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.

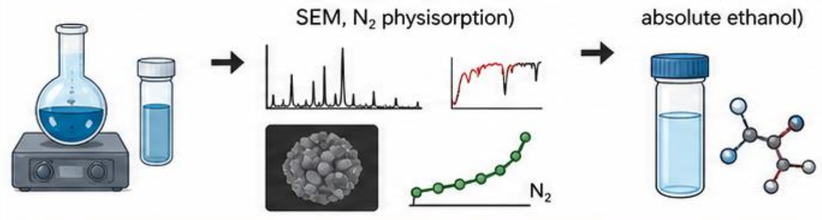
Diclofenac (DCF) widely used NSAID, frequently detected in water bodies.

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

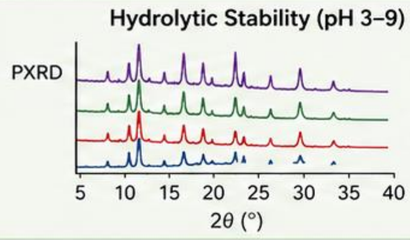
OBJECTIVE:
Evaluate diclofenac adsorption on HKUST-1 and MOF-5 in a controlled non-aqueous medium.

2. METHODOLOGY

Synthesis (reflux method) → **Characterization** (PXRD, FTIR, Raman, SEM, N_2 physisorption) → **Adsorption Tests** (non-aqueous – absolute ethanol)



Hydrolytic Stability (pH 3–9)



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 ($\Delta G°$, $\Delta H°$, $\Delta S°$)

3. KEY RESULTS

Adsorption Capacity (Sips model, 298 K)

MOF-5: 195.3 mg g^{-1} — HKUST-1: 119.6 mg g^{-1} — Higher capacity in MOF-5

Surface Area and Porosity (BET, 77 K)

MOF-5	HKUST-1
2886 m^2 g^{-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

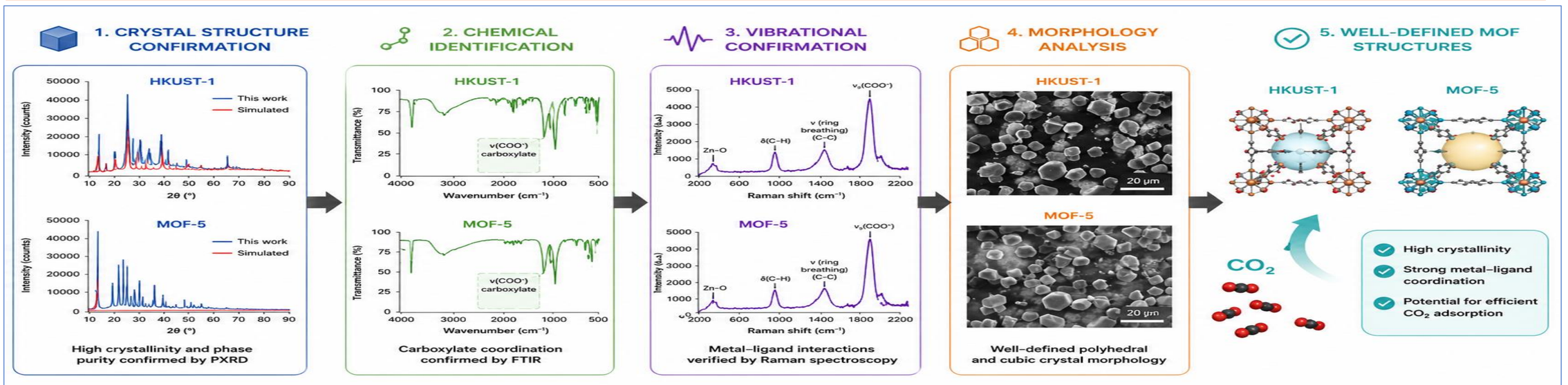
Thermodynamic Behavior

HKUST-1: $\Delta H° = -48.6$ kJ mol^{-1} Chemisorption — Exothermic — MOF-5: $\Delta H° = -21.4$ kJ mol^{-1} Physisorption

Kinetics and Mechanism

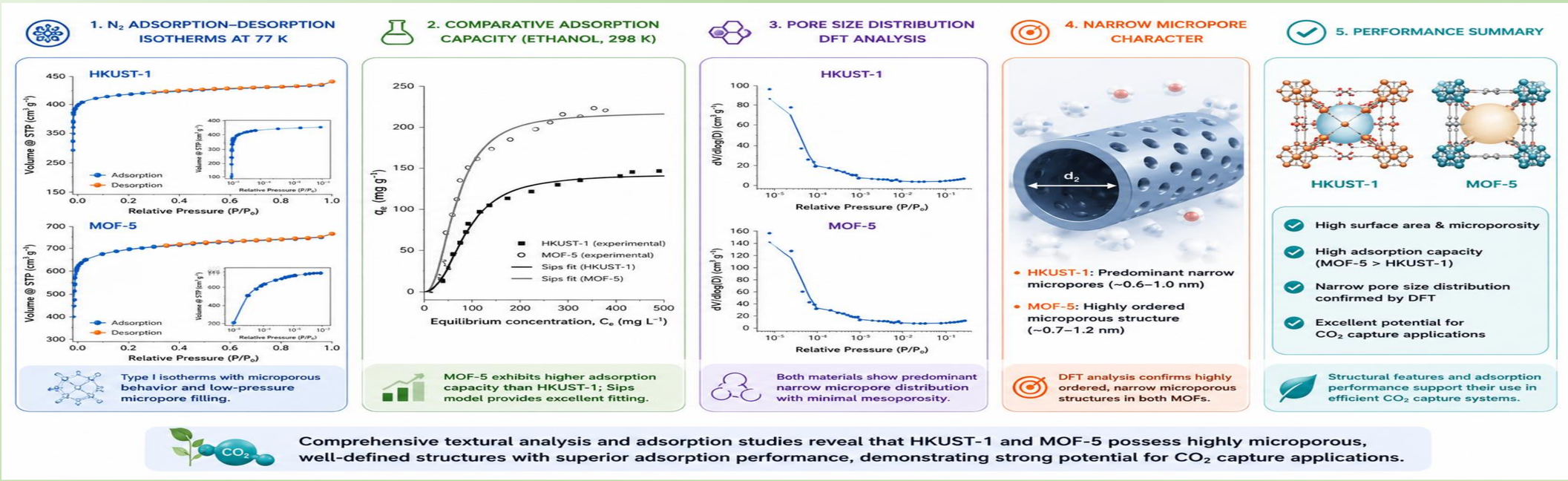
- Pseudo-first-order kinetics
- Multistep mechanism
- External mass transfer and intraparticle diffusion are co-limiting.

4. RESULTS AND DISCUSSION



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 CO_2 capture applications.

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



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 CO_2 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.

ACKNOWLEDGEMENTS

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