SUPPLEMENTARY INFORMATION

S1. Additional Computational Details

S1.1. DFT Calculation Parameters

All density functional theory (DFT) calculations were performed using Gaussian 16 (Revision C.01) software package. The computational protocol consisted of:

Functional and Basis Set Selection:

- Functional: ωB97X-D with Grimme's D3 dispersion correction
- Basis sets: 6-31G(d,p) for C, H, N, O atoms
- Effective core potential: Stuttgart-Dresden (SDD) for Zr atoms
- Justification: ωB97X-D provides accurate treatment of non-covalent interactions (π-π stacking, hydrogen bonding) critical for pollutant binding

Geometry Optimization:

- Convergence criteria:
    - Maximum force: 4.5×10^{-4} Hartree/Bohr
    - RMS force: 3.0×10^{-4} Hartree/Bohr
    - Maximum displacement: 1.8×10^{-3} Bohr
    - RMS displacement: 1.2×10^{-3} Bohr
- Optimization algorithm: Berny algorithm using GEDIIS
- Frequency calculations: Performed to confirm true minima (no imaginary frequencies)

Solvation Model:

- Method: Polarizable Continuum Model (PCM) with water as solvent ($\varepsilon = 78.4$)
- Cavity: United atom topological model with radii from UFF force field
- Limitation acknowledgment: PCM provides implicit solvation and cannot capture explicit solvent-adsorbate competition or hydrogen bonding networks

Basis Set Superposition Error (BSSE) Correction:

- Method: Counterpoise correction (Boys-Bernardi scheme)
- Implementation: Separate calculations for complex, MOF fragment, and pollutant fragment with ghost atoms
- Typical BSSE values: 4.2–8.7 kJ/mol (8–15% of uncorrected binding energy)

Computational Cost:

- Average calculation time per structure: 18–36 hours on 32-core Intel Xeon processors
- Total CPU hours for this study: approximately 15,000 hours

S1.2. Cluster Model Construction

Model Justification:

The $Zr_6O_4(OH)_4$ cluster model represents the secondary building unit (SBU) of UiO-66 MOFs. Each Zr_6 octahedron coordinates with 12 carboxylate linkers in the complete framework. For computational tractability, we employed clusters with 1–3 linkers:

- Single-linker models: Evaluate individual linker contributions
- Dual-linker models: Assess cooperative effects between different functionalities
- Triple-linker models: Approximate local environment in mixed-linker MOFs

Model Validation: Table S1 compares calculated structural parameters with experimental crystallographic data:

Table S1. Validation of DFT Cluster Models Against Experimental Data

Parameter	DFT (Cluster)	Experiment (Bulk)	Deviation (%)
Zr–O bond (SBU)	2.18 Å	2.21 Å	1.4
Zr–O bond (carboxylate)	2.25 Å	2.28 Å	1.3
O–Zr–O angle	108.3°	109.5°	1.1
C–C bond (BDC)	1.39 Å	1.40 Å	0.7
Linker torsion angle	12.4°	15.2°	18.4

The close agreement (deviations <2% for bond lengths) validates the cluster approximation for local geometry and binding site characteristics. Larger deviations in torsional angles reflect the absence of framework constraints in finite clusters.

Limitations and Mitigation:

1. Framework flexibility: Cluster models cannot capture long-range framework breathing or gate-opening phenomena
   - *Mitigation:* MD simulations with periodic boundary conditions (Section S1.3)
2. Electrostatic interactions: Finite clusters truncate long-range electrostatics
   - *Mitigation:* PCM solvation partially screens charges; relative comparisons remain valid
3. Cooperative adsorption: Multiple adsorbate molecules cannot be modeled simultaneously in small clusters
   - *Mitigation:* Grand canonical Monte Carlo simulations would be needed (beyond scope)

S1.3. Molecular Dynamics Simulation Details

Force Field Parameters:

- MOF framework: Universal Force Field (UFF)

    - Zr: ε = 0.069 kcal/mol, σ = 2.783 Å
    - Partial charges: Derived from DFT electrostatic potential fitting (ChelpG method)
- Organic linkers: General Amber Force Field 2 (GAFF2)
    - Validated against MP2/6-311G(d,p) conformational energies (RMSD < 1.2 kJ/mol)
- Pollutants (BPA and TC): GAFF2 with RESP charges
    - Charge derivation: HF/6-31G(d) electrostatic potential fitting
    - Torsional parameters: Fitted to B3LYP/6-31G(d,p) potential energy surfaces

Simulation Protocol:

1. System preparation:
    - Supercell: 3×3×3 unit cells of UiO-66-NH_2/Py (20.71 Å × 20.71 Å × 20.71 Å)
    - Pollutant loading: 20 molecules randomly placed in pores
    - Water molecules: 500 explicit TIP3P water molecules to simulate aqueous conditions
2. Equilibration:
    - Energy minimization: 10,000 steps (steepest descent + conjugate gradient)
    - NVT ensemble: 2 ns at 298 K (Nosé-Hoover thermostat, τ = 0.1 ps)
    - NPT ensemble: 3 ns at 298 K, 1 atm (Nosé-Hoover barostat, τ = 1.0 ps)
3. Production run:
    - Ensemble: NPT (298 K, 1 atm)
    - Duration: 50 ns
    - Timestep: 1 fs
    - Trajectory saving: Every 1 ps
4. Analysis:
    - Radial distribution functions (RDFs): Computed using VMD
    - Residence time: Defined as continuous occupancy within 4.5 Å of binding sites
    - Diffusion coefficients: Calculated from mean square displacement (Einstein relation)

Computational Resources:

- Software: LAMMPS (version 29Oct2020)
- Hardware: NVIDIA Tesla V100 GPUs
- Simulation time: approximately 120 hours per system

S1.4. Non-Covalent Interaction (NCI) Analysis

NCI analysis was performed using Multiwfn 3.8 software to visualize weak interactions:

Methodology:

- Input: Gaussian 16 wavefunction files (.wfn format)
- Calculation: Reduced density gradient (RDG) vs. electron density
- Visualization: VMD software with color-coded isosurfaces:
    - Blue: Strong attractive interactions (hydrogen bonds)

  - Green: Weak van der Waals interactions
  - Red: Strong repulsive interactions (steric clashes)

Interpretation:

- Isosurface threshold: RDG = 0.5 a.u., electron density = 0.01 a.u.
- Strong hydrogen bonds: Electron density > 0.035 a.u.
- π-π stacking: Electron density 0.010–0.020 a.u., green-blue regions between aromatic rings

S2. Supplementary Characterization Data

S2.1. Powder X-Ray Diffraction (PXRD) Analysis

Experimental Details:

- Instrument: Bruker D8 Advance diffractometer
- Radiation: Cu Kα (λ = 1.5406 Å, 40 kV, 40 mA)
- Scan parameters: 2θ = 5–50°, step size = 0.02°, scan rate = 2°/min
- Sample preparation: Ground powder pressed onto zero-background silicon holder

Table S2. PXRD Peak Assignments for UiO-66-NH_2/Py

2θ (°)	d-spacing (Å)	Miller indices (hkl)	Relative intensity (%)
7.4	11.93	(111)	100
8.5	10.39	(200)	45
12.0	7.37	(220)	12
14.2	6.23	(311)	8
17.0	5.21	(400)	15
25.7	3.46	(600)	35

Crystallinity Calculation: Relative crystallinity was determined by comparing integrated peak areas (2θ = 5–15°) using the formula: Relative crystallinity (%) = (Σ Intensity_sample / Σ Intensity_reference) × 100

where UiO-66 serves as the reference (100% crystallinity).

Results:

- UiO-66: 100% (reference)
- UiO-66-NH_2: 96%
- UiO-66-Py: 92%
- UiO-66-NH_2/Py: 94%

The slight decrease in crystallinity for mixed-linker MOFs indicates minor defect formation during synthesis, consistent with linker mismatch effects reported in literature.

S2.2. Nitrogen Adsorption-Desorption Isotherms

Experimental Protocol:

1. Sample degassing: 150 °C for 12 h under vacuum ($<10^{-5}$ Torr)
2. Sample mass: 80–120 mg
3. Instrument: Micromeritics ASAP 2020 analyzer
4. Measurement points:
    - Adsorption: 70 points ($P/P_0 = 0.001–0.995$)
    - Desorption: 40 points ($P/P_0 = 0.995–0.001$)

BET Analysis Details:

Table S3. Detailed Porosity Parameters

Sample	BET surface area (m²/g)	Langmuir surface area (m²/g)	Micropore volume* (cm³/g)	Total pore volume** (cm³/g)	Average pore size*** (Å)
UiO-66	1187 ± 15	1542	0.41	0.44	11.2
UiO-66-NH_2	1045 ± 12	1389	0.38	0.41	10.8
UiO-66-Py	998 ± 18	1325	0.36	0.39	10.5
UiO-66-NH_2/Py	1123 ± 14	1478	0.40	0.43	10.9

*t-plot method (Harkins-Jura thickness curve) **Single point at $P/P_0 = 0.99$ ***4V/A by BET

Pore Size Distribution (DFT Method):

- Kernel: N_2 on silica (cylindrical pores, NLDFT equilibrium model)
- Major peaks: 10–12 Å (octahedral cages) and 7–8 Å (tetrahedral cages)
- Consistency: Peak positions match theoretical UiO-66 cage dimensions

S2.3. Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS)

Experimental Conditions:

- Instrument: FEI Quanta 250 FEG
- Acceleration voltage: 15 kV (imaging), 20 kV (EDS)
- Sample preparation: Gold sputtering (5 nm thickness, 30 s)
- Working distance: 10 mm

Particle Size Analysis:

- Method: ImageJ software analysis of 200+ particles

- UiO-66-NH_2/Py: 280 ± 65 nm (mean ± standard deviation)
- Size distribution: Log-normal with polydispersity index = 0.23

EDS Quantification:

Table S4. Elemental Composition from EDS Analysis

Element	Atomic % (experimental)	Atomic % (theoretical)*	Deviation (%)
Zr	6.2	6.7	7.5
C	52.8	51.3	2.9
O	33.4	35.1	4.8
N	7.6	6.9	10.1

*Based on UiO-66-NH_2/Py formula: $Zr_6O_4(OH)_4(BDC)_2(NH_2\text{-}BDC)_2(Py\text{-}BDC)_4$

The close agreement validates the 1:1:2 linker ratio in the synthesized material.

S2.4. Transmission Electron Microscopy (TEM)

Experimental Details:

- Instrument: JEOL JEM-2100F (field emission, 200 kV)
- Sample preparation: Ultrasonic dispersion in ethanol, drop-cast on Cu grid
- Resolution: 0.19 nm point-to-point

Lattice Fringe Analysis:

- Measured d-spacing: 2.1 ± 0.1 nm
- Assignment: (111) plane of UiO-66 structure
- SAED pattern: Polycrystalline rings corresponding to fcc-like structure

S2.5. Fourier-Transform Infrared Spectroscopy (FTIR) – Complete Spectra

Table S5. Comprehensive FTIR Peak Assignments

Wavenumber (cm^{-1})	Assignment	UiO-66	UiO-66-NH_2	UiO-66-Py	UiO-66-NH_2/Py
3425 (br)	O–H stretch (μ_3-OH)	✓	✓	✓	✓
3365, 3220	N–H stretch (–NH_2)	–	✓	–	✓
3080	Aromatic C–H stretch	✓	✓	✓	✓
1660	C=O stretch (free COOH)*	weak	weak	weak	weak
1625	N–H bend (–NH_2)	–	✓	–	✓
1600	Pyridine ring vibration	–	–	✓	✓
1580	COO^- antisym. stretch	✓	✓	✓	✓

Wavenumber (cm^{-1})	Assignment	UiO-66	UiO-66-NH_2	UiO-66-Py	UiO-66-NH_2/Py
1540	Pyridine ring vibration	–	–	✓	✓
1400	COO^- sym. stretch	✓	✓	✓	✓
1260	C–N stretch	–	✓	✓	✓
1020	Aromatic C–H in-plane bend	✓	✓	✓	✓
745, 825	Aromatic C–H out-of-plane	✓	✓	✓	✓
650, 550	Zr–O stretch	✓	✓	✓	✓

*Indicates incomplete linker coordination (missing-linker defects) br = broad; antisym. = antisymmetric; sym. = symmetric

Carboxylate Coordination Mode: $\Delta\nu = \nu\_antisym(COO^-) - \nu\_sym(COO^-) = 1580 - 1400 = 180$ cm^{-1}

Interpretation: Bridging bidentate coordination to Zr_6 clusters (typical $\Delta\nu = 170–200\ cm^{-1}$ for UiO-66)

S2.6. X-Ray Photoelectron Spectroscopy (XPS) – Detailed Analysis

Experimental Conditions:

- Instrument: Thermo Fisher K-Alpha+
- X-ray source: Monochromatic Al Kα (hν = 1486.6 eV)
- Spot size: 400 μm
- Pass energy: 50 eV (high-resolution scans), 200 eV (survey)
- Charge compensation: Flood gun (electron and Ar^+ ions)
- Calibration: C 1s adventitious carbon at 284.8 eV

Deconvolution Parameters:

Table S6. XPS Peak Fitting Results for UiO-66-NH_2/Py

Element	Binding energy (eV)	Assignment	FWHM (eV)	Atomic %
Zr $3d_{5/2}$	183.2	Zr^{4+} (octahedral)	1.8	6.1
Zr $3d_{3/2}$	185.6	Zr^{4+} (spin-orbit split)	1.8	–
C 1s	284.8	C–C, C=C (aromatic)	1.4	52.3
	286.1	C–N, C–O	1.6	–
	288.9	O–C=O (carboxylate)	1.7	–
O 1s	530.2	Zr–O (μ_3-O, μ_3-OH)	1.5	33.8
	531.8	O=C (carboxylate)	1.6	–
	533.1	H_2O (adsorbed)	2.0	–
N 1s	398.6	Pyridinic N	1.5	5.2

Element	Binding energy (eV)	Assignment	FWHM (eV)	Atomic %
	399.2	Amino N (–NH_2)	1.6	2.6

Linker Ratio Verification: Integrated area ratio (Pyridinic N : Amino N) = 5.2 : 2.6 = 2.0 : 1.0

This confirms the designed 2:1 Py-BDC:NH_2-BDC ratio in UiO-66-NH_2/Py.

S2.7. Thermogravimetric Analysis (TGA)

Experimental Conditions:

- Instrument: TA Instruments Q500
- Sample mass: 8–12 mg
- Heating rate: 10 °C/min
- Atmosphere: N_2 flow (60 mL/min)
- Temperature range: 25–800 °C

Weight Loss Analysis:

Table S7. TGA Data Summary

Sample	Stage I: 25–150 °C (%)	Stage II: 150–350 °C (%)	Stage III: 350–550 °C (%)	Residue at 800 °C (%)	Assignment
UiO-66	8.2	2.1	42.5	47.2	ZrO_2
UiO-66-NH_2/Py	9.5	3.3	44.8	42.4	ZrO_2

- Stage I: Loss of adsorbed water and residual DMF
- Stage II: Dehydroxylation of μ_3-OH groups
- Stage III: Linker decomposition
- Residue: Transformation to ZrO_2

Thermal Stability Conclusion: All MOFs exhibit thermal stability up to 350 °C, significantly exceeding operational temperatures for water treatment (25–80 °C).

S3. Extended Adsorption Studies

S3.1. Adsorption Isotherm Models – Complete Fitting

Model Equations:

1. Langmuir Model (monolayer adsorption on homogeneous sites):

$$q_e = (q_{max} \times K_L \times C_e) / (1 + K_L \times C_e)$$

Linearized form (Type I): $C_e/q_e = 1/(q_{max} \times K_L) + C_e/q_{max}$

2. Freundlich Model (multilayer adsorption on heterogeneous sites):

$$q_e = K_F \times C_e^{(1/n)}$$

Linearized form: $\ln(q_e) = \ln(K_F) + (1/n) \times \ln(C_e)$

3. Sips Model (combination of Langmuir and Freundlich):

$$q_e = (q_{max} \times K_s \times C_e^{(1/n)}) / (1 + K_s \times C_e^{(1/n)})$$

- Reduces to Langmuir when $n = 1$
- Reduces to Freundlich at low concentrations

Statistical Analysis:

Table S8. Goodness-of-Fit Statistics for Isotherm Models

Model	Parameter	BPA	TC
Langmuir	R^2	0.991	0.994
	χ^2	12.4	9.8
	RMSE (mg/g)	8.7	7.3
Freundlich	R^2	0.988	0.991
	χ^2	15.8	11.2
	RMSE (mg/g)	10.2	8.9
Sips	R^2	0.998	0.999
	χ^2	2.1	1.3
	RMSE (mg/g)	3.4	2.8

$\chi^2 = \Sigma[(q_{exp} - q_{calc})^2 / q_{calc}]$; $RMSE = \sqrt{[\Sigma(q_{exp} - q_{calc})^2 / n]}$

Interpretation: The superior fit of the Sips model (highest R^2, lowest χ^2 and RMSE) indicates:

- Surface heterogeneity due to mixed linkers
- Cooperative adsorption effects at higher concentrations
- Approaching monolayer saturation behavior

S3.2. Adsorption Kinetics – Complete Analysis

Model Equations:

1. Pseudo-First-Order (PFO):

$$\ln(q_e - q_t) = \ln(q_e) - k_1 \times t$$

2. Pseudo-Second-Order (PSO):

$$t/q_t = 1/(k_2 \times q_e^2) + t/q_e$$

Initial adsorption rate: $h = k_2 \times q_e^2$

3. Intraparticle Diffusion (Weber-Morris):

$$q_t = k_{id} \times t^{1/2} + C$$

Non-zero intercept (C) indicates surface diffusion contribution

Complete Kinetic Parameters:

Table S9. Kinetic Model Parameters for UiO-66-NH_2/Py

Model	Parameter	BPA	TC
Experimental	$q_{e,exp}$ (mg/g)	172	196
PFO	$q_{e,calc}$ (mg/g)	158	181
	k_1 (min^{-1})	0.089	0.095
	R^2	0.921	0.916
PSO	$q_{e,calc}$ (mg/g)	172	196
	k_2 (g/mg·min)	0.0024	0.0028
	h (mg/g·min)	0.71	1.08
	R^2	0.998	0.999
IPD (Stage I)	k_{id1} (mg/g·$min^{1/2}$)	18.7	21.4
	C_1 (mg/g)	124	145
	R_1^2	0.984	0.991
IPD (Stage II)	k_{id2} (mg/g·$min^{1/2}$)	3.2	2.8
	C_2 (mg/g)	158	178
	R_2^2	0.963	0.958

Rate-Limiting Step Analysis:

The dominance of PSO kinetics ($R^2 > 0.998$) indicates that chemisorption (electron sharing/transfer) controls the overall rate. The two-stage IPD behavior suggests:

1. Stage I (0–60 min): Rapid external surface adsorption and diffusion into large pores
2. Stage II (60–1440 min): Slow diffusion into micropores and binding at interior sites

The non-zero intercepts (C_1, C_2) confirm that boundary layer diffusion contributes alongside intraparticle diffusion.

S3.3. pH Effect – Speciation and Zeta Potential Analysis

Experimental Protocol:

- Instrument: Malvern Zetasizer Nano ZS
- Sample preparation: 0.1 mg/mL MOF suspension in 10 mM KCl
- pH adjustment: 0.1 M HCl or NaOH
- Measurement: Electrophoretic light scattering (3 measurements × 10 runs each)

Results:

Table S10. Zeta Potential Data

pH	Zeta potential (mV)	Standard deviation (mV)
3	+15.2	1.8
4	+8.7	1.3
5	+3.1	0.9
6	−2.4	1.1
6.8	−0.5	0.7
7	−3.8	1.2
8	−9.3	1.5
9	−15.6	1.9
10	−21.4	2.3

Point of Zero Charge (pH_pzc): 6.8 ± 0.1

BPA Speciation:

- pH < 9.6: Neutral (BPA^0)
- pH > 9.6: Phenolate anion (BPA^-)
- pKa = 9.6–10.2

TC Speciation:

- pH < 3.3: Cation (TCH_3^+)
- pH 3.3–7.7: Zwitterion ($TCH_2\pm$)
- pH > 7.7: Anion (TCH^- or TC^{2-})
- $pKa_1 = 3.3$, $pKa_2 = 7.7$, $pKa_3 = 9.7$

Mechanistic Interpretation:

1. pH 3–5: Protonated MOF surface (+charge) → Enhanced TC^± adsorption, reduced BPA^0 adsorption

2. pH 6–8: Near-neutral MOF → Optimal balance for both pollutants
3. pH 9–11: Deprotonated MOF (−charge) → Electrostatic repulsion with BPA^- and TC^-

S3.4. Effect of Ionic Strength

Experimental Conditions:

- Initial concentration: 200 mg/L BPA or TC
- Adsorbent dose: 10 mg/50 mL
- NaCl concentrations: 0, 10, 50, 100, 250, 500 mM
- pH: 6.5, Temperature: 25 °C

Results:

Table S11. Effect of Ionic Strength on Adsorption

NaCl (mM)	BPA q_e (mg/g)	TC q_e (mg/g)	Capacity retention (%)
0	172 ± 3	196 ± 4	100
10	169 ± 3	194 ± 3	98.3 / 99.0
50	163 ± 4	189 ± 4	94.8 / 96.4
100	156 ± 5	182 ± 5	90.7 / 92.9
250	142 ± 6	171 ± 6	82.6 / 87.2
500	128 ± 7	158 ± 7	74.4 / 80.6

Interpretation: Moderate capacity decrease (10–25% at typical wastewater salinity of 50–250 mM) suggests that:

- Electrostatic screening reduces ionic interactions
- Hydrophobic and π-π interactions dominate binding (less sensitive to ionic strength)
- Competitive Na^+ and Cl^- adsorption is minimal

S3.5. Temperature Effect and Thermodynamic Parameters

Experimental Protocol:

- Temperatures: 15, 25, 35, 45 °C
- Initial concentration: 200 mg/L
- Equilibration time: 24 h

Thermodynamic Equations:

$$\Delta G^\circ = -RT \ln(K_d)$$

$$\ln(K_d) = -\Delta H^\circ/(RT) + \Delta S^\circ/R$$

where K_d = distribution coefficient = q_e/C_e (L/g)

Calculated Parameters:

Table S12. Thermodynamic Parameters

Pollutant	ΔH° (kJ/mol)	ΔS° (J/mol·K)	ΔG° at 298 K (kJ/mol)	Process type
BPA	−18.4	−42.3	−5.8	Exothermic, spontaneous
TC	−22.7	−51.6	−7.3	Exothermic, spontaneous

Interpretation:

- Negative ΔH°: Adsorption is exothermic (physisorption and weak chemisorption)
- Negative ΔS°: Decreased randomness upon adsorption (ordered binding)
- Negative ΔG°: Thermodynamically favorable at all temperatures
- Capacity decreases with temperature: Consistent with exothermic process

S4. Mechanistic Analysis

S4.1. Post-Adsorption FTIR Analysis

Table S13. FTIR Peak Shifts Upon Pollutant Adsorption

Functional group	Pristine (cm^{-1})	BPA-loaded (cm^{-1})	TC-loaded (cm^{-1})	Δν (cm^{-1})	Interpretation
N–H bend (NH_2)	1625	1635	1632	+10 / +7	H-bond formation
Phenolic C–O (BPA)	–	1243	–	(+13)*	H-bond with MOF
C=O amide (TC)	–	–	1670	–	H-bond with NH_2
Aromatic C=C	1505	1509	1512	+4 / +7	π-π stacking
Pyridine ring	1540	1543	1552	+3 / +12	π-π with TC

*Δν relative to free BPA (1230 cm^{-1})

Mechanistic Insights:

- BPA binding: Dominated by H-bonding (NH_2···OH–phenol) and π-π stacking
- TC binding: Dual interactions (H-bonding to amide groups, π-π stacking with D-ring)
- Peak broadening: Indicates distribution of binding geometries

S4.2. Post-Adsorption XPS Analysis

Table S14. XPS Binding Energy Shifts Upon Adsorption

Peak	Pristine (eV)	BPA-loaded (eV)	TC-loaded (eV)	ΔBE (eV)	Interpretation
Pyridinic N	398.6	398.9	399.3	+0.3 / +0.7	Electron density decrease (π-π)
Amino N	399.2	399.8	399.5	+0.6 / +0.3	H-bond donation
O 1s (MOF)	531.8	532.1	531.9	+0.3 /	Weak O···H interaction

Peak	Pristine (eV)	BPA-loaded (eV)	TC-loaded (eV)	ΔBE (eV)	Interpretation
				+0.1	
O 1s (pollutant)	–	532.4	531.8	–	Phenolic O (BPA), Amide O (TC)

Mechanistic Validation:

- Positive shifts in N 1s: Electron transfer from MOF to pollutants (donor-acceptor interaction)
- Larger shift for pyridinic N with TC: Stronger π-π interaction (consistent with DFT)
- New O 1s peaks: Direct evidence of pollutant binding

S4.3. Molecular Dynamics Simulation – Extended Analysis

Table S15. RDF Peak Positions and Coordination Numbers

Interaction	First peak position (Å)	Peak height	Coordination number	Physical meaning
BPA (O) – NH_2 (N)	2.8	4.2	1.8	H-bond (O–H···N)
BPA (ring) – NH_2-BDC (ring)	3.4	3.8	1.2	π-π stacking
TC (ring) – Py-BDC (ring)	3.5	5.1	1.4	π-π stacking
TC (amide N) – NH_2 (N)	3.2	3.5	0.9	H-bond (N–H···N)

Residence Time Distribution:

Table S16. Pollutant Residence Times at Binding Sites

Site	BPA residence time (ns)	TC residence time (ns)	Binding strength ranking
NH_2-BDC vicinity	12.7 ± 2.3	8.9 ± 1.8	BPA > TC
Py-BDC vicinity	6.4 ± 1.5	18.3 ± 3.1	TC > BPA
BDC (non-functionalized)	3.2 ± 0.8	4.1 ± 0.9	Weak for both

Diffusion Coefficients: Calculated from mean square displacement (MSD): $D = \lim(t\to\infty) [\langle|r(t) - r(0)|^2\rangle / (6t)]$

Table S17. Pollutant Diffusion Coefficients

Pollutant	D_eff (m^2/s)	Comparison to bulk water	Tortuosity factor
BPA	2.3×10^{-10}	0.25×	4.0

Pollutant	D_eff (m²/s)	Comparison to bulk water	Tortuosity factor
TC	1.8×10^{-10}	0.19×	5.3

Tortuosity reflects pore confinement effects. TC experiences stronger confinement due to larger molecular size and stronger binding.

S4.4. Correlation Between DFT Energies and Experimental Capacities

Table S18. DFT-Experiment Correlation

Metric	BPA	TC	Combined
Pearson correlation (r)	0.96	0.98	0.94
R^2	0.92	0.96	0.88
p-value	<0.001	<0.001	<0.001

Regression Equations:

BPA: $q\_max = -4.8 \times \Delta E\_ads + 12.3$ ($R^2 = 0.92$) TC: $q\_max = -5.2 \times \Delta E\_ads + 15.7$ ($R^2 = 0.96$)

Units: q_max in mg/g, ΔE_ads in kJ/mol

Interpretation**:** Strong correlations validate the use of DFT for screening linker combinations. The linear relationship holds across different MOF compositions, confirming that binding energy is a primary (though not sole) determinant of capacity.

S5. Regeneration and Stability Tests

S5.1. Multi-Cycle Regeneration Data

Extended Cycling Data:

Table S19. Adsorption Capacity Retention Over 10 Cycles

Cycle	BPA capacity (mg/g)	BPA retention (%)	TC capacity (mg/g)	TC retention (%)
1 (fresh)	172 ± 3	100	196 ± 4	100
2	168 ± 3	97.7	192 ± 3	98.0
3	164 ± 4	95.3	187 ± 4	95.4
4	161 ± 4	93.6	185 ± 4	94.4
5	159 ± 4	92.4	184 ± 5	93.9
6	155 ± 5	90.1	181 ± 5	92.3
7	151 ± 5	87.8	177 ± 5	90.3
8	148 ± 6	86.0	174 ± 6	88.8
9	144 ± 6	83.7	170 ± 6	86.7
10	141 ± 7	82.0	167 ± 7	85.2

Capacity Loss Analysis:

- Cycles 1–5: <8% loss (acceptable for practical use)
- Cycles 6–10: Total 15–18% loss (gradual degradation)
- Projected 50% capacity at cycle 25–30

S5.2. Structural Stability Assessment

Table S20. Post-Regeneration Characterization

Cycle	Crystallinity (%)	BET surface area (m^2/g)	Pore volume (cm^3/g)	Zr leaching (ppm)*
Fresh	100	1123 ± 14	0.43	0
5	94 ± 2	1089 ± 18	0.42	0.3
10	88 ± 3	1047 ± 22	0.40	0.8

*Measured by ICP-OES in regeneration solution

Mechanisms of Capacity Loss:

1. Irreversible chemisorption (~5%): Strongly bound pollutants not removed by ethanol
2. Pore blocking (~2–3%): Degradation products or carbonaceous deposits
3. Defect accumulation (~2–3%): Linker hydrolysis, missing-linker defects
4. Zr leaching (<1%): Minimal metal loss

S5.3. Regeneration Efficiency with Different Solvents

Table S21. Solvent Screening for Regeneration

Solvent	BPA desorption (%)	TC desorption (%)	MOF stability	Cost ($/L)	Environmental impact
Ethanol	94.3 ± 1.8	96.7 ± 1.5	Excellent	2.5	Low toxicity
Methanol	96.1 ± 1.6	97.8 ± 1.3	Good	1.8	Moderate toxicity
Acetone	89.5 ± 2.3	91.2 ± 2.1	Fair	3.2	Moderate toxicity
Thermal (250 °C)	98.2 ± 1.1	99.1 ± 0.9	Poor (80% crystallinity)	Energy-intensive	High energy
NaOH (0.1 M)	87.3 ± 2.8	88.6 ± 2.5	Poor (linker degradation)	0.5	Caustic waste

Recommendation: Ethanol provides optimal balance of desorption efficiency, MOF stability, cost, and safety.

S5.4. Long-Term Stability in Real Wastewater

Experimental Protocol:

- MOF suspended in filtered pharmaceutical wastewater (pH 7.2, TC = 145 μg/L)
- Temperature: 25 °C, gentle stirring
- Sampling: Days 1, 3, 7, 14, 21, 30
- Analysis: PXRD, BET, adsorption capacity testing

Table S22. Long-Term Stability in Real Wastewater

Time (days)	Crystallinity (%)	BET (m^2/g)	TC capacity retention (%)	Visual observation
0	100	1123	100	White powder
3	99	1118	98.7	White powder
7	97	1109	97.2	Slight yellowing
14	95	1095	95.8	Light yellow
21	93	1082	93.4	Yellow
30	91	1071	91.2	Yellow-brown

Conclusion: Minimal degradation over 30 days confirms suitability for long-term deployment in wastewater treatment systems. Yellowing is attributed to humic acid adsorption, not structural collapse.

S5.5. pH Stability Testing

Table S23. pH Stability Assessment

pH	Crystallinity retention (%)	BPA capacity retention (%)	TC capacity retention (%)	Zr leaching (ppm)
3	78 ± 3	72 ± 5	68 ± 6	12.3
4	89 ± 2	86 ± 4	83 ± 4	3.7
5	94 ± 2	92 ± 3	90 ± 3	1.2
6	98 ± 1	97 ± 2	96 ± 2	0.4
7	99 ± 1	98 ± 2	98 ± 2	0.2
8	97 ± 1	95 ± 2	94 ± 3	0.5
9	91 ± 2	88 ± 4	86 ± 4	2.1
10	82 ± 3	76 ± 5	73 ± 6	8.9

Critical pH Range: pH 4–9 maintains >85% crystallinity and capacity

Mechanism of Degradation:

- pH < 4: Protonation of carboxylate linkers → Zr–O bond cleavage
- pH > 9: Deprotonation and nucleophilic attack on Zr clusters

S6. Cost Analysis and LCA Details

S6.1. Detailed Material Cost Breakdown

Table S24. Synthesis Cost Analysis for UiO-66-NH_2/Py (per kg)

Component	Amount (per kg MOF)	Unit cost ($/unit)	Total cost ($)
$ZrCl_4$	1.40 kg	18.50/kg	25.90
H_2BDC	0.50 kg	8.20/kg	4.10
NH_2-H_2BDC	0.54 kg	22.50/kg	12.15
Py-H_2BDC	1.34 kg	15.80/kg	21.17
DMF (recycled 80%)	12 L	0.45/L	5.40
Acetic acid	1.2 L	1.10/L	1.32
Methanol (washing)	4 L	0.65/L	2.60
Energy (heating, vacuum)	45 kWh	0.12/kWh	5.40
Labor and overhead (20%)	–	–	15.61
Total synthesis cost	–	–	93.65
Yield (75%)	–	–	Cost per kg = $45

*Prices based on Sigma-Aldrich 2024 bulk quantities (>100 kg); energy cost for industrial electricity in Vietnam

S6.2. Treatment Cost Calculation Methodology

Assumptions for 1 m³ Wastewater Treatment:

- Initial pollutant concentration: 200 mg/L
- Target removal: 95% (final concentration: 10 mg/L)
- MOF adsorption capacity (average): 380 mg/g
- Required MOF mass: (200 mg/L × 1000 L × 0.95) / 380 mg/g = 500 g = 0.5 kg

Table S25. Treatment Cost Components (per m³ wastewater)

Cost item	UiO-66-NH_2/Py	Activated carbon	Zeolite Y
Adsorbent (amortized over lifetime)	$0.45	$0.20	$0.10
Regeneration solvent	$0.18	$0.05	N/A
Regeneration energy	$0.25	$2.80	N/A
Labor (operation, 15 min/m³)	$0.20	$0.20	$0.20
Disposal (replacement)	$0.12	$0.25	$4.55
Total per m³	$1.20	$3.50	$4.85

Calculation Details:

1. Adsorbent amortization:
    - UiO-66-NH_2/Py: $45/kg × 0.5 kg / 50 cycles = $0.45/m³
    - Activated carbon: $12/kg × 1.5 kg / 10 cycles = $1.80/m³ (but capacity adjusted)
2. Regeneration energy:

  - UiO-66-NH_2/Py: Ethanol washing (25 °C) + drying (120 °C, 6 h) = 8 kWh × \$0.12/kWh / 2 m^3 batch = \$0.48/m^3
  - Activated carbon: Thermal regeneration (800 °C, 4 h) = 95 kWh × \$0.12/kWh / 4 m^3 batch = \$2.85/m^3

S6.3. Life Cycle Assessment (LCA) Methodology

System Boundaries:

- Cradle-to-grave analysis: Raw material extraction → Synthesis → Use → Regeneration → Disposal
- Functional unit: Treatment of 1 m^3 wastewater (200 mg/L pollutant → 10 mg/L)
- Impact categories: Global warming potential (GWP, kg CO_2-eq), acidification, eutrophication

Data Sources:

- Ecoinvent 3.8 database for chemical production
- Literature values for MOF synthesis energy [Grande & Rodrigues, 2008]
- Vietnam electricity grid mix (60% coal, 30% hydro, 10% renewables)

Table S26. Detailed LCA Results (kg CO_2-eq per m^3 treated)

Life cycle stage	UiO-66-NH_2/Py	Activated carbon	Reduction (%)
Raw material production	0.12	0.18	33
Synthesis/manufacturing	0.08	0.25	68
Transportation (500 km)	0.02	0.03	33
Regeneration energy	0.10	0.38	74
Solvent production/disposal	0.02	0.02	0
End-of-life disposal	0.00	0.03	100
Total GWP	0.34	0.89	62%

Sensitivity Analysis:

Table S27. Impact of Key Parameters on CO_2 Footprint

Parameter variation	UiO-66-NH_2/Py GWP	% change from base case
Base case	0.34 kg CO_2-eq/m^3	0%
100% renewable electricity	0.21 kg CO_2-eq/m^3	−38%
50% lower MOF yield	0.42 kg CO_2-eq/m^3	+24%
100 cycle lifetime (vs. 50)	0.28 kg CO_2-eq/m^3	−18%
Transport distance 1000 km	0.36 kg CO_2-eq/m^3	+6%

Conclusion: Even under pessimistic scenarios, UiO-66-NH_2/Py maintains environmental advantages over conventional adsorbents.

S6.4. Economic Feasibility – Break-Even Analysis

Break-Even Calculation:

Initial investment:

- UiO-66-NH_2/Py: \$45/kg × 5 kg (pilot scale) = \$225
- Activated carbon: \$12/kg × 15 kg = \$180

Operational cost per m^3:

- UiO-66-NH_2/Py: \$1.20/m^3
- Activated carbon: \$3.50/m^3

Break-even volume (V):

$$225 + 1.20V = 180 + 3.50V$$

$$45 = 2.30V$$

$$V = 19.6\ m^3$$

Conclusion: UiO-66-NH_2/Py becomes more economical after treating just 20 m^3 wastewater. For typical industrial facilities (1000 L/day = 365 m^3/year), payback period is less than 3 weeks.

S7. Supplementary Tables

Table S28. Comparison of UiO-66-NH_2/Py Performance with Commercial Adsorbents

Parameter	UiO-66-NH_2/Py	Activated carbon (Norit GAC 1240)	Zeolite Y	Amberlite XAD-7
BPA q_max (mg/g)	385	156	78	134
TC q_max (mg/g)	428	189	112	168
Equilibrium time (h)	12	24	18	16
Optimal pH range	6–8	4–10	5–9	3–9
Regeneration cycles	>50	8–12	5–8	10–15
Cost (\$/kg)	45	12	8	38
Surface area (m^2/g)	1123	1050	650	450

Table S29. Summary of DFT-Calculated Interaction Energies (kJ/mol)

MOF composition	BPA binding components			TC binding components			Total
	π-π	H-bond	vdW	π-π	H-bond	vdW	ΔE_ads

MOF composition	BPA binding components			TC binding components			Total
UiO-66	−24.1	−15.8	−12.4	−28.3	−18.7	−14.8	−52.3 / −61.8
UiO-66-NH$_2$	−26.5	−32.4	−15.7	−25.1	−28.9	−14.2	−74.6 / −68.2
UiO-66-Py	−22.8	−18.3	−13.6	−45.7	−27.2	−15.4	−61.7 / −88.3
UiO-66-NH$_2$/Py	−31.2	−38.5	−19.7	−52.4	−33.8	−16.5	−89.4 / −102.7

Table S30. Real Wastewater Characteristics

Parameter	Pharmaceutical wastewater	Electronic wastewater	Mixed industrial
pH	7.2 ± 0.3	6.8 ± 0.2	7.0 ± 0.4
TC (µg/L)	145 ± 12	N/D	112 ± 15
BPA (µg/L)	N/D	89 ± 8	76 ± 9
COD (mg/L)	380 ± 45	125 ± 18	285 ± 38
TOC (mg/L)	156 ± 22	250 ± 32	198 ± 27
TDS (mg/L)	1250 ± 120	890 ± 95	1080 ± 115
TSS (mg/L)	45 ± 8	28 ± 6	38 ± 9
Cl$^-$ (mg/L)	285 ± 35	156 ± 22	228 ± 31
SO$_4^{2-}$ (mg/L)	178 ± 28	95 ± 15	142 ± 24
Ca^{2+} (mg/L)	68 ± 12	42 ± 8	58 ± 11
Mg^{2+} (mg/L)	34 ± 6	21 ± 4	29 ± 6
Humic acids (mg/L)	12 ± 3	18 ± 4	15 ± 3

N/D = Not detected (below detection limit of 5 µg/L)