

Adsorption of Diclofenac onto MOF-Based Adsorbents: Kinetic, Equilibrium, and Thermodynamic Insights in a Controlled Non-Aqueous Medium



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1. INTRODUCTION

Pharmaceutical micropollutants persist in aquatic environments and resist conventional wastewater treatment.

Diclofenac (DCF) widely used NSAID, frequently detected in water bodies.

MOFs are promising adsorbents due to high surface area, tunable porosity and active sites.

OBJECTIVE: Evaluate diclofenac adsorption on HKUST-1 and MOF-5 in a controlled non-aqueous medium.

2. METHODOLOGY

Synthesis (reflux method) → Characterization (PXRD, FTIR, Raman, SEM, N₂ physisorption) → Adsorption Tests (non-aqueous – absolute ethanol)

Hydrolytic Stability (pH 3–9): PXRD plots at pH 3, 5, 7, 9. Aqueous instability of HKUST-1 and MOF-5 justifies the use of a non-aqueous medium.

Adsorption Modeling: Isotherms (Langmuir, Freundlich, Sips), Kinetics (Pseudo-first, Pseudo-second, Intraparticle diffusion), Thermodynamics (ΔG° , ΔH° , ΔS°)

3. KEY RESULTS

Adsorption Capacity (Sips model, 298 K)

MOF-5	195.3 mg g ⁻¹	HKUST-1	119.6 mg g ⁻¹
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Higher capacity in MOF-5

Surface Area and Porosity (BET, 77 K)

MOF-5	2886 m ² g ⁻¹	HKUST-1	1420 m ² g ⁻¹
	1.15 cm ³ g ⁻¹		0.70 cm ³ g ⁻¹

Higher surface area and pore volume in MOF-5

Thermodynamic Behavior

HKUST-1	Exothermic	MOF-5	Exothermic
$\Delta H^\circ = -48.6$ kJ mol ⁻¹	Chemisorption	$\Delta H^\circ = -21.4$ kJ mol ⁻¹	Physisorption

Kinetics and Mechanism

- Pseudo-first-order kinetics
- Multistep mechanism
- External mass transfer and intraparticle diffusion are co-limiting.

4. RESULTS AND DISCUSSION

1. CRYSTAL STRUCTURE CONFIRMATION

Intensity (counts) vs 2θ (°) for HKUST-1 and MOF-5. High crystallinity and phase purity confirmed by PXRD.

2. CHEMICAL IDENTIFICATION

Transmittance (%) vs Wavenumber (cm⁻¹) for HKUST-1 and MOF-5. Carboxylate coordination confirmed by FTIR.

3. VIBRATIONAL CONFIRMATION

Intensity (a.u.) vs Raman shift (cm⁻¹) for HKUST-1 and MOF-5. Metal-ligand interactions verified by Raman spectroscopy.

4. MORPHOLOGY ANALYSIS

SEM images of HKUST-1 and MOF-5. Well-defined polyhedral and cubic crystal morphology.

5. WELL-DEFINED MOF STRUCTURES

Structural models of HKUST-1 and MOF-5. High crystallinity, strong metal-ligand coordination, potential for efficient CO₂ adsorption.

Comprehensive structural, chemical, and morphological characterization confirms the successful synthesis of HKUST-1 and MOF-5 with well-defined frameworks, paving the way for effective CO₂ capture applications.

5. Structure-Adsorption Relationships in Microporous MOFs: HKUST-1 vs MOF-5

1. N₂ ADSORPTION-DESORPTION ISOTHERMS AT 77 K

Volume @ STP (cm³ g⁻¹) vs Relative Pressure (P/P₀) for HKUST-1 and MOF-5. Type I isotherms with microporous behavior and low-pressure micropore filling.

2. COMPARATIVE ADSORPTION CAPACITY (ETHANOL, 298 K)

q_e (mg g⁻¹) vs Equilibrium concentration, C_e (mg L⁻¹) for HKUST-1 and MOF-5. MOF-5 exhibits higher adsorption capacity than HKUST-1; Sips model provides excellent fitting.

3. PORE SIZE DISTRIBUTION DFT ANALYSIS

dV/dlog(D) (cm³ g⁻¹) vs Relative Pressure (P/P₀) for HKUST-1 and MOF-5. Both materials show predominant narrow micropore distribution with minimal mesoporosity.

4. NARROW MICROPORE CHARACTER

Diagram of narrow micropore (d₂). HKUST-1: Predominant narrow micropores (~0.6–1.0 nm). MOF-5: Highly ordered microporous structure (~0.7–1.2 nm). DFT analysis confirms highly ordered, narrow microporous structures in both MOFs.

5. PERFORMANCE SUMMARY

- High surface area & microporosity
- High adsorption capacity (MOF-5 > HKUST-1)
- Narrow pore size distribution confirmed by DFT
- Excellent potential for CO₂ capture applications

Structural features and adsorption performance support their use in efficient CO₂ capture systems.

Comprehensive textural analysis and adsorption studies reveal that HKUST-1 and MOF-5 possess highly microporous, well-defined structures with superior adsorption performance, demonstrating strong potential for CO₂ capture applications.

6. CONCLUSIONS

- Non-aqueous conditions (ethanol) preserve MOF integrity, avoiding hydrolytic degradation and ensuring reliable adsorption data.
- MOF-5 exhibits higher adsorption capacity, governed by its larger surface area and pore volume (pore-filling mechanism).
- HKUST-1 shows stronger adsorption affinity, driven by coordinatively unsaturated Cu(II) sites (specific interactions).
- Adsorption follows pseudo-first-order kinetics with a multistep diffusion mechanism (film + intraparticle control).
- Thermodynamics confirms the spontaneity and exothermicity of adsorption for HKUST-1 (chemisorption) and MOF-5 (physisorption).

7. IMPACT

Environmental Impact

- Improved reliability in pollutant removal studies, avoiding misleading results from MOF degradation in water.
- Supports development of efficient materials for pharmaceutical removal, addressing emerging water contaminants.
- Provides a pathway toward more sustainable wastewater treatment strategies, reducing environmental risk.
- Enables rational design of water-stable MOFs, critical for real-world environmental applications.

Scientific Impact

- Establishes a robust non-aqueous methodology for studying hydrolytically unstable MOFs.
- Clarifies true adsorption mechanisms, decoupling adsorption from structural degradation.
- Defines structure-property-performance relationships in MOF-based systems.
- Provides a reproducible framework for future adsorption studies, improving data comparability across the field.

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