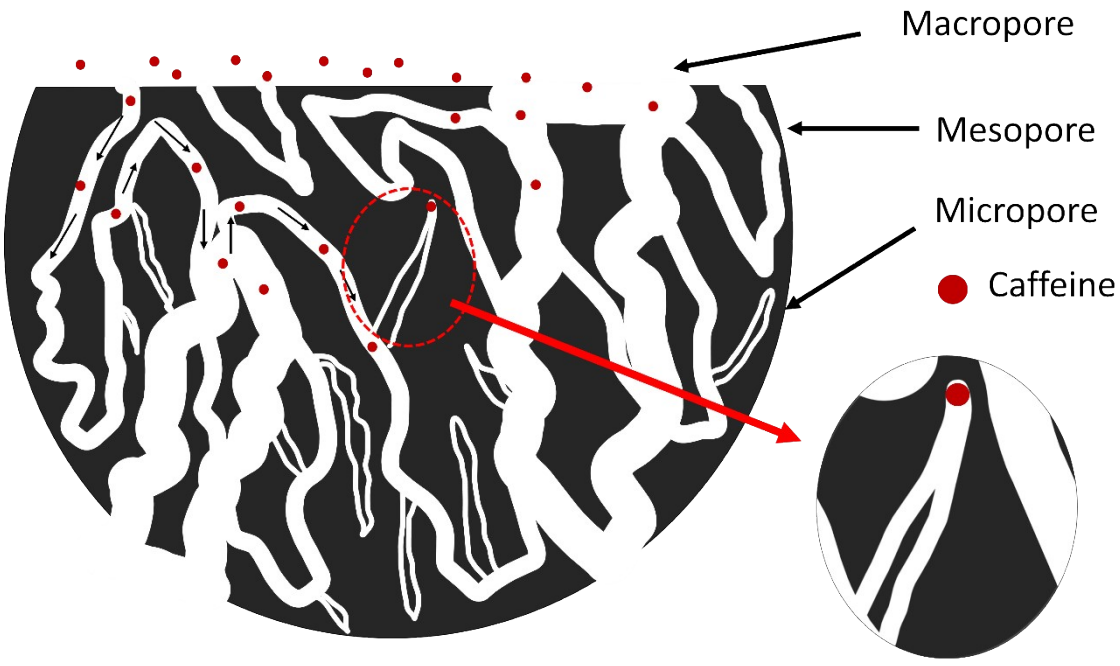

Figure S14 A schematic representation of the caffeine diffusion process through the pore network of HPC_T until its adsorption within the micropores.

4. References

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