Supporting Information

Amine Functionalized Metal-organic Frameworks and Covalent Organic Polymers as Potential Sorbents for Removal of Formaldehyde in Aqueous Phase: Experimental Vs. Theoretical Study

Kowsalya Vellingiri[a,b1], Ya-Xin Deng[c1], Ki-Hyun Kim[a*], Jheng-Jie Jiang[d], Taejin Kim[e], Jin Shang[f], Wha-Seung Ahn[g], Deepak Kukkar[h*], Danil W. Boukhvalov[I,j]

[a]Department of Civil and Environmental Engineering, Hanyang University, 222 Wangsimni-Ro, Seoul 04763, Korea, [b]Environmental and Water Resources Engineering Division, Department of Civil Engineering, IIT Madras, Chennai 600 036, India, [c]Science and Technology on Reactor System Design Technology Laboratory Nuclear Power Institution of China Chengdu, 610213, China, [d]Department of Environmental Engineering, Chung Yuan Christian University, Taoyuan 32023, Taiwan, [e]Department of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook,, NY 11794, USA, [f]School of Energy and Environment, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong SAR, [g]Department of Chemistry and Chemical Engineering, Inha University, Incheon 402-751, South Korea, [h]Department of Nanotechnology, Sri Guru Granth Sahib World University, Fatehgarh Sahib, Punjab-140406, India, [i]College of Science, Institute of Materials Physics and Chemistry, Nanjing Forestry University, Nanjing 210037, P. R. China a, [j]Theoretical Physics and Applied Mathematics Department, Ural Federal University, Mira Street 19, 620002 Yekaterinburg, Russia

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*Correspondence: kkim61@hanyang.ac.kr; dr.deepakkukkar@gmail.com

[1]These authors are considered to be co-first authors because they contributed equally to this work.

1. Experimental methods

1.1. Chemicals

Reagent grade chemicals including terephthalic acid (TPA) (≥98%), 2-aminoterephthalic acid (TPA-NH_2) (≥ 99%), zirconyl chloride octahydrate ($ZrOCl_2$-$8H_2O$: ≥ 98%), N, N′-dimethylformamide (DMF: ≥ 99.0%), trimethylamine (≥ 99%), terephthaloyl chloride (TC), 1,3,5-benzenetricarbonyl trichloride (BTC), 1,3,5-triphenylbenzene, biphenyl, anhydrous $AlCl_3$, 1,2-ethylenediamine (EDA), diethylenetriamine (DETA), sodium borohydride, dichloromethane (DCM), ethanol (≥ 99.5%), and methanol (≥ 99.5%) were purchased from Sigma Aldrich, USA. Chloroform was purchased from Daejung Chemicals & Metals, Korea. Concentrated HCl was obtained from Junsei Chemical, Japan. The primary standard (PS) (formaldehyde solution: 36.5-38%) of FA was purchased from Sigma Life Science, USA. The AC granules were purchased from Duksan Pure Chemicals, Korea.

1.2. Synthesis of adsorbents

U6 and U6N were synthesized by following the procedure discussed by Katz et al.[1] In summary, two aliquots of $ZrOCl_2$-$8H_2O$ were prepared by separately solubilizing 125 mg of $ZrOCl_2$-$8H_2O$ in 5 mL DMF and 1 mL concentrated HCl solution. The aliquots were stirred well for proper mixing at room temperature (RT), followed by sonication for 20 minutes. In a parallel experiment, ligands (U6: 123 mg of TPA; and U6N: 123 mg of TPA-NH_2) were separately

solubilized in 10 mL of DMF and added to the metal aliquots as stated above. The two solution mixtures were further sonicated for 30 min before heating in an oven at 80 °C for 12 h. The resulting solid was filtered and washed twice with DMF (30 mL each). Subsequently, each of the resulting solids was exchanged with 10 mL of ethanol three times in three days. Finally, the MOF products were dried in oven at 90 °C for 12 h.

CBAP-1 was synthesized using the reported procedure with some modifications.[2] In summary, 3.05 g TC, 3.06 g 1,3,5-triphenylbenzene, and 180 mL DCM were mixed and purged with N_2 for 15 min. Subsequently, 2 g anhydrous $AlCl_3$ was added to the reaction mixture, followed by refluxing for 12 h to produce dark brown powder. The powdered product was filtered and washed with DCM and methanol many times (30 mL each). Finally, the product was dried under vacuum at 130 °C, producing a dark brown solid of CBAP-1. From this product, 1 g of CBAP-1 was solubilized in 40 mL methanol, followed by addition of 2 mL EDA (for CE synthesis) or DETA (for CD synthesis). The mixture was refluxed at 80 °C for 15 h under vigorous stirring and finally cooled to RT. The resulting Schiff-base intermediate was reduced with excess NaBH4 before being vigorously stirred for 10 h at RT. Then, the products were filtered and washed with methanol and water several times. Finally, the resulting products of CBAP-1-EDA (CE) and CBAP-1-DETA (CD) were dried in an oven at 130 °C for 12 h and designated as CE and CD, respectively.

1.3. Characterization methods

FTIR spectroscopy was carried out using a PerkinElmer L1600400–IR spectrometer (Akron, OH, U.S.A) with an attenuated reflectance method (ATR). PXRD patterns were recorded using a high-resolution x-ray diffractometer (HR-XRD; Rigaku, Japan). The powder was smear mounted onto a glass slide and then analyzed using Cu K_α radiation (1.54 A°). The data were obtained for an angular 2θ range, step size, scan speed, X-ray voltage, and current of 5°-60°, 0.02°, 1 °C min^{-1}, 45 kV, and 200 mA, respectively. The morphology of the particles was determined using NOVA nano SEM-450 field emission (FE)-SEM (Hillsboro, OR) microscopy. TGA experiments were performed on a SDT Q600, Auto-DSCQ20 system (Eden Prairie, MN, U.S.A). For TGA analysis, samples were placed in alumina pans and heated from 20 to 800 °C at a ramping rate of 10 °C min^{-1} with N_2 supplied at a rate of 100 mL min^{-1}. XPS measurements were collected on an XPS-theta probe instrument (Albany, USA). The BET surface area of synthesized materials was determined using a Micromeritics ASAP 2010 (Norcross, U.S.A) surface analyzer at 77 K. An HPLC system (Thermo Scientific, USA) equipped with a pump (Spectra System P4000) and UV detector (wavelength 360 nm, Spectra System UV2000) was used for sample analysis.

1.4. Computational modeling studies

Modeling was performed using density functional theory (DFT, implemented by means of the pseudopotential code SIESTA),[3] as in our previous study.[4] All calculations were performed using

the generalized gradient approximation (GGA-PBE) including spin polarization[5] by taking into account van der Waals correction.[6] Full optimization of the atomic positions was carried out. During this optimization, the ion cores were described by norm-conserving nonrelativistic pseudopotentials[7] with cutoff radii of 1.14, 1.48, 1.47, 2.52, and 1.25 a.u. for C, N, O, Zr, and H, respectively. The wave functions were expanded with a double-ζ plus polarization basis of localized orbitals for non-hydrogen atoms and with a double-ζ basis for H. Optimization of the force and total energy was performed with accuracies of 0.04 eV/Å and 1 meV, respectively. This procedure was considered to reflect realistic atomic structures of U6N taken from Valenzano et al.[8]. For calculation of U6N, we substituted the amine groups with hydrogen atoms and performed full optimization. For the modeling of COPs (e.g., CD and CE), we used the periodic part of the polymers with substitution of hydrogen atoms (see Fig. S8).

2. Results and discussion

2.1. Modeling studies

In an aqueous environment, the equation for the calculation of H(W) was as follows:

$$H(W) = H_{vapor} - [E(host + H_2O) - E(host) + E(H_2O))],$$

where E(host) is the total energy of the host system, E (H_2O) is the total energy of a single water molecule, E(host+H_2O) is the energy of the host with adsorbed water, and H_{vapor} is the enthalpy

of water evaporation (40.7 kJ mol^{-1}). The terms in the square parentheses of the above noted equation describe the enthalpy of adsorption of water molecules on the active sites of adsorbents. On the other hand, the equation for the enthalpy of FA adsorption was as follows:

$$H(FA) = [E(host + FA) - E(host) + E(FA))] - H(FA - water),$$

where the terms in square parenthesis are the enthalpy of the adsorption of FA molecules on the active sites of adsorbents, and H(FA-water) is the estimated enthalpy of the interaction of FA molecules with water. Unlike gaseous phases, several interactions were possible in an aqueous system, while building an exact model for the aqueous environment is a difficult and expensive process. In this regard, we estimated the energy of water molecules with FA by summarizing the interactions between water and the hydrophilic (C=O)/hydrophobic groups (C-H) of FA. The calculated energy for interaction of water molecules with the hydrophilic groups of FA was approximately -0.1 eV, while the value for the hydrophobic group was estimated to be -0.02 eV.[9] From this value, E (FA-water) was determined to be equal to -0.14 eV or 13.5 kJ mol^{-1}.

Table S1. Generalized equations for the kinetic models used in this study.

Kinetic model	Principle/Assumptions	Expression	Plot	References
Pseudo-first-order	• It depends on the concentration of the solution and adsorption capacity of the adsorbent. As time increases, the closeness to equilibrium decreases, and, finally, when equilibrium is reached, q_e-q_t = 0. • This kinetic model is based on physisorption.	$ln\,(q_e - q_t) = lnq_e - K_1 t$	$ln\,(q_e - q_t) vs$ t	10
Pseudo-second-order	• Chemisorption is the rate limiting step. • It describes the valency forces between the shared electrons of the adsorbent and adsorbate.	$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{t}{q_e}$	$\frac{t}{q_t} vs$ t	11
Intra-particle diffusion	• It describes the boundary layer effect. • Thickness of the boundary layer is the rate-limiting step.	$q_t = K_{ID} t^{1/2} + C$	$q_t\, vs\, t^{1/2}$	12
Elovich	• Activation energy and the degree of surface coverage of active sites.	$q_t = \frac{1}{\beta} ln\alpha\beta + \frac{1}{\beta} ln\, t$	$q_t\, vs ln\, t$	13

Table S2. Generalized equations for the adsorption isotherm models used in this study.

Model Name	Equation	Linear expression	Assumption/principle	Plot	References
Langmuir	$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}}$	$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e}$	• Monolayer adsorption accompanied by physical forces.	$\frac{1}{q_e}\ vs\ \frac{1}{C_e}$	14
Freundlich	$q_e = K_F C_e^{\frac{1}{n}}$	$lnq_e = ln\,K_F + {}^{1}/_{n} lnC_e$	• Multilayer (heterogeneous) adsorption. • The binding site decreases with increasing degree of site occupation. • Stronger binding sites will be occupied first.	$lnq_e\ vs\ lnC_e$	15
Temkin	$q_e =$ B $ln(A_T C_e)$	$q_e = BlnA_T + BlnC_e$	• Heat of sorption (Q) is linear rather than logarithmic. • Due to sorbate-sorbent interactions, the Q of all of the molecules in the adsorption layer will decrease linearly with coverage.	$q_e\ vs\ ln\,C_e$	16-17
Dubinin–Radushkevich	$q_e = q_m\, exp\left(-K_{DR}\varepsilon^2\right)$	$lnq_e = ln\left(q_m\right) - \left(K_{DR}\varepsilon^2\right)$	• Adsorption characteristics of the adsorbent on both homogeneous and heterogeneous adsorption sites. • It helps to identify the adsorption mechanism with the help of the adsorption energy.	$lnq_e\ vs\ \varepsilon^2$	18
Elovich	$\frac{q_e}{q_m} = K_E C_e\, exp\left[-\frac{q_e}{q_m}\right]$	$ln\frac{q_e}{C_e} = lnK_E q_m - \frac{1}{q_m} q_e$	• Multilayer adsorption in which the adsorption sites increase exponentially with adsorption.	$ln\frac{q_e}{C_e}\ vs\ q_e$	19

Table S3. The surface properties of the diverse adsorbents used in this study.

Adsorbents	BET surface area	Single point surface area (P/P_o)	Pore volume	Adsorption average pore diameter (4V/A BET)
	$m^2\ g^{-1}$	$m^2\ g^{-1}$	$cm^3\ g^{-1}$	nm
U6	1,328	1,038	0.79	1.56
U6N	963	749	0.58	1.55
CD	667	541	0.32	1.90
CE	674	558	0.23	1.69

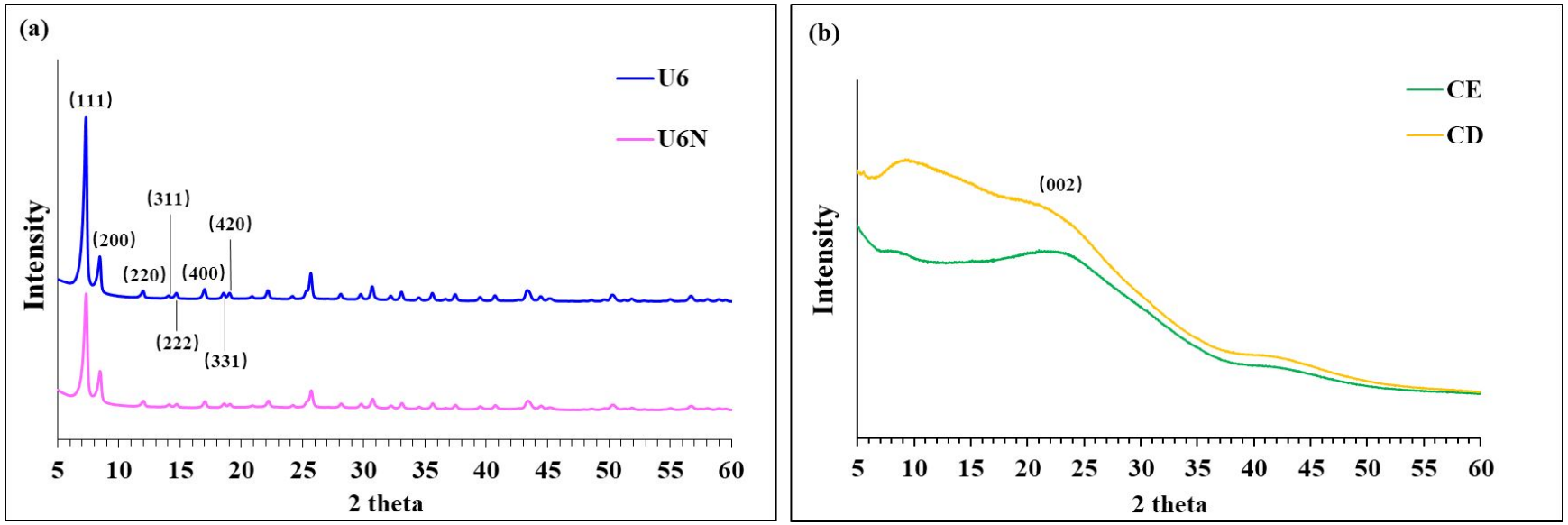

Fig. S1. PXRD patterns of MOFs ((a) U6 (blue) and U6N (pink)) and COPs ((b) CE (green) and CD (yellow)) investigated in this work.

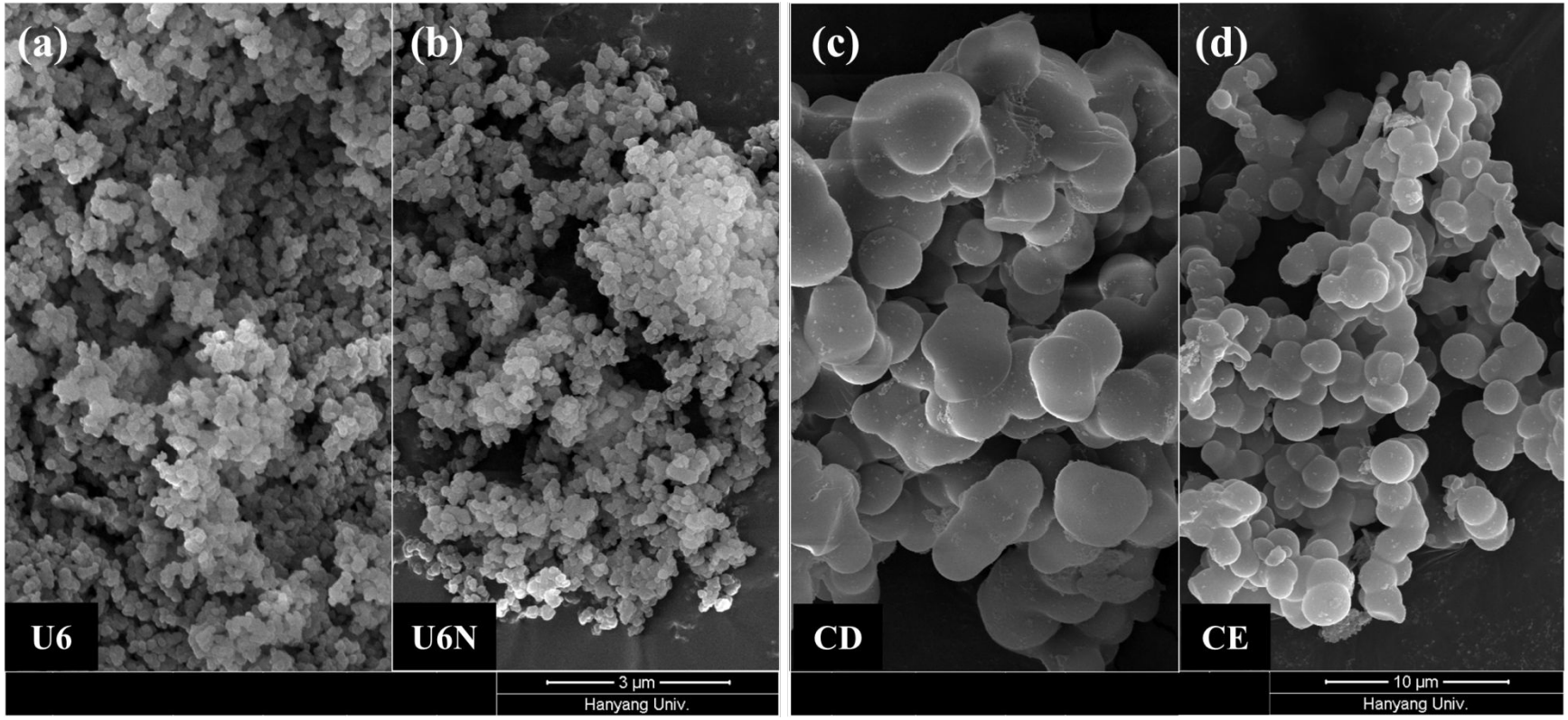

Fig. S2. SEM images of MOFs ((a) U6 and (b) U6N) and COPs ((c) CD and (d) CE) investigated in this research:.

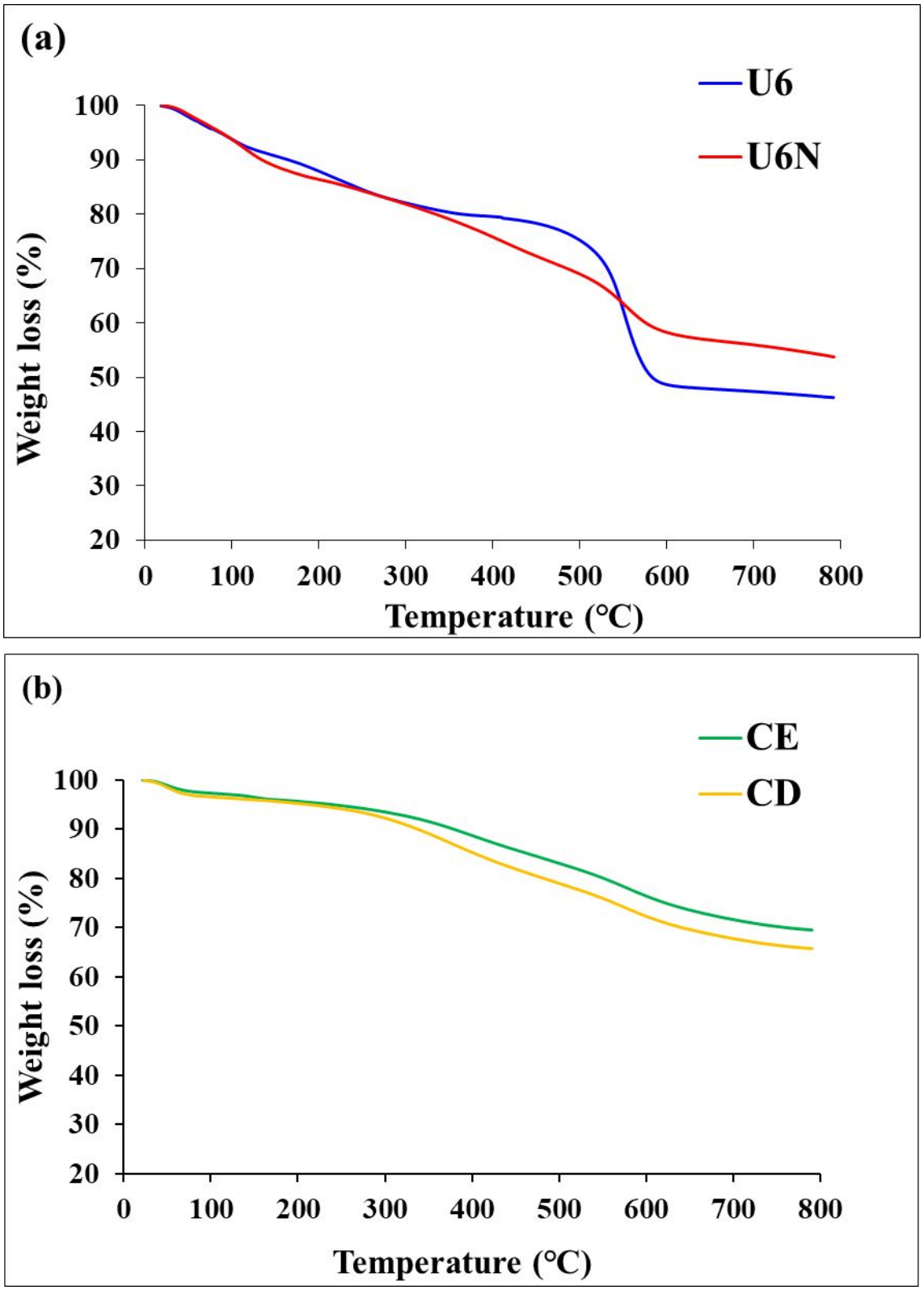

Fig. S3. Summary of TGA patterns of (a) two MOFs (U6 and U6N) and (b) two COPs (CE and CD).

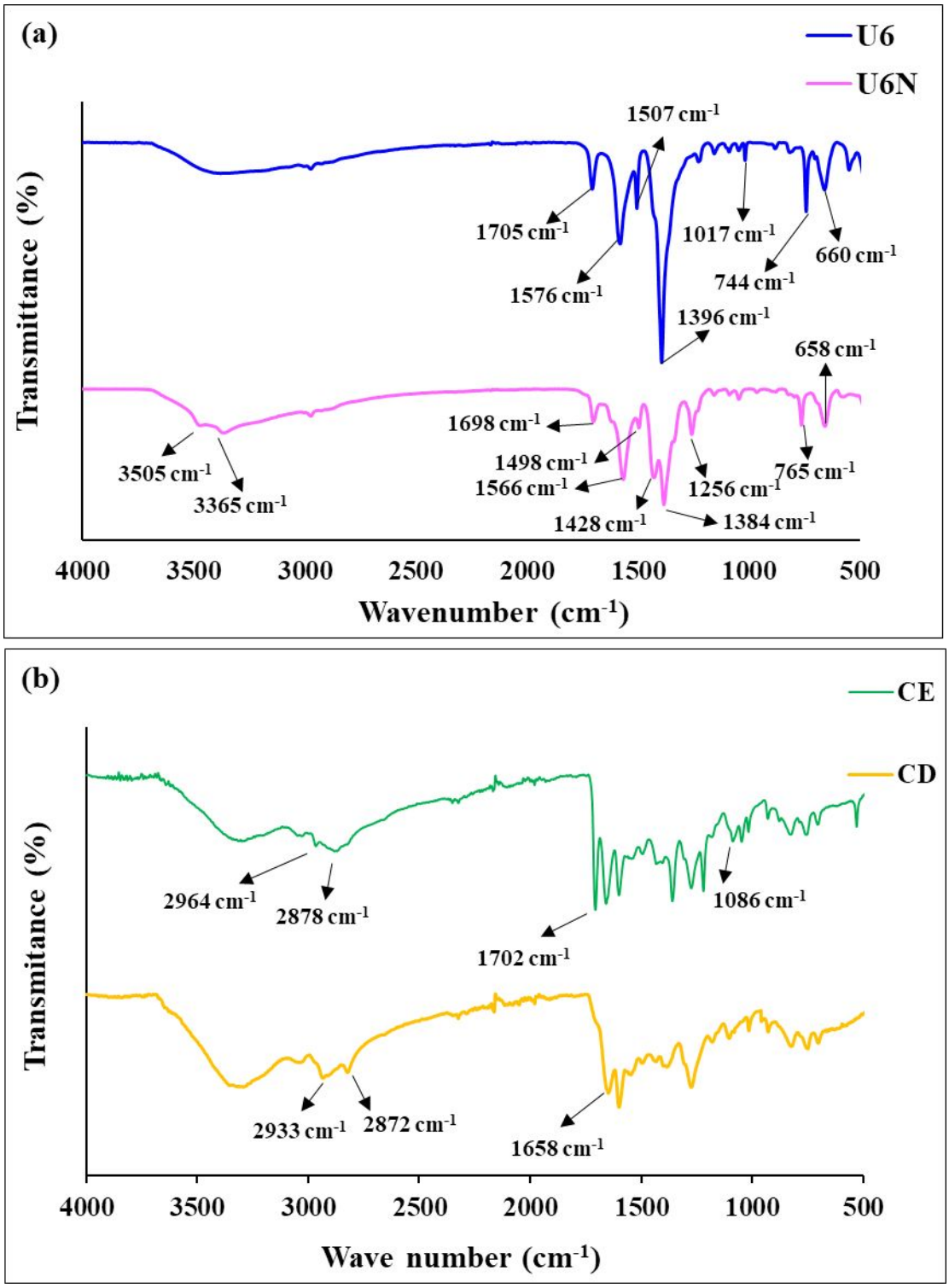

Fig. S4. FTIR spectrums of (a) two MOFs (U6 and U6N) and (b) two COPs (CE and CD).

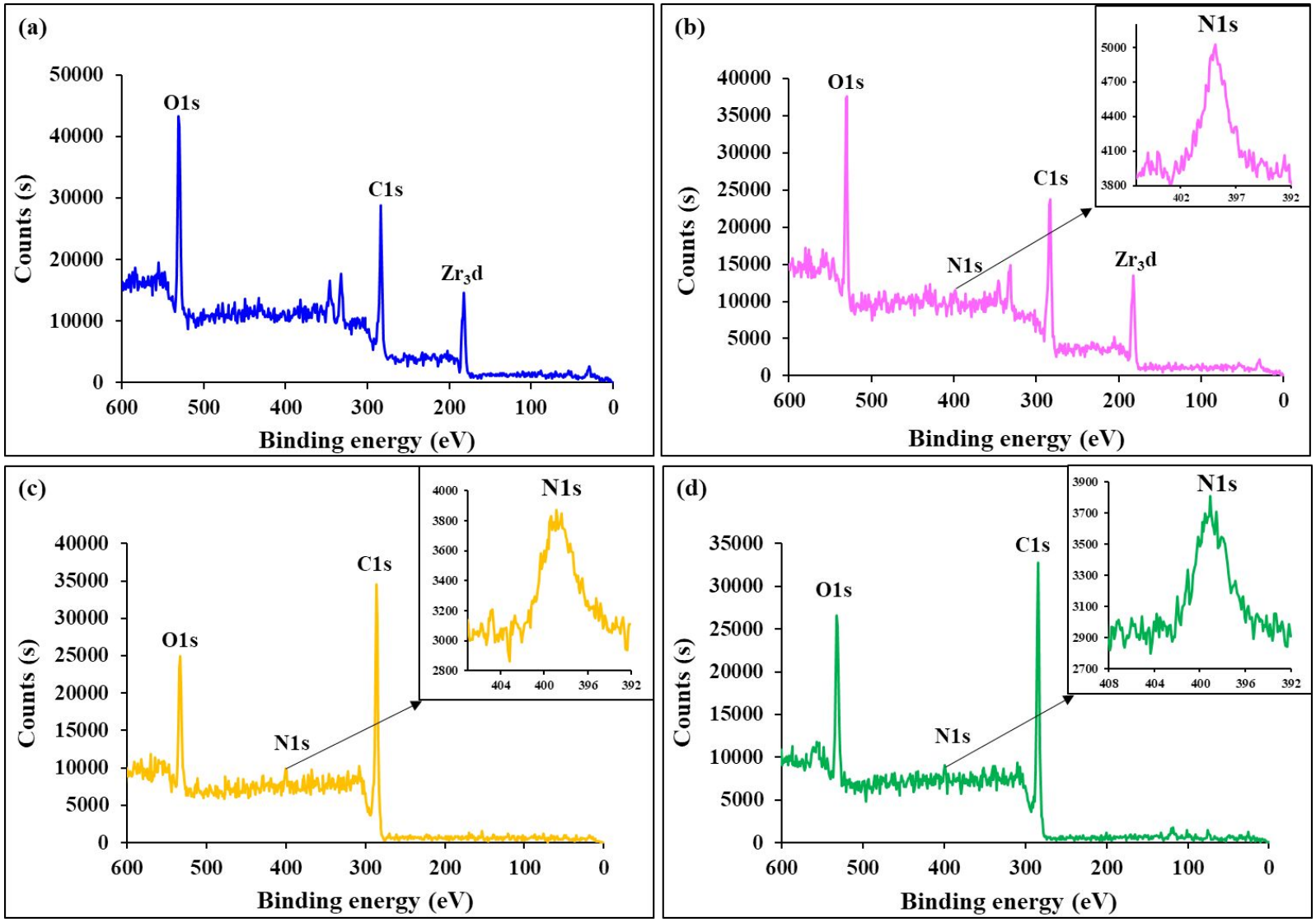

Figure S5. The wide-scan XPS profiles of the originally synthesized porous materials: (a) U6, (b) U6N, (c) CD, and (d) CE.

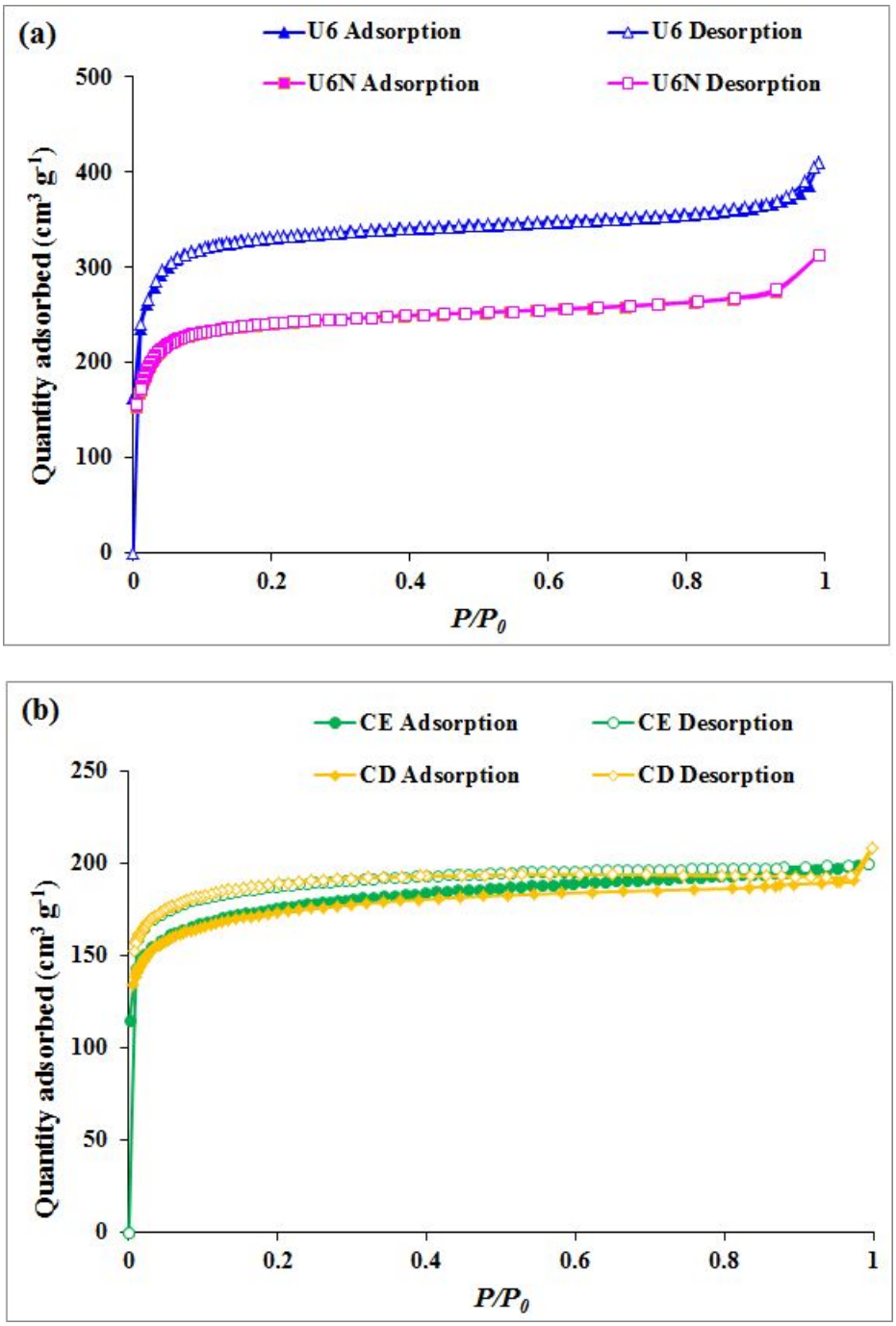

Fig. S6. Plot of the N_2 adsorption-desorption isotherms of (a) two MOFs (U6 and U6N) and (b) two COPs (CE and CD).

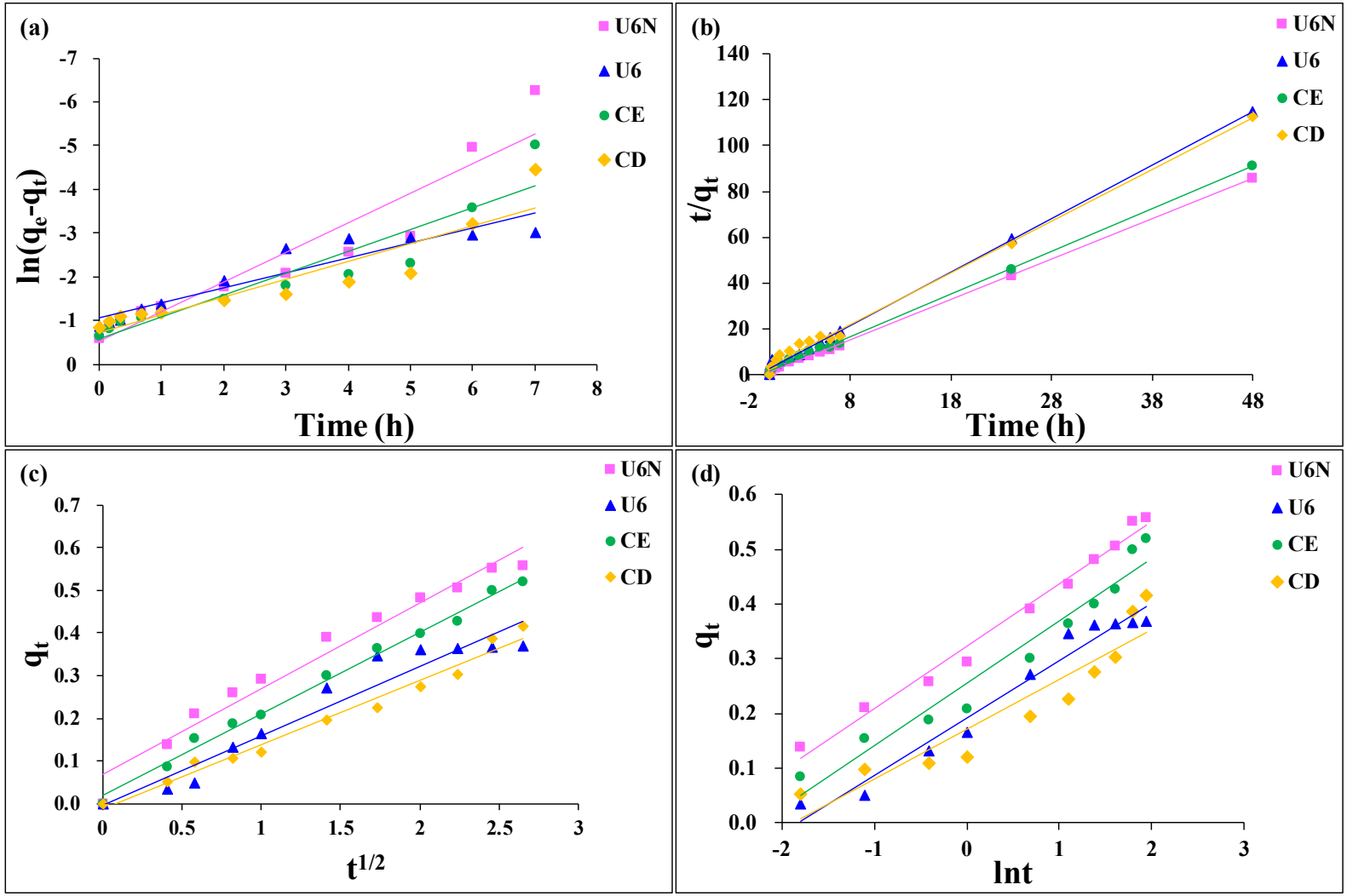

Fig. S7. The kinetic studies of porous materials U6, U6N, CD, CE, and AC for FA in water: (a) the pseudo-first-order model, (b) the pseudo-second-order model, (c) Intra-particle diffusion model, and (d) Elovich model.

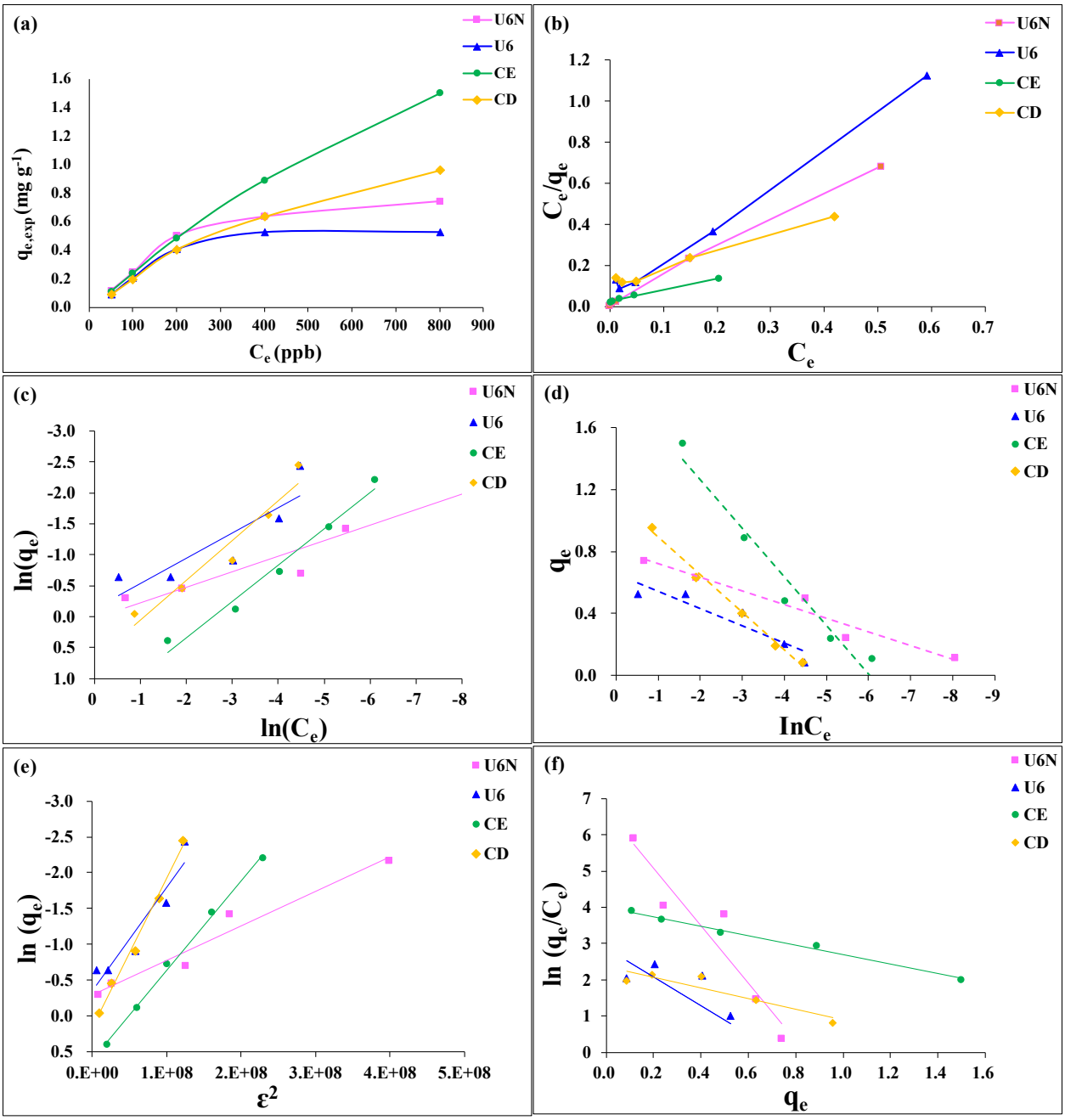

Fig. S8. Adsorption isotherm models of FA removed by four sorbents: U6N, U6, CD, and CE. (a) Adsorption isotherm experiment at different concentrations, (b) Langmuir model, (c) Freundlich model, (d) Temkin model, (e) Dubinin-Radushkevich model, and (f) Elovich model.

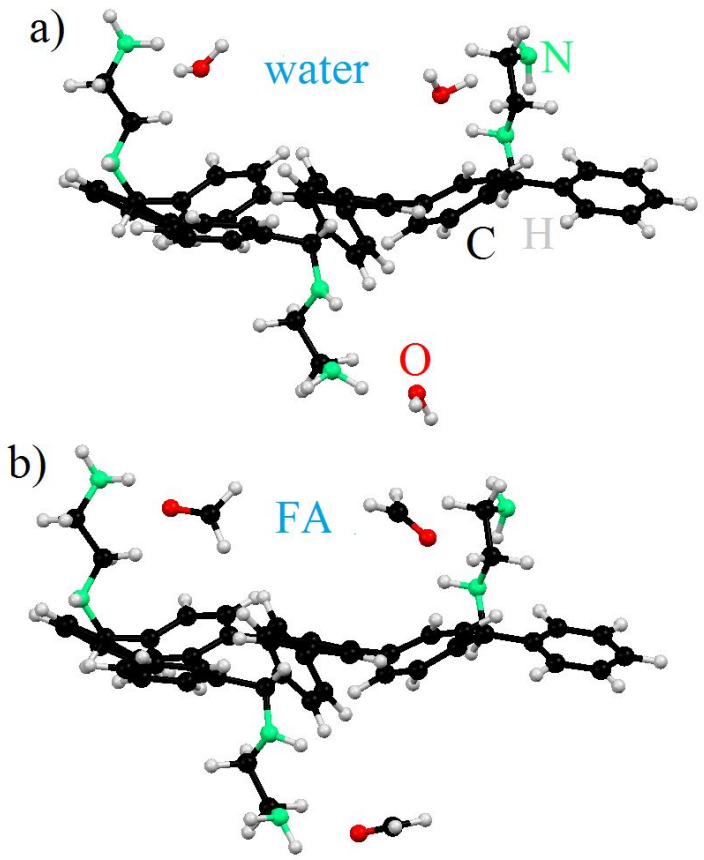

Fig. S9. Optimized atomic structure of the model system used for imitation of the CD compound: (a) after adsorption of water molecules on the active sites of CD and (b) after adsorption of FA molecules on the active sites of CD.

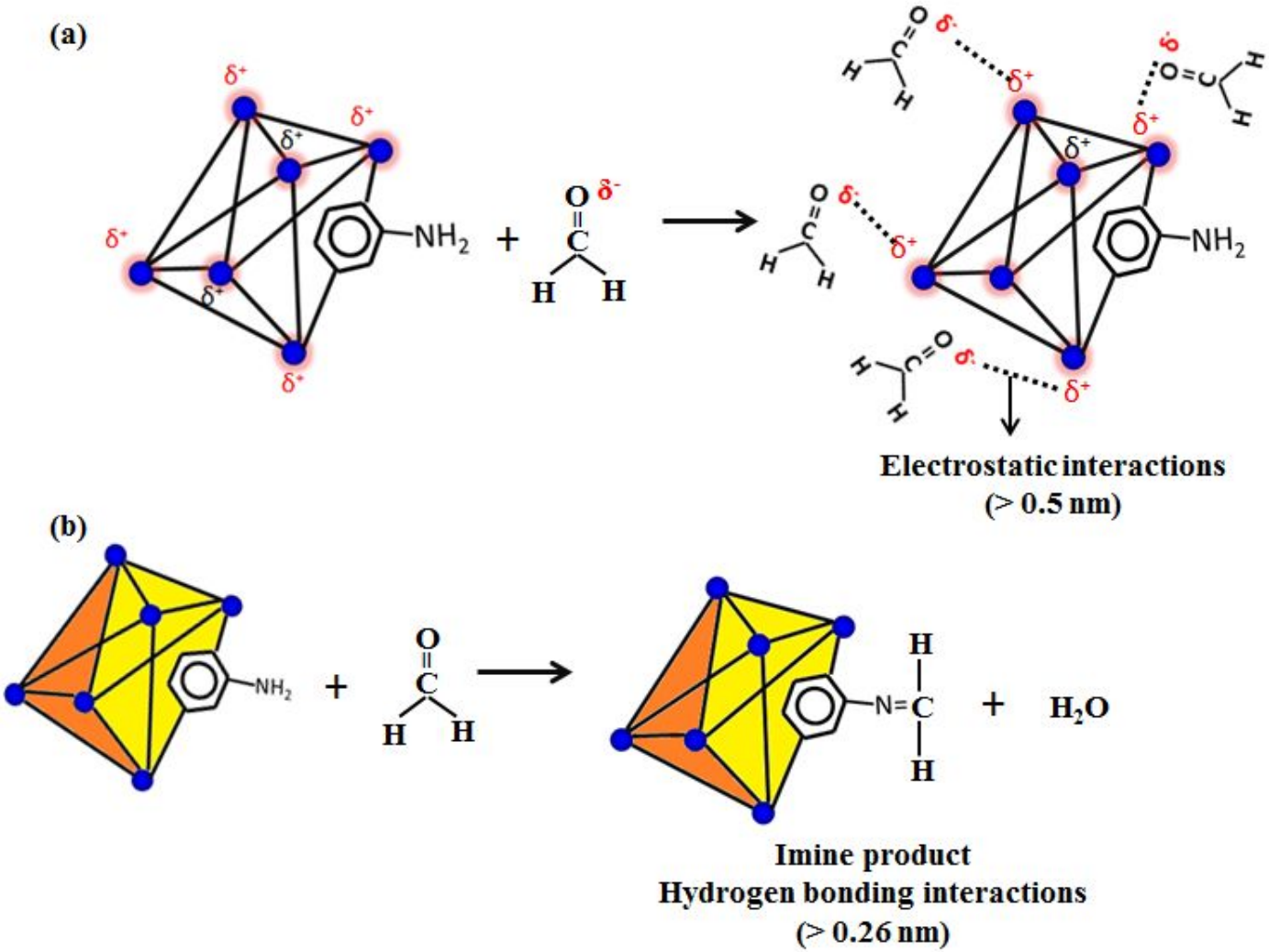

Fig. S10. Adsorption mechanism of U6N toward FA in the aqueous phase in terms of interaction with (a) metal-clusters and (b) amine groups

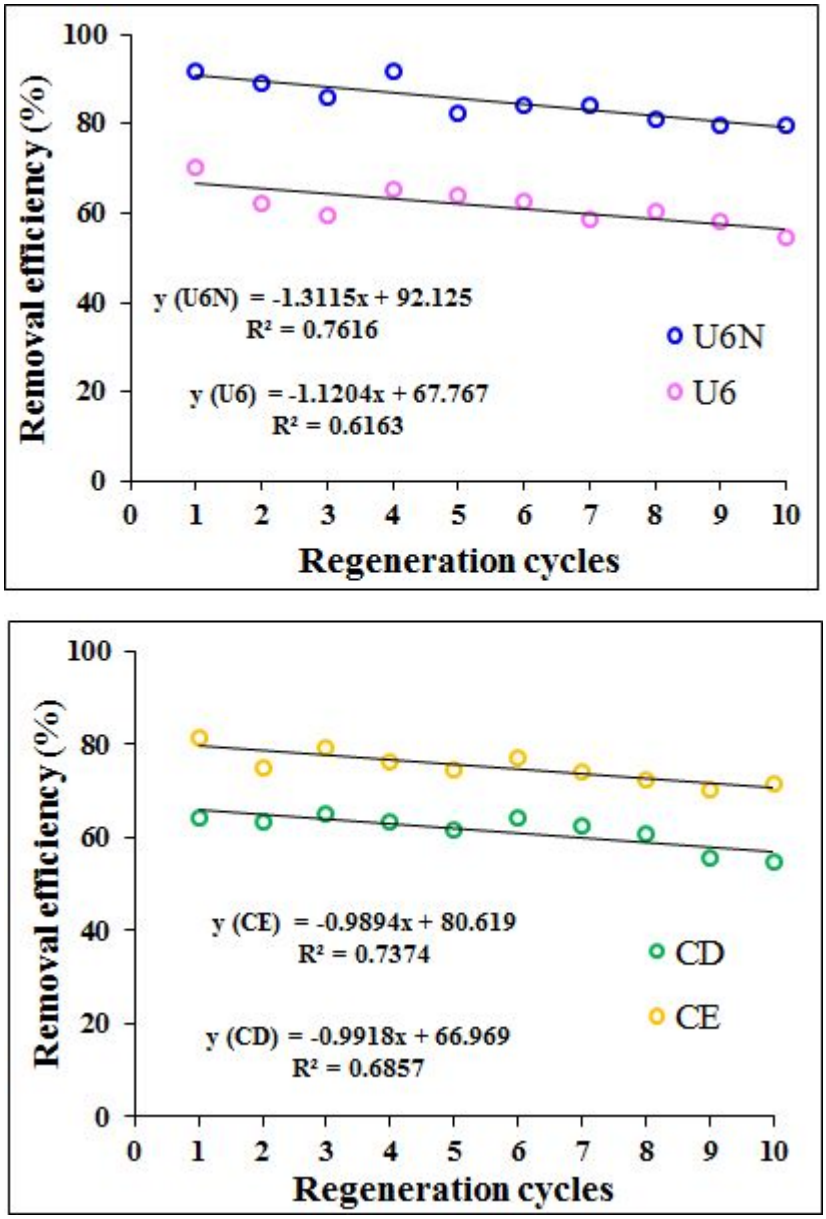

Fig. S11. Linear plot of MOFs and COPs verses number of regeneration cycles.

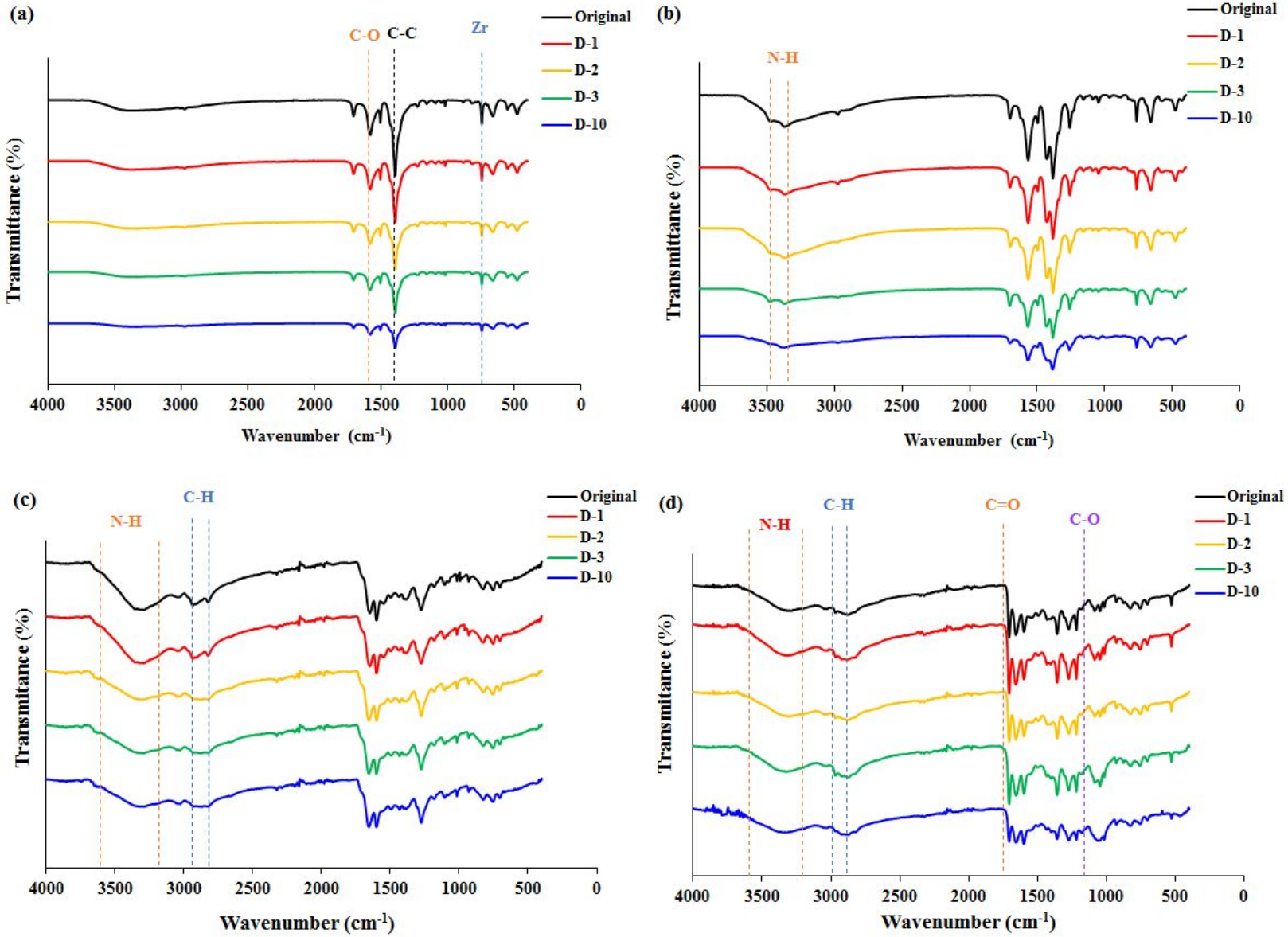

Fig. S12. FTIR spectrum of four porous materials after adsorption of aqueous FA at diverse time intervals: (a) U6, (b) U6N, (c) CD, and (d) CE.

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