Supplementary Materials

Amine-functionalized porous aromatic frameworks for efficient adsorption of hazardous organic micropollutants in water

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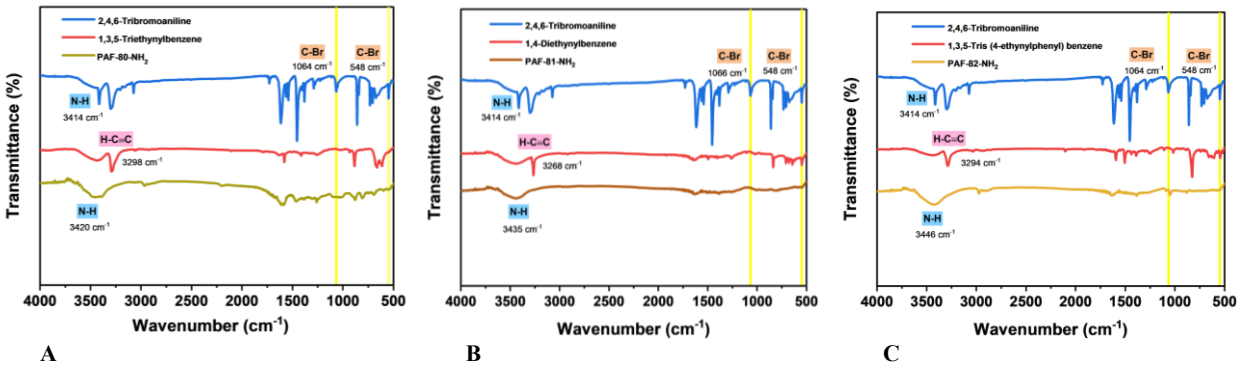
Supplementary Table 1. Mole ratios of building units and catalysts for amine-functionalized PAF materials

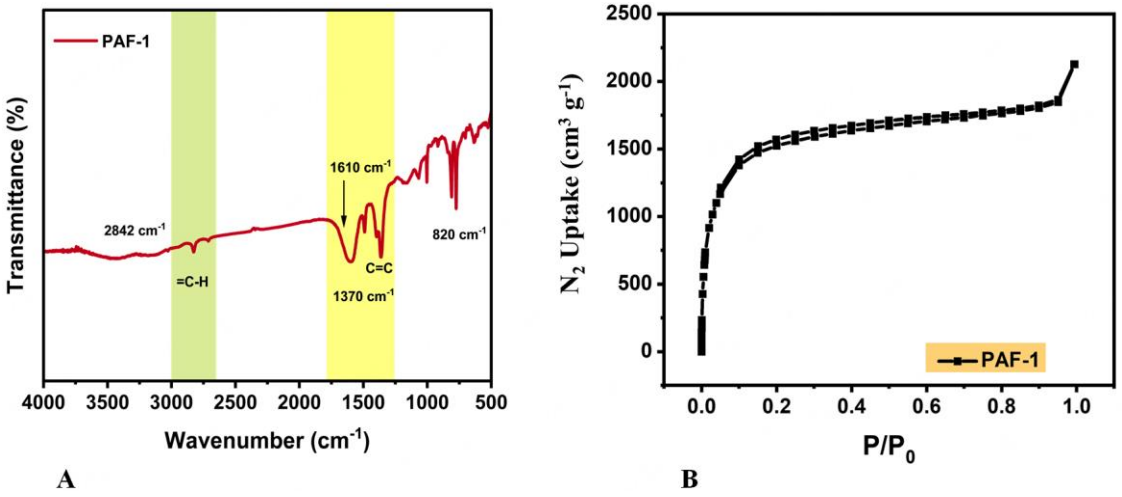
Materials	2,4,6-tribromo aniline	Building units	Tetrakis(triphenyl-phosphine) palladium	CuI	Triethylamine /DMF V: V	Yield (%)
PAF-80-NH_2	0.6 mmole	0.6 mmole	457 mg	15mg	15 ml:15 ml	91
PAF-81-NH_2	0.6 mmole	0.9 mmole	457 mg	15mg	15 ml:15 ml	89
PAF-82-NH_2	0.6 mmole	0.6 mmole	457 mg	15mg	15 ml:15 ml	96

Supplementary Section 1. Synthetic procedure of PAF-1

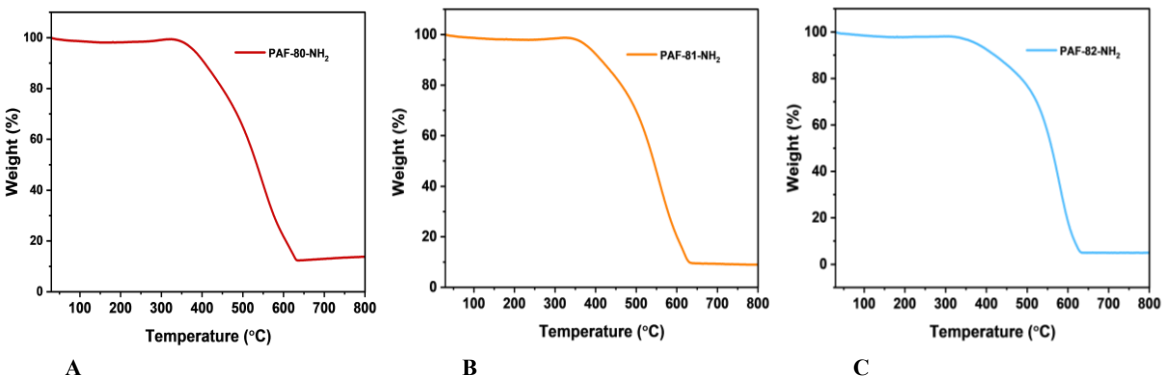
PAF-1 was synthesized following the procedure in already reported literature[1]. For its synthesis, 1,5-cyclooctadiene (cod, 1.05 mL, 8.32 mmol) was introduced into the solution of the catalyst as bis(1,5-cyclooctadiene) nickel(0) {[$Ni(cod)_2$]} (2.25 g, 8.18 mmol), and 2,2'-bipyridyl (1.28 g, 8.18 mmol) in extra dry DMF (50 mL). Then, this round bottom flask was left at 80 ℃ for 1 h for activation of catalyst. On the other hand, monomer tetrakis(4-bromophenyl) methane (1 g, 1.57 mmol) was completely dispersed in the same solvent, extra dry DMF (70 mL), then added to purple catalyst solution at 80 ℃. This resultant mixture was stirred overnight at the same temperature to get a deep purple suspension. Concentrated HCl was added to the mixture after cooling it to room temperature to stop the reaction. Consequently, three washings with $CHCl_3$, THF, and H_2O were carried out after filtration. After Soxhlet extraction in THF and vacuum, drying, off-white colored powder was obtained as PAF-1.



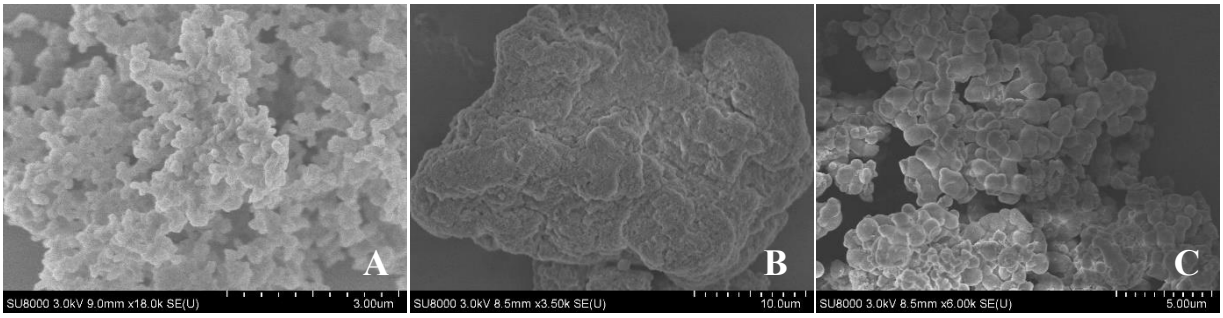
Supplementary Figure 1. FTIR spectra of synthesized amine-functionalized PAFs: (A) FTIR spectra of PAF-80-NH_2; (B) FTIR spectra of PAF-81-NH_2; (C) FTIR spectra of PAF-82-NH_2.



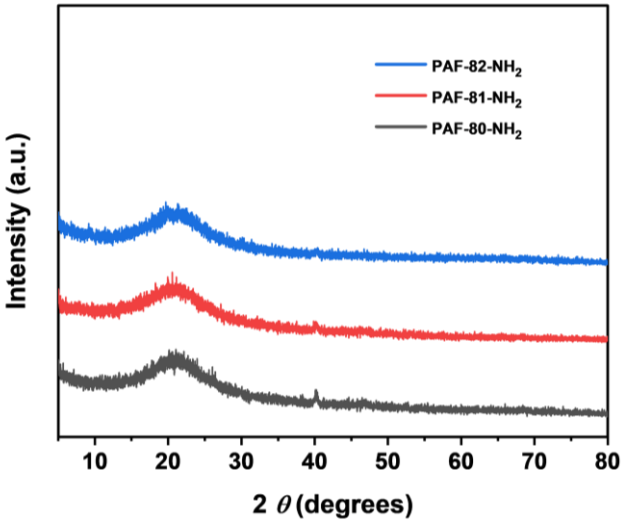
Supplementary Figure 2. Characterization of PAF-1: (A) FTIR of PAF-1; (B) N_2 isotherm of PAF-1.



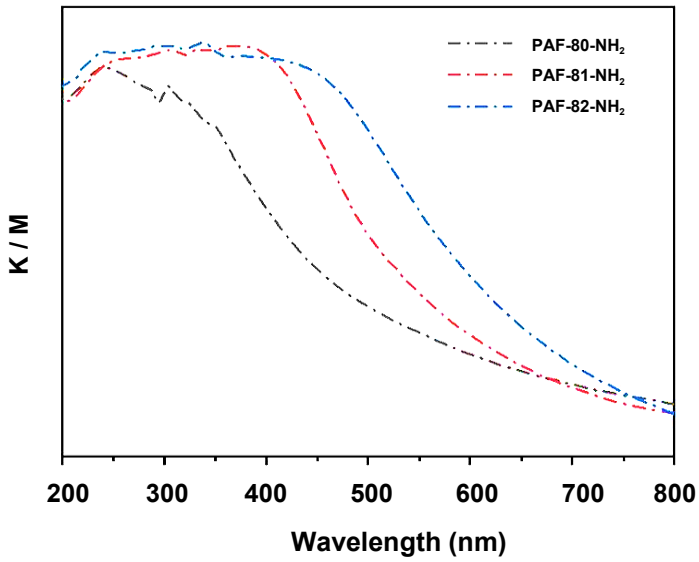
Supplementary Figure 3. TGA curves of synthesized amine-functionalized PAFs under air at 10 °C/min: (A) TGA curve of PAF-80-NH2; (B) TGA curve of PAF-81-NH2; (C) TGA curve of PAF-82-NH2.



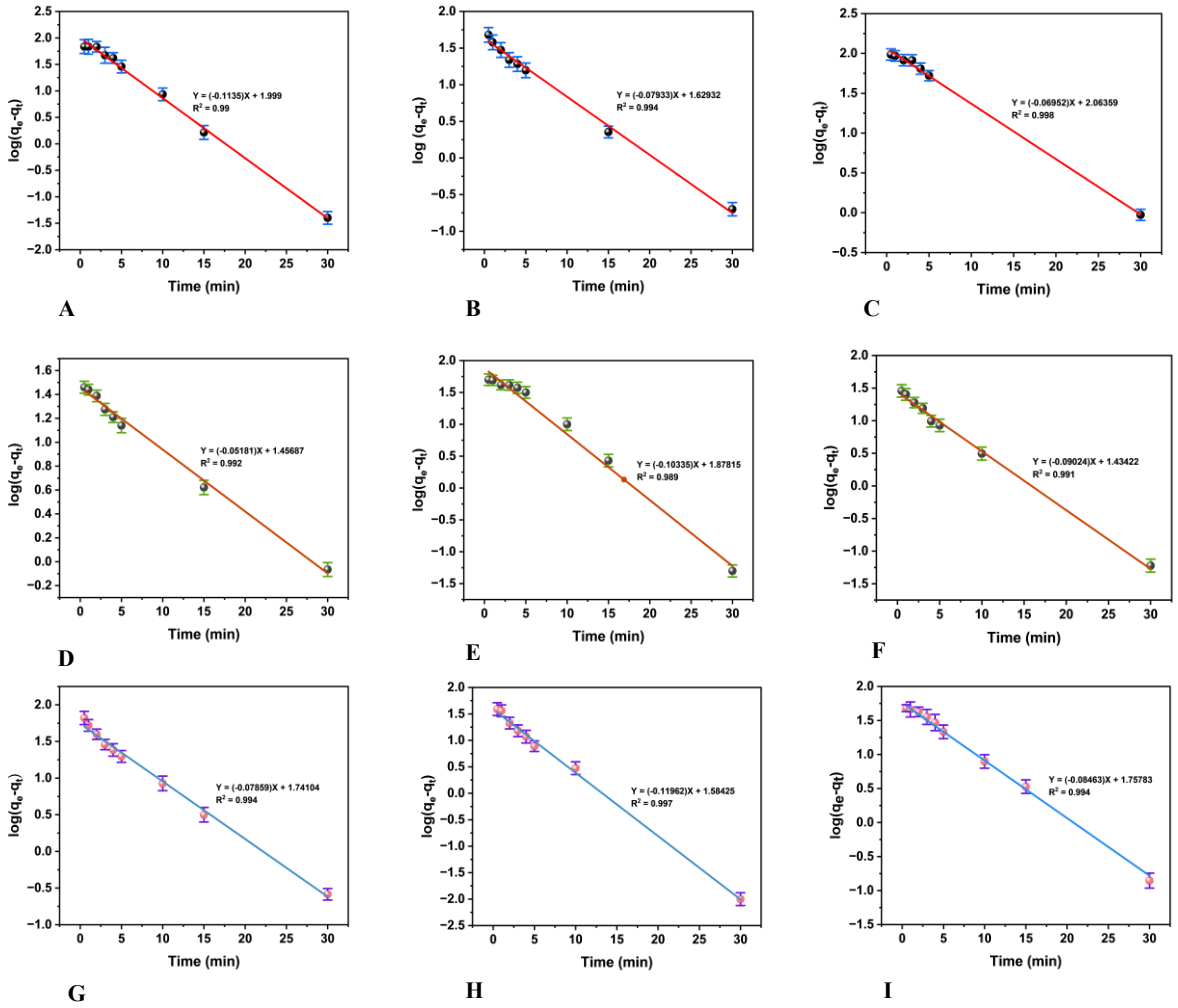
Supplementary Figure 4. SEM images of synthesized amine-functionalized PAFs: (A) SEM image of PAF-80-NH_2; (B) SEM image of PAF-81-NH_2; (C) SEM image of PAF-82-NH_2.



Supplementary Figure 5. PXRD pattern of PAF-80-NH_2 (**black**), PAF-81-NH_2 (**red**), and PAF-82-NH_2 (**blue**).



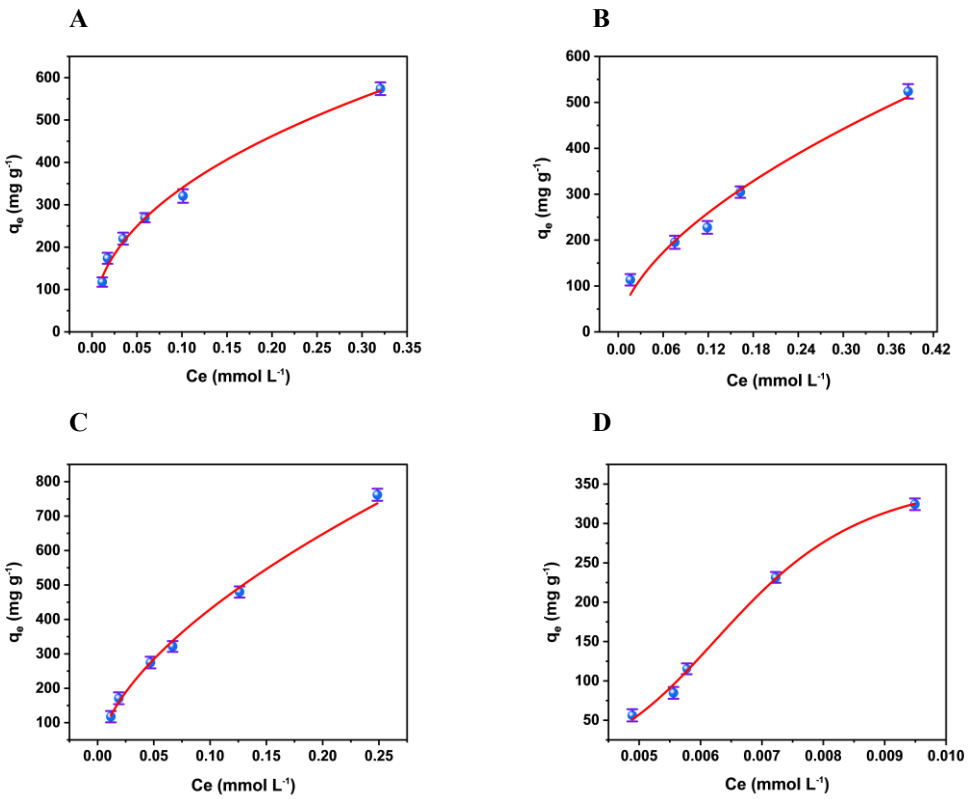
Supplementary Figure 6. UV-visible reflectance spectra of PAF-80-NH_2 (**black**), PAF-82-NH_2 (**red**) and PAF-81-NH_2 (**blue**).



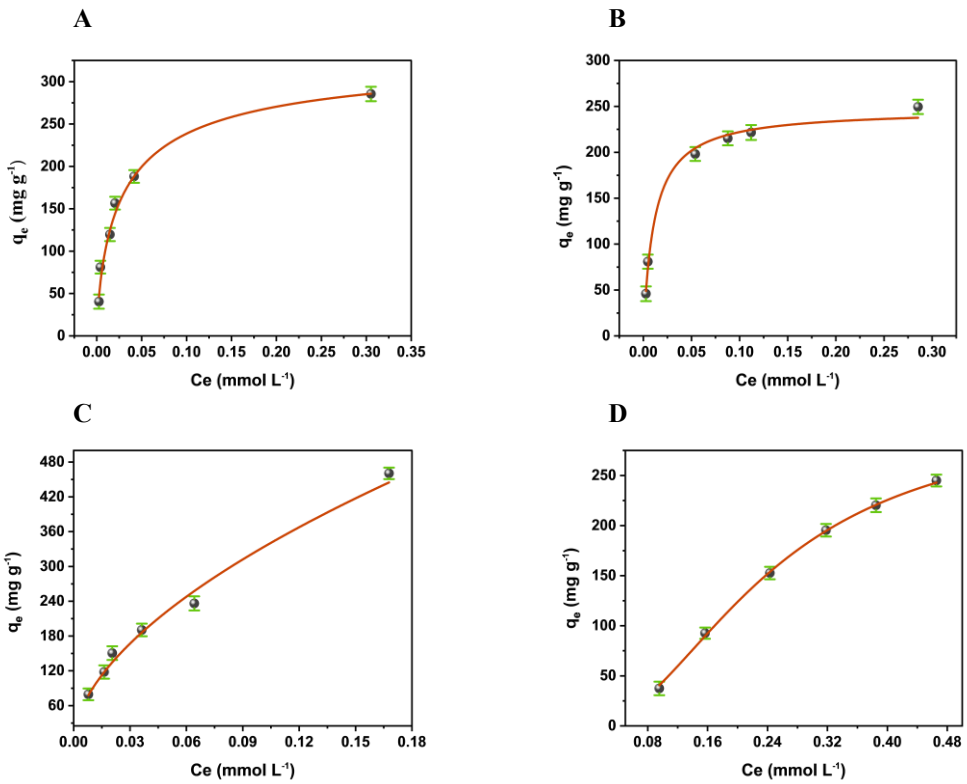
Supplementary Figure 7. Linear fitting curves of Pseudo-first-order kinetic data: (A) BPA adsorption by PAF-80-NH_2; (B) BPA adsorption by PAF-81-NH_2; (C) BPA adsorption by PAF-82-NH_2; (D) 2-NO adsorption by PAF-80-NH_2; (E) 2-NO adsorption by PAF-81-NH_2; (F) 2-NO adsorption by PAF-82-NH_2; (G) PCMX adsorption by PAF-80-NH_2; (H) PCMX adsorption by PAF-81-NH_2; (I) PCMX adsorption by PAF-82-NH_2.

Supplementary Table 2. Fitting parameters of pseudo-first-order kinetics and pollutant uptake rates by amine-functionalized PAF materials.

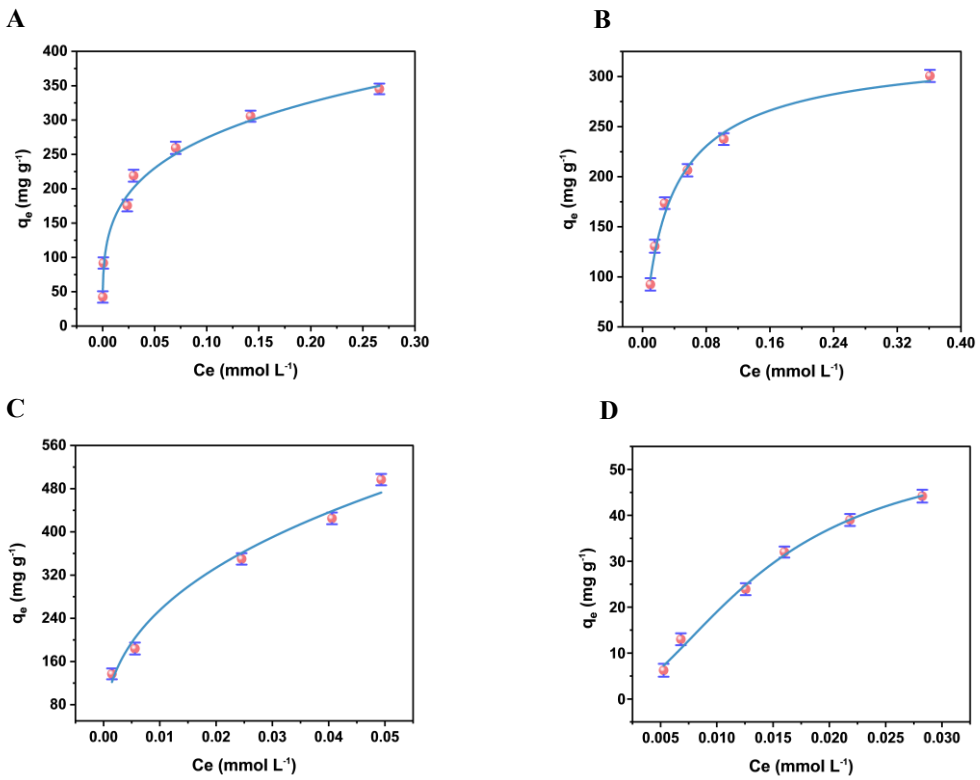
	BPA			2-NO			PCMX		
Sorbent	**K ($g \cdot mg^{-1} \cdot min^{-1}$)**	**R^2**	**t_{eq} (min)**	**K ($g \cdot mg^{-1} \cdot min^{-1}$)**	**R^2**	**t_{eq} (min)**	**K ($g \cdot mg^{-1} \cdot min^{-1}$)**	**R^2**	**t_{eq} (min)**
PAF-80-NH_2	0.2614	0.990	20	0.1193	0.994	20	0.1810	0.998	25
PAF-81-NH_2	0.1827	0.992	30	0.2380	0.989	25	0.2755	0.991	30
PAF-82-NH_2	0.1601	0.99	15	0.2078	0.99	20	0.19	0.994	10



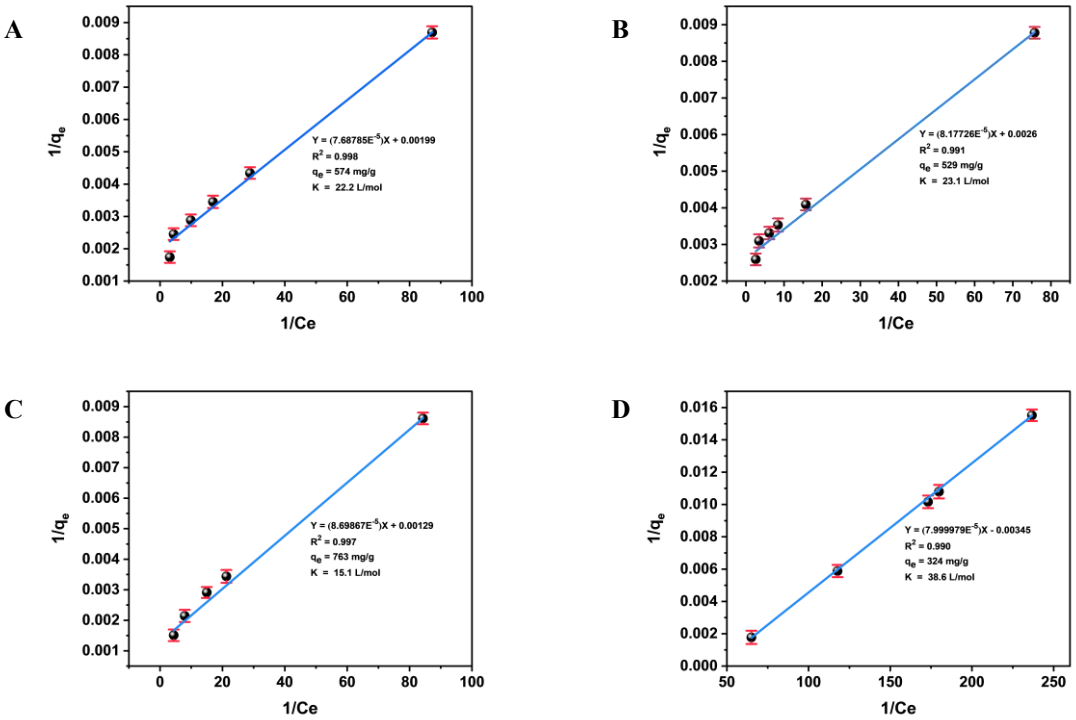
Supplementary Figure 8. Langmuir adsorption isotherms: (A) BPA adsorption onto PAF-80-NH_2; (B) BPA adsorption onto PAF-81-NH_2; (C) BPA adsorption onto PAF-82-NH_2; (D) BPA adsorption onto PAF-1.



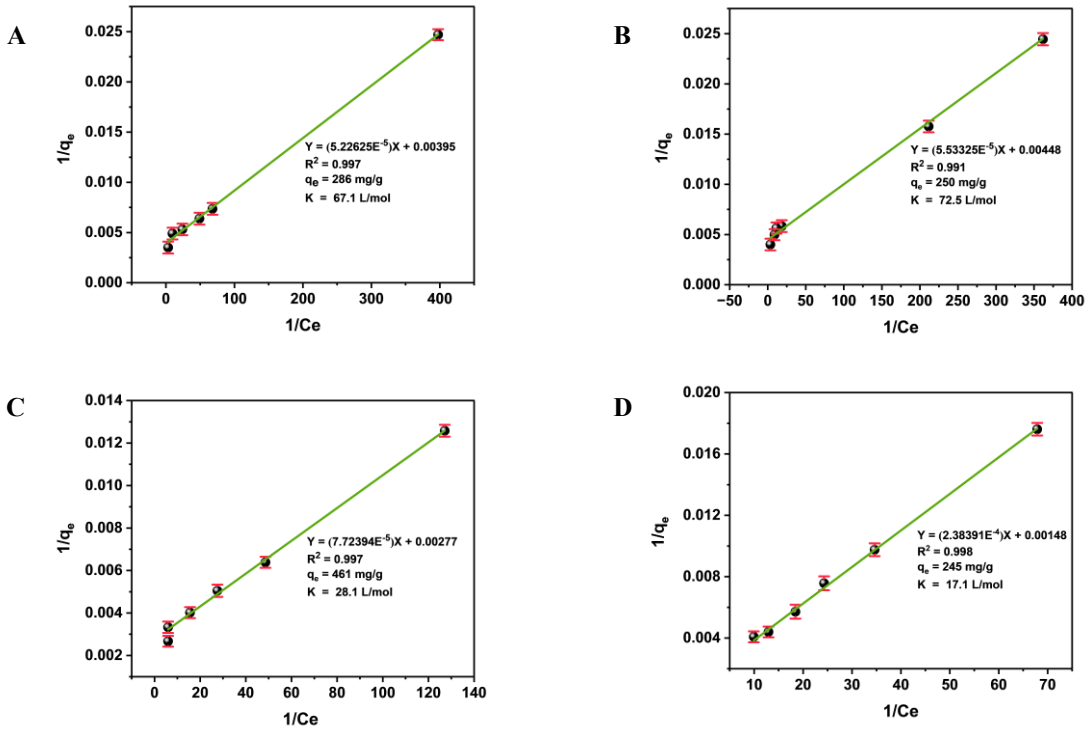
Supplementary Figure 9. Langmuir adsorption isotherms. (A) 2-NO adsorption onto PAF-80-NH_2; (B) 2-NO adsorption onto PAF-81-NH_2; (C) 2-NO adsorption onto PAF-82-NH_2; (D) 2-NO adsorption onto PAF-1.



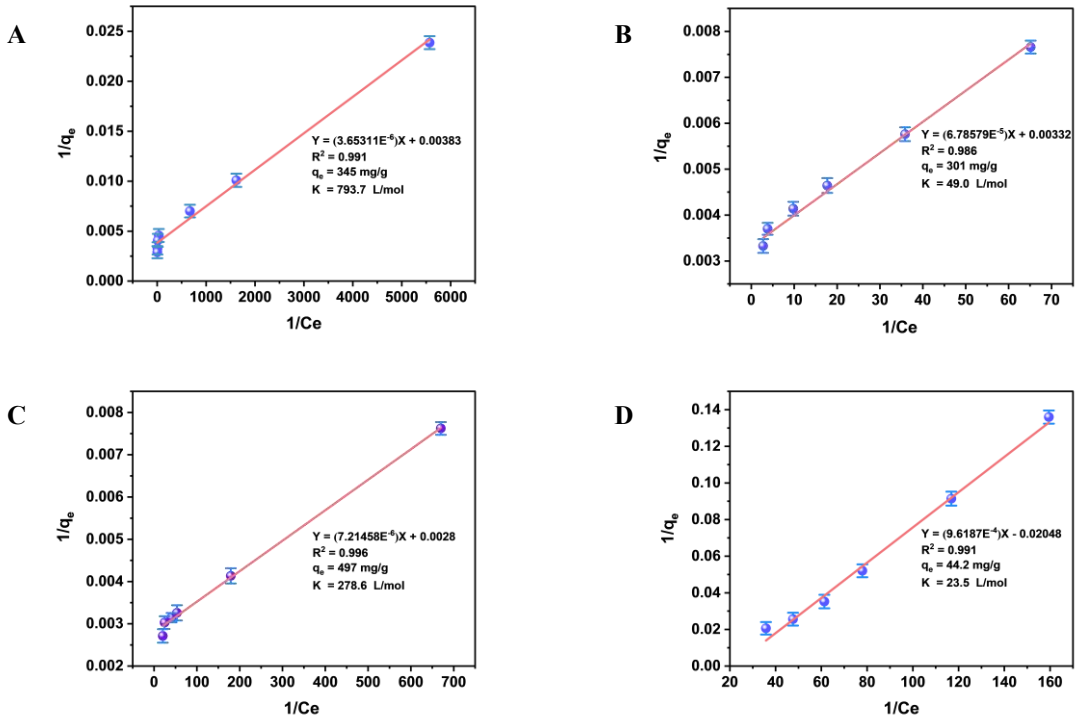
Supplementary Figure 10. Langmuir adsorption isotherms: (A) PCMX adsorption onto PAF-80-NH_2; (B) PCMX adsorption onto PAF-81-NH_2; (C) PCMX adsorption onto PAF-82-NH_2; (D) PCMX adsorption onto PAF-1.



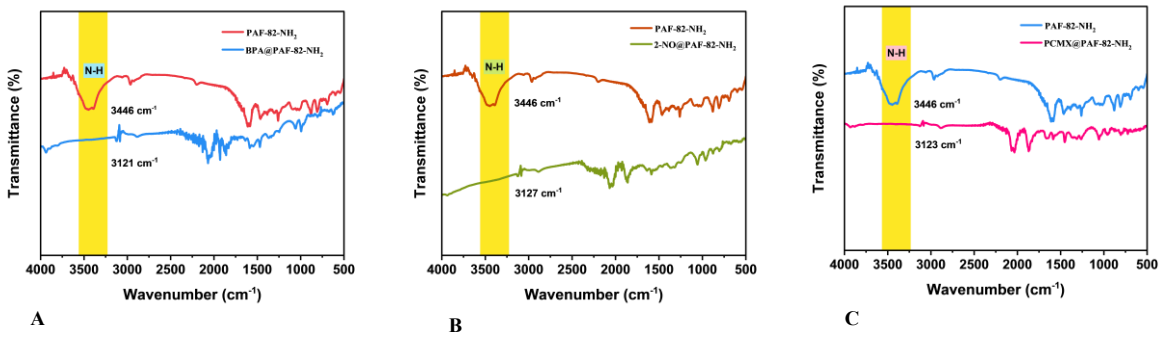
Supplementary Figure 31. Langmuir linear plots: (A) BPA adsorption onto PAF-80-NH_2; (B) BPA adsorption onto PAF-81-NH_2; (C) BPA adsorption onto PAF-82-NH_2; (D) BPA adsorption onto PAF-1.



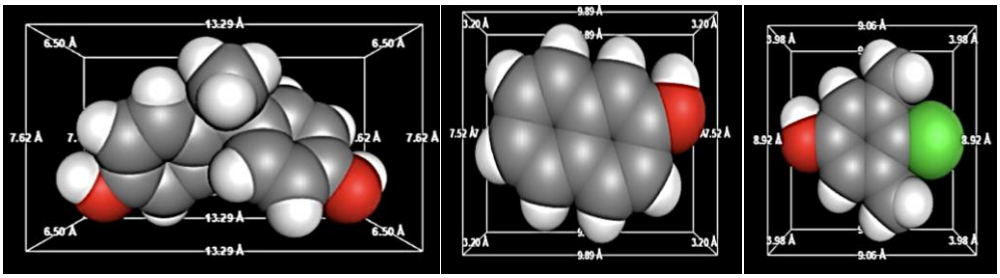
Supplementary Figure 42. Langmuir linear plots: (A) 2-NO adsorption onto PAF-80-NH_2; (B) 2-NO adsorption onto PAF-81-NH_2; (C) 2-NO adsorption onto PAF-82-NH_2; (D) 2-NO adsorption onto PAF-1.



Supplementary Figure 13. Langmuir linear plots: (A) PCMX adsorption onto PAF-80-NH_2; (B) PCMX adsorption onto PAF-81-NH_2; (C) PCMX adsorption onto PAF-82-NH_2; (D) PCMX adsorption onto PAF-1.



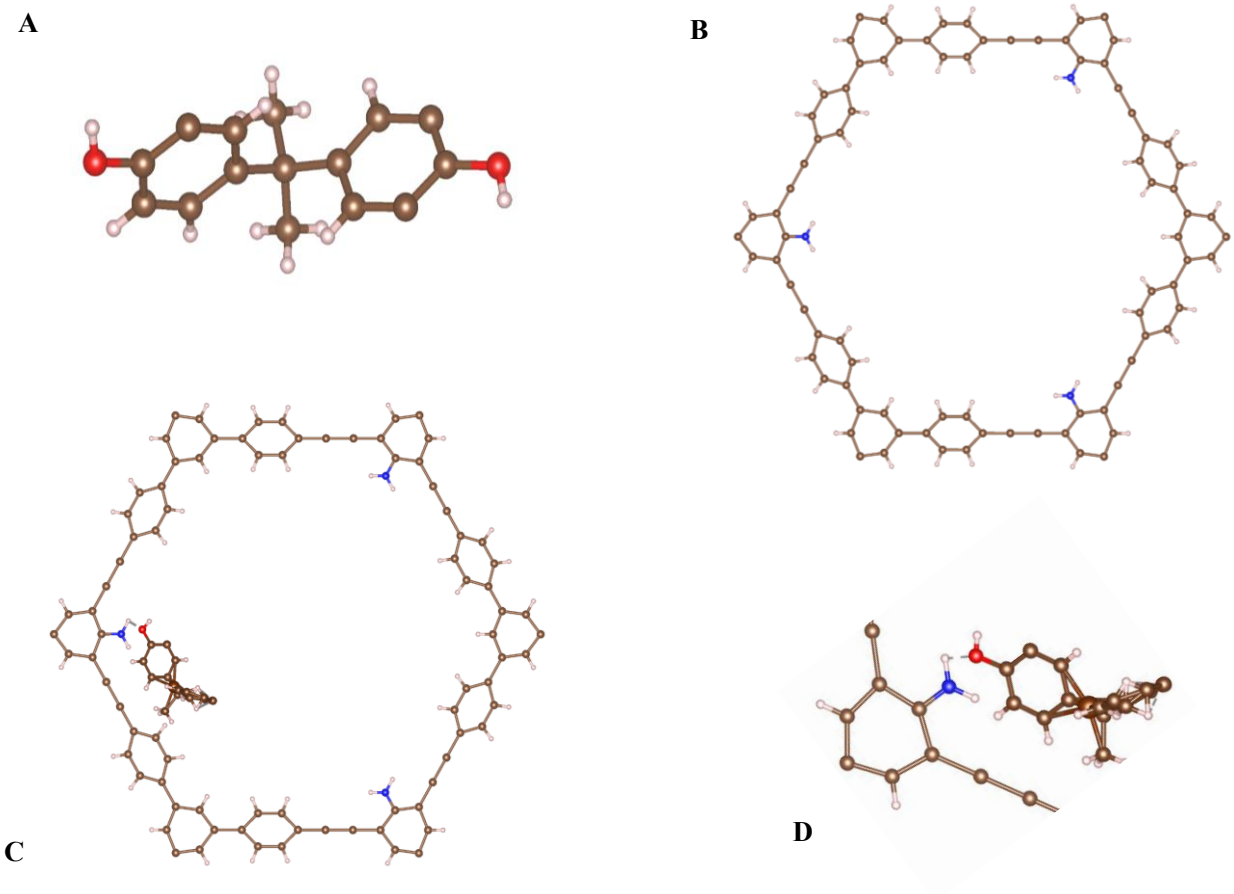
Supplementary Figure 5. FTIR spectra of Amine-functionalized PAFs before and after adsorption of OMP: (A) BPA adsorption onto PAF-82-NH_2; (B) 2-NO adsorption onto PAF-82-NH_2; (C) PCMX adsorption onto PAF-82-NH_2.



Supplementary Figure 6. Molecular dimensions of OMP: (A) BPA; (B) 2-NO; (C) PCMX.

Supplementary Table 3. Comparison of molecular dimensions of OMP with PAF-82-NH_2 pore size.

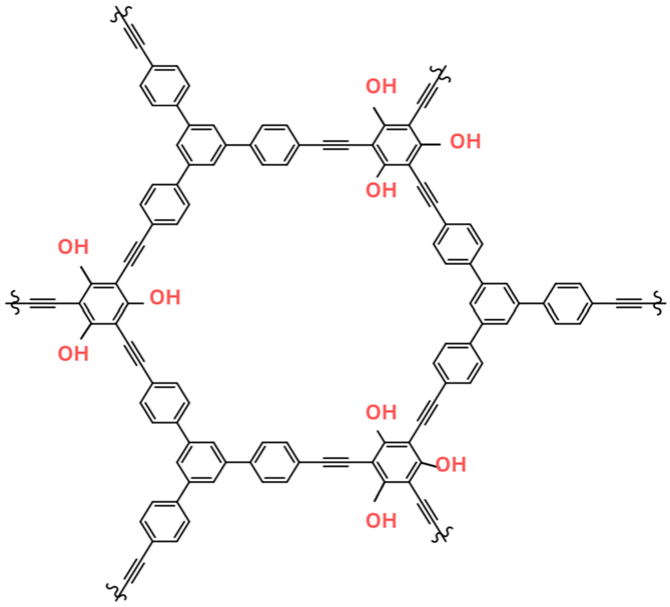
Model OMPs	OMP dimensions (Å)	Pore size (Å) (PAF-82-NH_2)	Accessibility
BPA	13.29 × 7.62 × 6.50	13.79	Accessible
2-NO	9.89 × 7.52 × 3.20	13.79	Accessible
PCMX	9.06 × 8.92 × 3.98	13.79	Accessible



Supplementary Figure 7. Representation of optimized structures: (A) BPA; (B) PAF-82-NH_2; (C) BPA adsorbed onto PAF-82-NH_2; (D) Zoomed view of BPA adsorption onto PAF-82-NH_2.

Supplementary Table 4. Adsorption capacities ($mg \cdot g^{-1}$) of some recently reported adsorbents

Adsorbents	Pollutants	Adsorption Capacity (mg/g)	References
PAF-82	BPA	689	[1]
lignin-based activated carbon (KLP)	BPA	220	[2]
hierarchically porous biochar (HBC)	BPA	246.13	[3]
Graphene oxide diethylenetriamine GO-DEA	BPA	334.4	[4]
Metal-organic-framework-derived carbon (MDC-800)	BPA	493	[5]
Al-MOF-NH_2	BPA	227.78	[5]
azine-linked COF	BPA	61.3	[5]
PAF-82-NH_2	BPA	763	This work
ZIF@wool	2-NO	371.2-391.1	[6]
PAF-82	2-NO	431	[1]
Biochar (200-1)	2-NO	230.45	[7]
PAF-82-NH_2	2-NO	461	This work
β-CDP	PCMX	144	[8]
PAF-82	PCMX	480	[1]
MONTs-pNIAPM sponge	PCMX	184	[9]
Co-NPC-800	PCMX	39	[10]
PAF-82-NH_2	PCMX	497	This work



Supplementary Figure 8. Structure of hydroxyl-functionalized PAF-82[1].

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