Supplementary material for the paper

Title: The influence of surface chemistry of activated carbons on adsorption and freezing/melting processes

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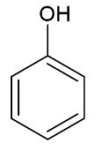
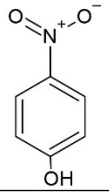
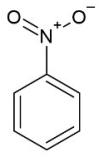
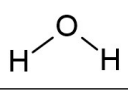
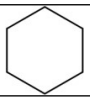
Table S1. Physicochemical properties of adsorbates.

Compound name	Phenol (P)	4-Nirophenol (4-NP)	Nitrobenzene (NB)
Molecular formula	C_6H_6O	$C_6H_5NO_3$	$C_6H_5NO_2$
Chemical formula*			
Molecular weight (g/mol)	94.11	139.11	123.11
Solubility in water (g/100 mL at 20 °C)	8.3	1.6	0.19
Solubility in cyclohexane (g/100 mL at 20°C)	1.5	<0.01	15
Ionization constant (pKa)	9.99	7.15	-
Melting point (°C)	40.5	113.0	5.7
Boiling point (°C)	181.7	210.9	279.0

*The molecule structures of adsorbate drawn up in ChemSketch/ACDLabs software (Toronto, Canada, USA)

Table S2. Physicochemical characteristics of diluents.

Compound name	Water (W)	Cyclohexane (CH)
Molecular formula	H_2O	C_6H_6
Molecular weight (g/mol)	18.02	84.16
Density (g/mL at 20 °C)	0.9982	0.7785
Polarity	Polar	Unpolar
Dielectric constant (20 °C)	80.1	2.02
Dipole moment (D)	1.84	0.00
Melting point (°C)	0	6.5
Boiling point (°C)	100	80.7
Chemical formula*		

*The molecule structures of diluentsdrawn up in ChemSketch/ACDLabs software (Toronto, Canada, USA)

Equations:

First-Order Equation and Pseudo-First-Order Equation (FOE and PFOE)

$$ln(c_{eq}-c)=ln(c_{eq}-c_o)-k_1t \quad or \quad ln(a_{eq}-a)=lna_{eq}-k_1t \tag{S1}$$

where c is the temporary concentration, a is the actual adsorbed amount, the o and eq subscripts are connected to the initial and equilibrium states, k_1 is the adsorption rate coefficient

Second-Order Equation and Pseudo-Second-Order Equation (SOE and PSOE)

$$a=a_{eq}\left[k_2t/(1+k_2t)\right] \tag{S2}$$

$$or\ t/a=\left(1/a_{eq}\right)(1/k_2+t) \text{ and } a=a_{eq}\left[k_2t/(1+k_2t)\right]$$

where $k_2 = k_{2a} \cdot a_{eq}$ and k_{2a} are the rate coefficients for pseudo-second-order kinetics[17,18]

1,2-Mixed-Order Equation (MOE)

$$F=a/a_{eq}=\frac{1-exp(-k_1t)}{1-f_2exp(-k_1t)} \text{ or } ln\left(\frac{1-F}{1-f_2F}\right)=-k_1t \tag{S3}$$

where F is the relative adsorption progress in time, $f_2<1$is the normalized share of the second-order process in the kinetics. In special cases, the MOE equation may be degraded to the simple kinetic equations of the first ($f_2=0$) and the second-order ($f_2=1$) type

Fractal-Like MOE Equation (f-MOE)

$$F=\frac{1-exp(-k_1t)^p}{1-f_2exp(-k_1t)^p} \tag{S4}$$

Multi-Exponential Equation (m-exp)

$$c=(c_o-c_{eq})\sum_{i=1}^{n}f_iexp(-k_it)+c_{eq} \quad \text{or} \quad c=c_0-c_ou_{eq}\sum_{i=1}^{n}f_i\left[1-exp(-k_it)\right] \tag{S5}$$

where i is the term of the m-exp equation, k_i is the rate coefficient and $u_{eq}=1-c_{eq}/c_o$ is the relative loss of adsorbate from the solution

Intraparticle Diffusion Model (IDM, Crank)

$$F=1-\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}exp\left(\frac{-\pi^2\cdot n^2\cdot D_a\cdot t}{r^2}\right) \tag{S6}$$

where r is the radius of the adsorbent particle, D_a is the effective diffusion coefficient:

$$D_a=\frac{D}{\tau_p\cdot(1+\rho\cdot K_H\cdot\varepsilon_p)} \tag{S7}$$

where D is the molecular diffusion coefficient, τ_p – the dimensionless pore tortuosity factor, ρ is the particle density, ε_p is the particle porosity, K_H – the Henry adsorption constant

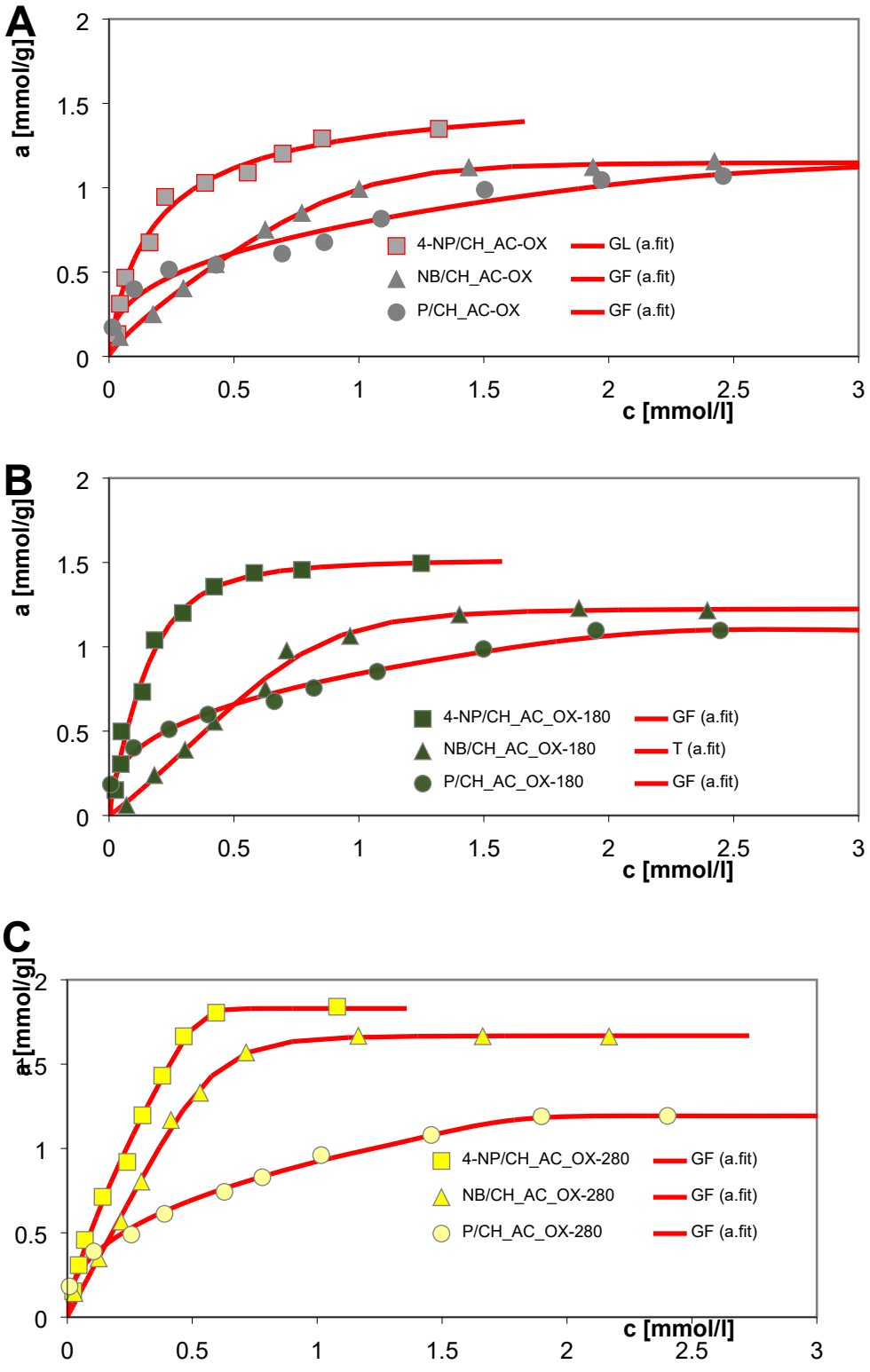
Pore Diffusion Model (PDM, McKay)

$$\frac{dF}{d\tau_s}=\frac{3\left(1-u_{eq}\cdot F\right)\cdot(1-F)^{\frac{1}{3}}}{1-B\cdot(1-F)^{\frac{1}{3}}} \tag{S8}$$

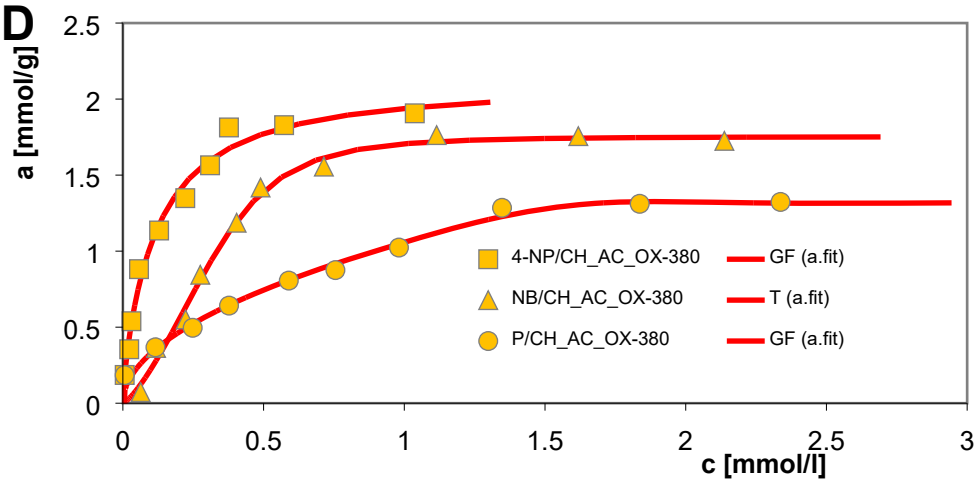
where u_{eq} is the relative adsorbate loss, the parameter $B = 1-1/B_i$, where$B_i=K_f/D_p$ is the Biot number, D_p is the pore diffusion coefficient, K_f is the external mass transfer coefficient, τ_s is the undersized model time:

$$\tau_s=\frac{1}{6\cdot u_{eq}}\left\{\left(2B-\frac{1}{b}\right)\cdot ln\left[\left|\frac{x^3+X^3}{1+X^3}\right|\right]+\frac{3}{a}ln\left[\left|\frac{x+X}{1+X}\right|\right]\right\}+\left\{arctan\left(\frac{2-X}{X\cdot\sqrt{3}}\right)\right\}-arctan\left(\frac{2\cdot x-X}{X\cdot\sqrt{3}}\right) \tag{S9}$$

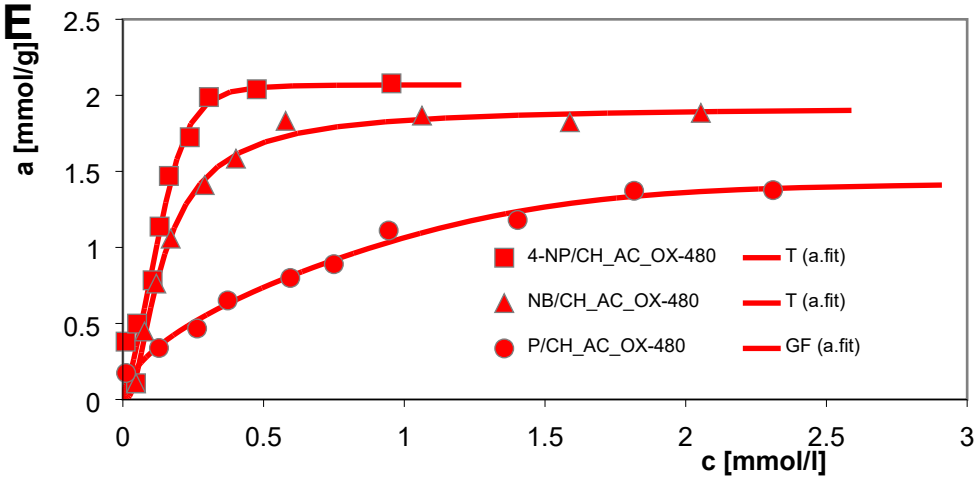
$$x = (1 - F)^{\frac{1}{3}}, b = \left(\frac{1}{1 - u_{eq}}\right)^{\frac{1}{3}} \quad \text{where} \quad {}^{23}. \tag{S10}$$



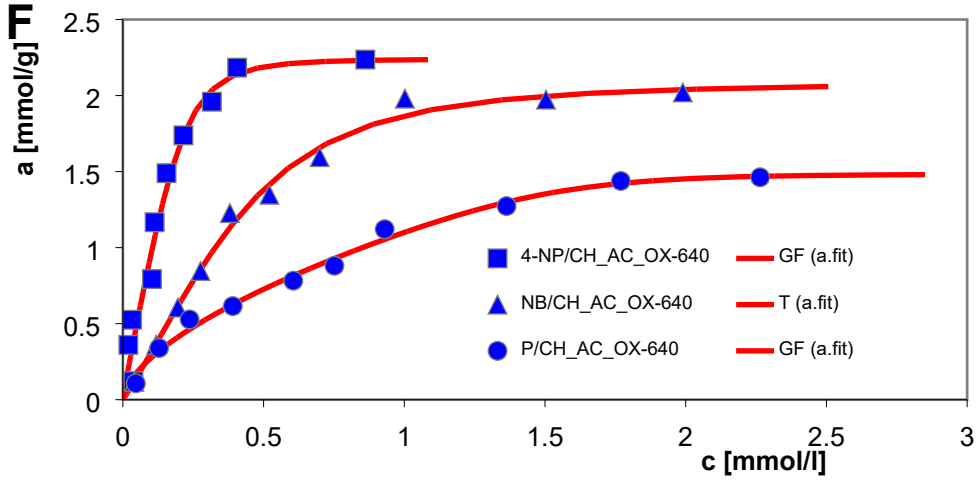
D


a [mmol/g]
c [mmol/l]
4-NP/CH_AC_OX-380
NB/CH_AC_OX-380
P/CH_AC_OX-380
GF (a.fit)
T (a.fit)
GF (a.fit)

E


a [mmol/g]
c [mmol/l]
4-NP/CH_AC_OX-480
NB/CH_AC_OX-480
P/CH_AC_OX-480
T (a.fit)
T (a.fit)
GF (a.fit)

F


a [mmol/g]
c [mmol/l]
4-NP/CH_AC_OX-640
NB/CH_AC_OX-640
P/CH_AC_OX-640
GF (a.fit)
T (a.fit)
GF (a.fit)

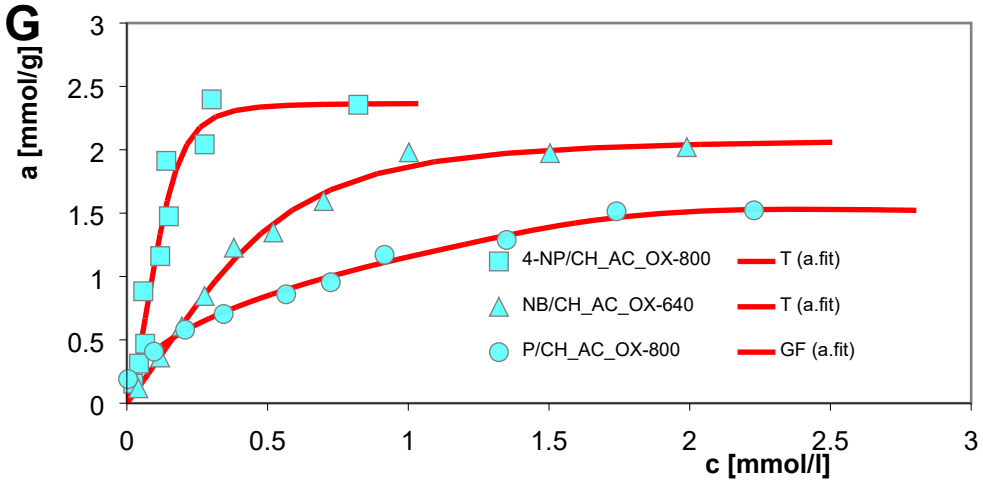


Figure S1. The isotherms of 4-NP, NB, and P adsorption from cyclohexane solutions on AC-OX (A), AC-OX-180 (B), AC-OX-280 (C), AC-OX-380 (D), AC-OX-480 (E), AC-OX-640 (F), and AC-OX-800 (G).

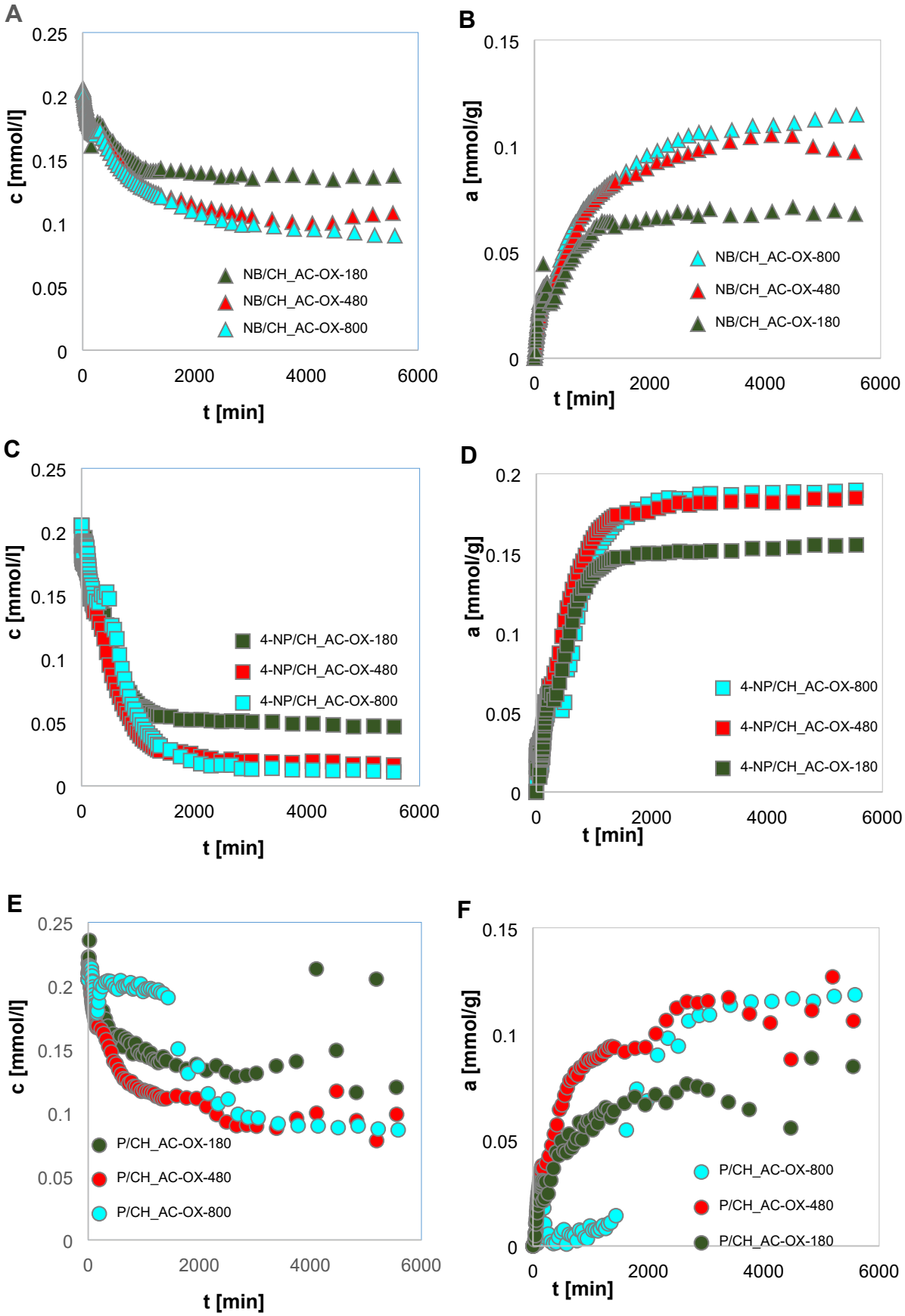


Figure S2. Adsorption kinetics for NB (A-B), 4-NP (C-D), and P (E-F) on AC-OX-180, AC-OX-480, and AC-OX-800 presented as changes in concentration over time (A, C, E) and changes in adsorption over time (B, D, F).

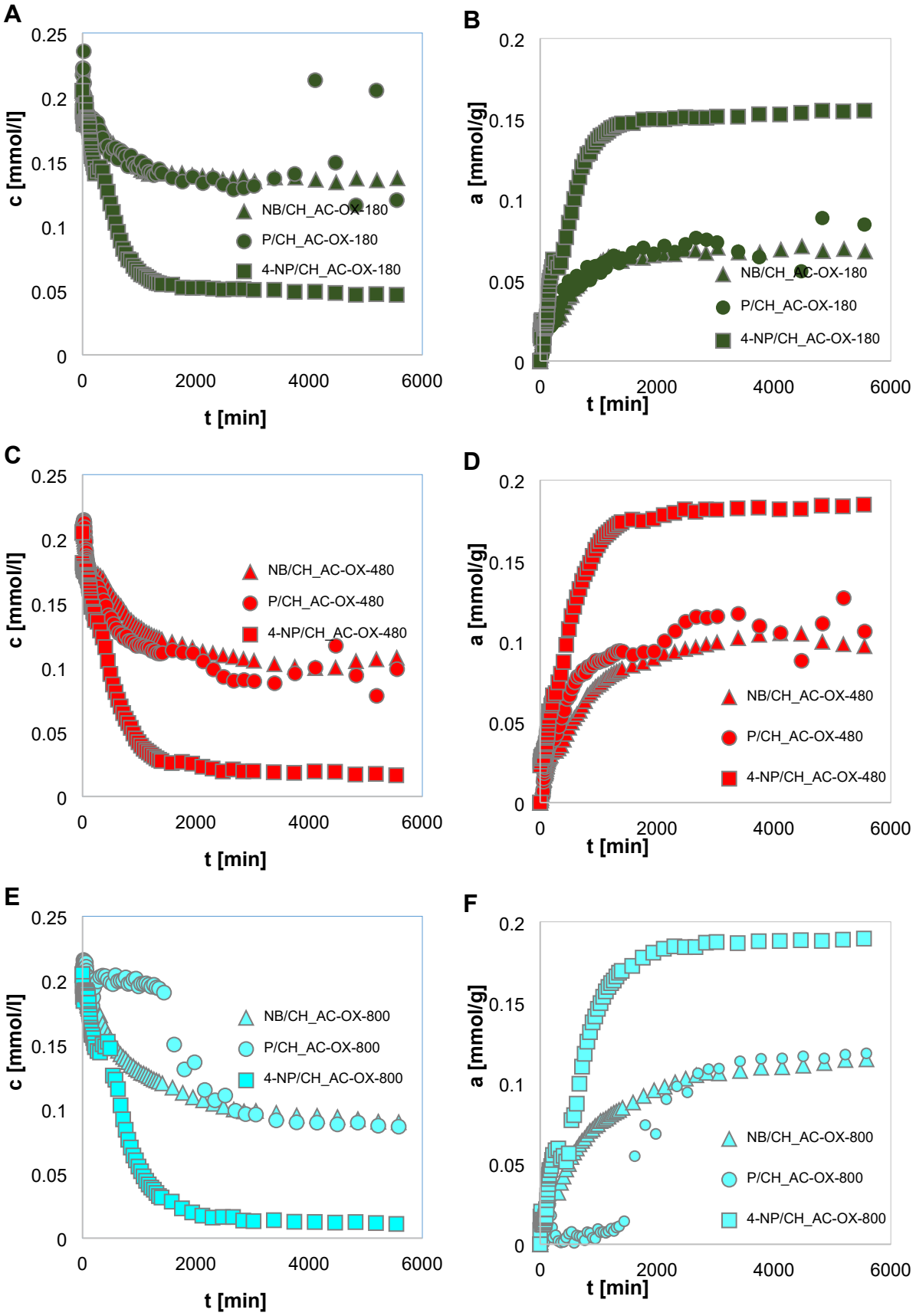


Figure S3. Adsorption kinetics for NB, 4-NP and P on AC-OX-180 (A-B), AC-OX-480 (C-D) and AC-OX-800 (E-F) presented as changes in concentration over time (A, C, E) and changes in adsorption over time (B, D, F).

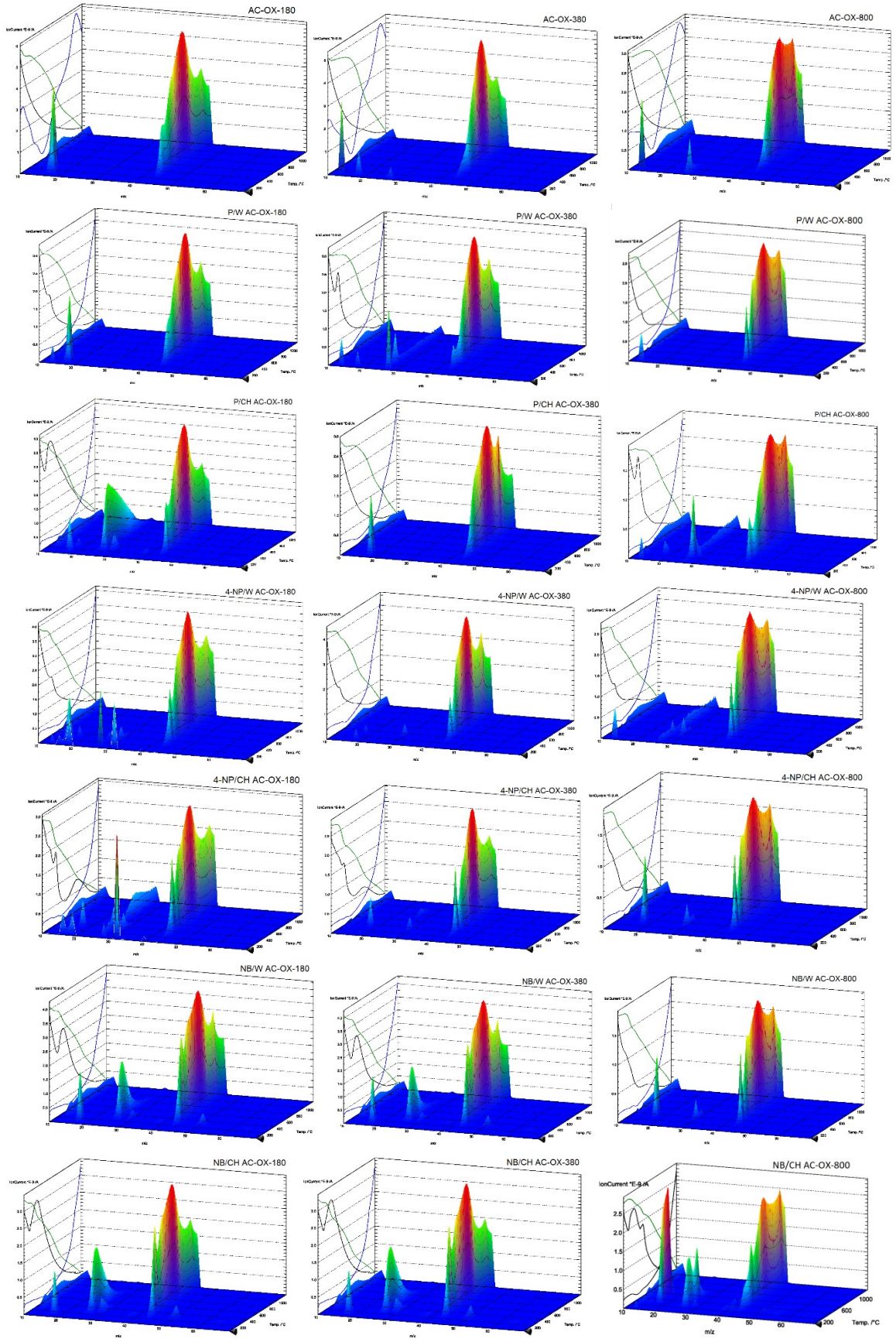
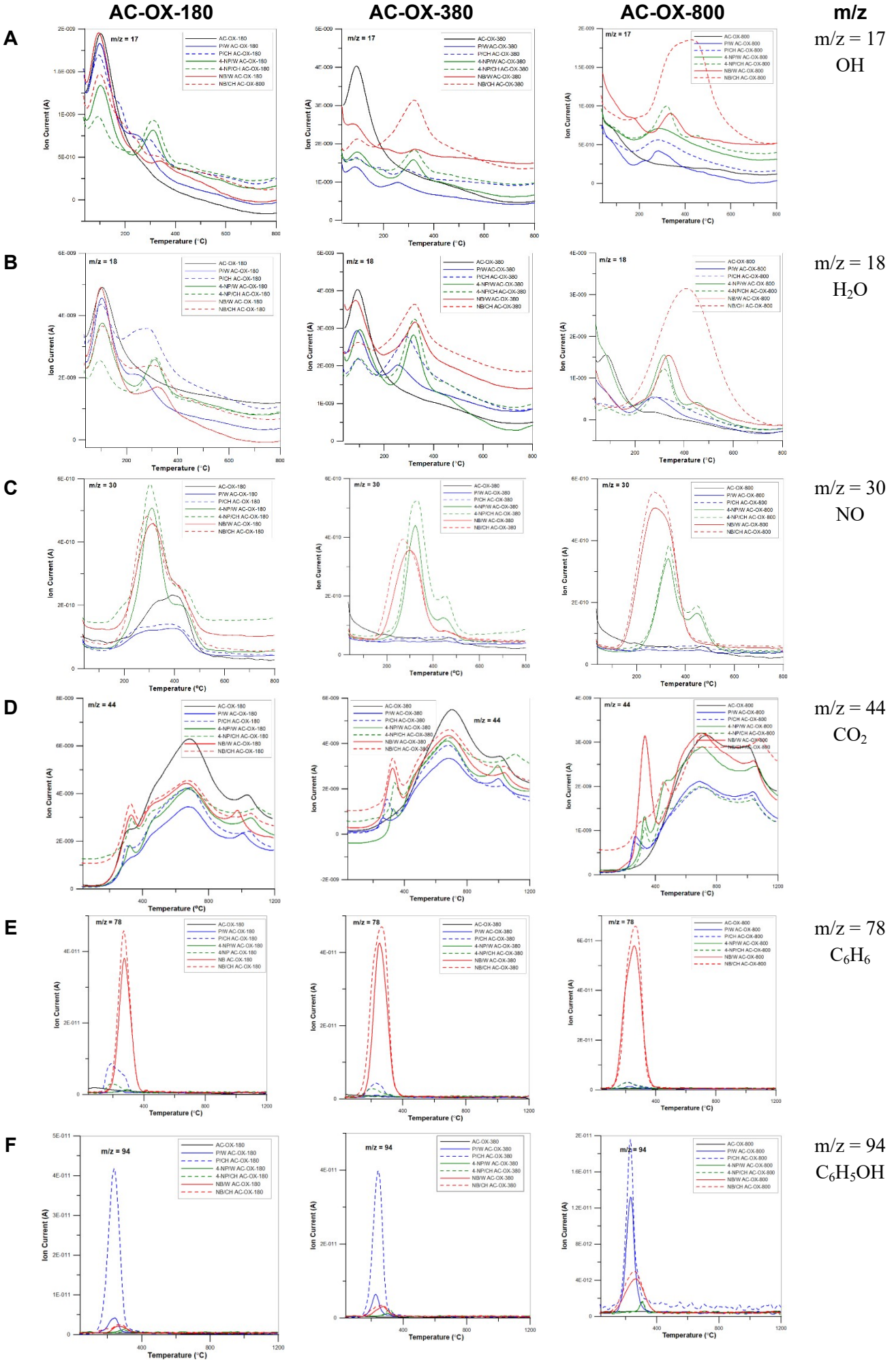


Figure S4. 3D MS profiles of decomposition of AC-OX-180, AC-OX-380 and AC-OX-800 samples.


AC-OX-180
AC-OX-380
AC-OX-800
m/z
A
m/z = 17
OH
B
m/z = 18
H2O
C
m/z = 30
NO
D
m/z = 44
CO2
E
m/z = 78
C6H6
F
m/z = 94
C6H5OH
Ion Current (A)
Temperature (°C)

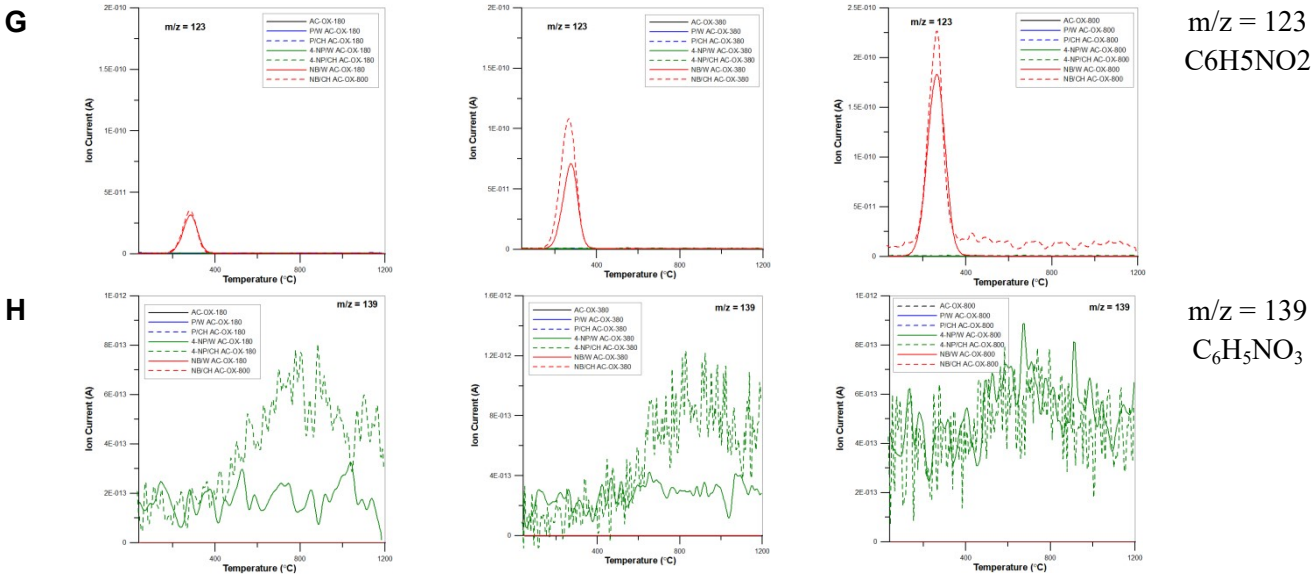


Figure S5. MS gaseous profiles registered during the thermal decomposition of AC-OX-180, AC-OX-380, and AC-OX-800 (m/z = 17 (A), m/z = 18 (B), m/z = 30 (C), m/z = 44 (D), m/z = 78 (E), m/z = 94 (F), m/z = 123 (G), m/z = 139 (H)) loaded with P/W and P/CH, 4-NP/W and 4-NP/CH, and NB/W and NB/CH, and modified ACs without solutes as a reference.