Development of Highly Efficient Bimetallic Metal Organic Frameworks for the Extraction of Pd(II) from Aqueous Solutions

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Determination of Pd(II) concentration using UV-vis spectroscopy

The colorimetric determination of Pd(II) was done using Thorin indicator as chromogenic agent, which tends to form 1:1 violet complex with divalent palladium which shows λ_{max} around 540 nm. 1 mL of 0.05 % (w/V) thorin indicator was used for the studies. pH of the solution to be analyzed was maintained at 3.7 using sodium acetate-acetic acid buffer. A series of solutions ranging from 1 ppm to 10 ppm was prepared from a standard Pd(II) stock solution of concentration 1 g/L. The calibration was done with these standard solutions which yielded a linear calibration plot. The value of molar extinction coefficient, obtained from the slope of calibration plot was found to be 6598.04 L mol^{-1} cm^{-1}. Similar procedure for palladium(II) determination was reported in literature.[1]

PXRD

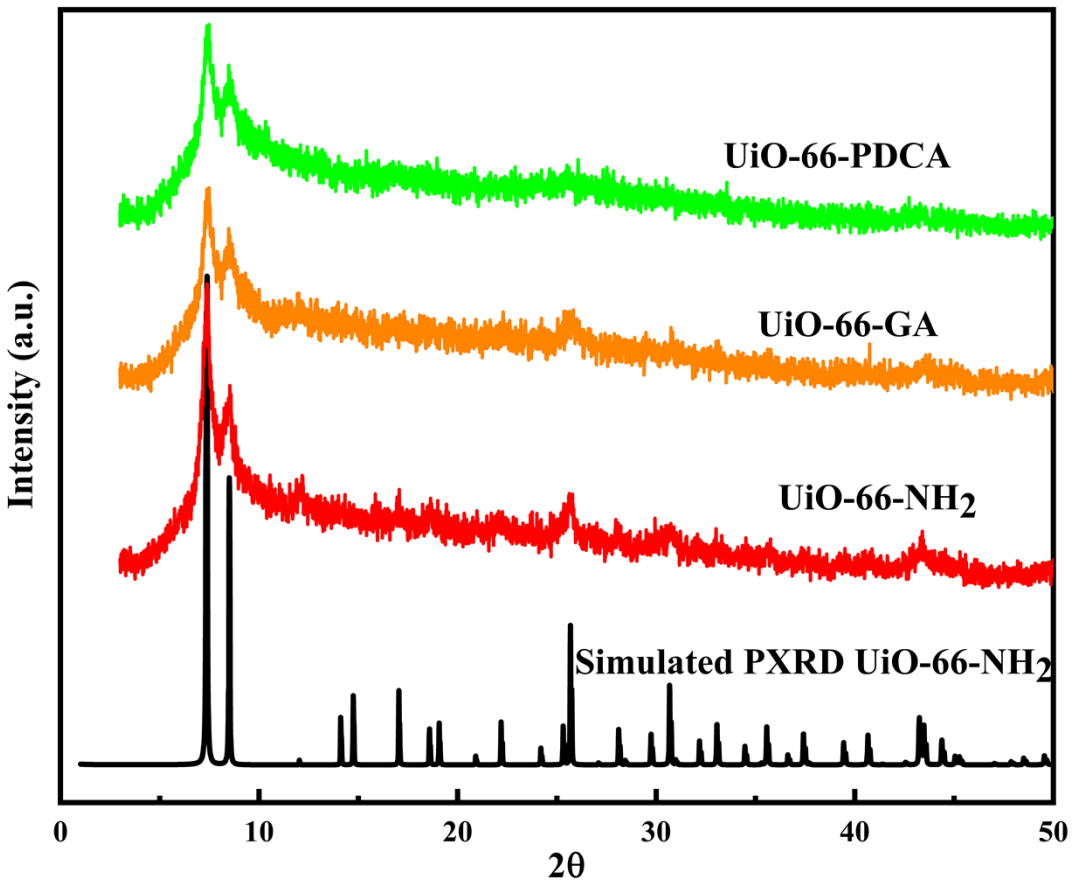


Fig. S1 PXRD of UiO-66-NH_2, UiO-66-GA and UiO-66-PDCA

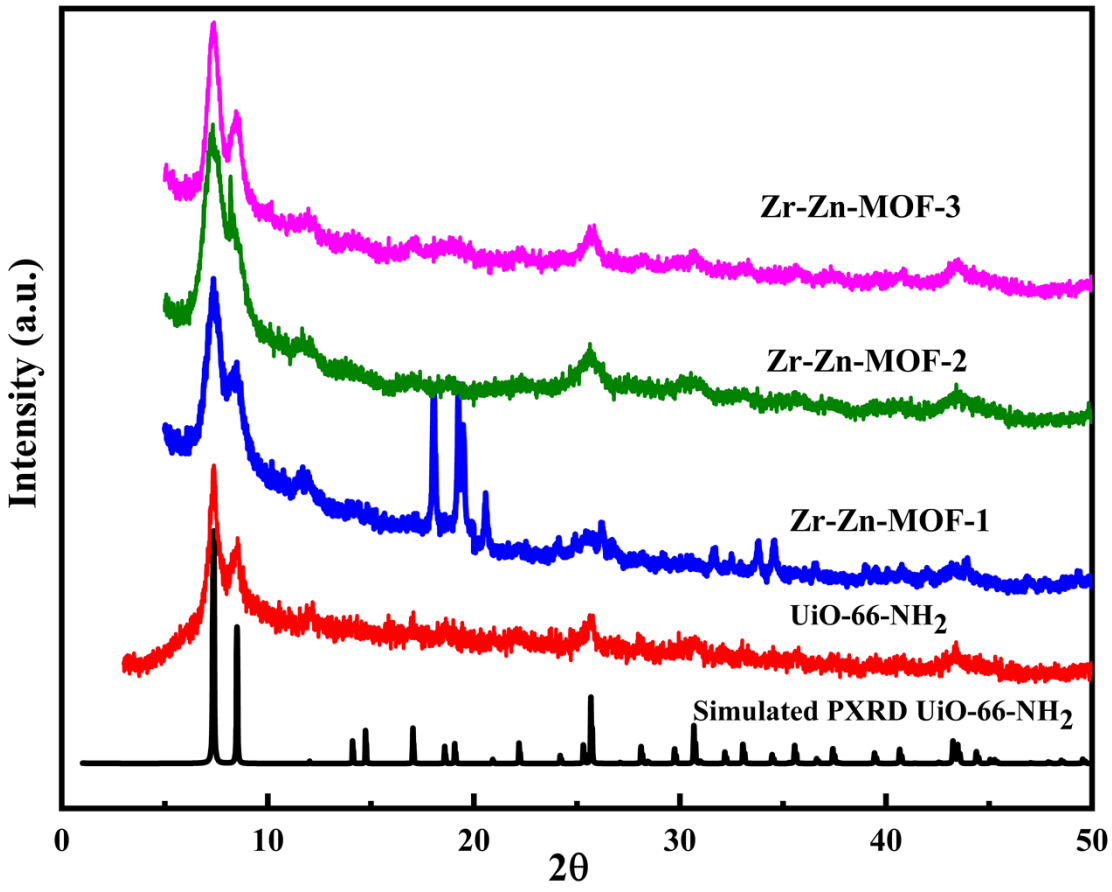


Fig. S2 PXRD of UiO-66-NH_2 and bimetallic MOFs

BET Surface Area Analysis

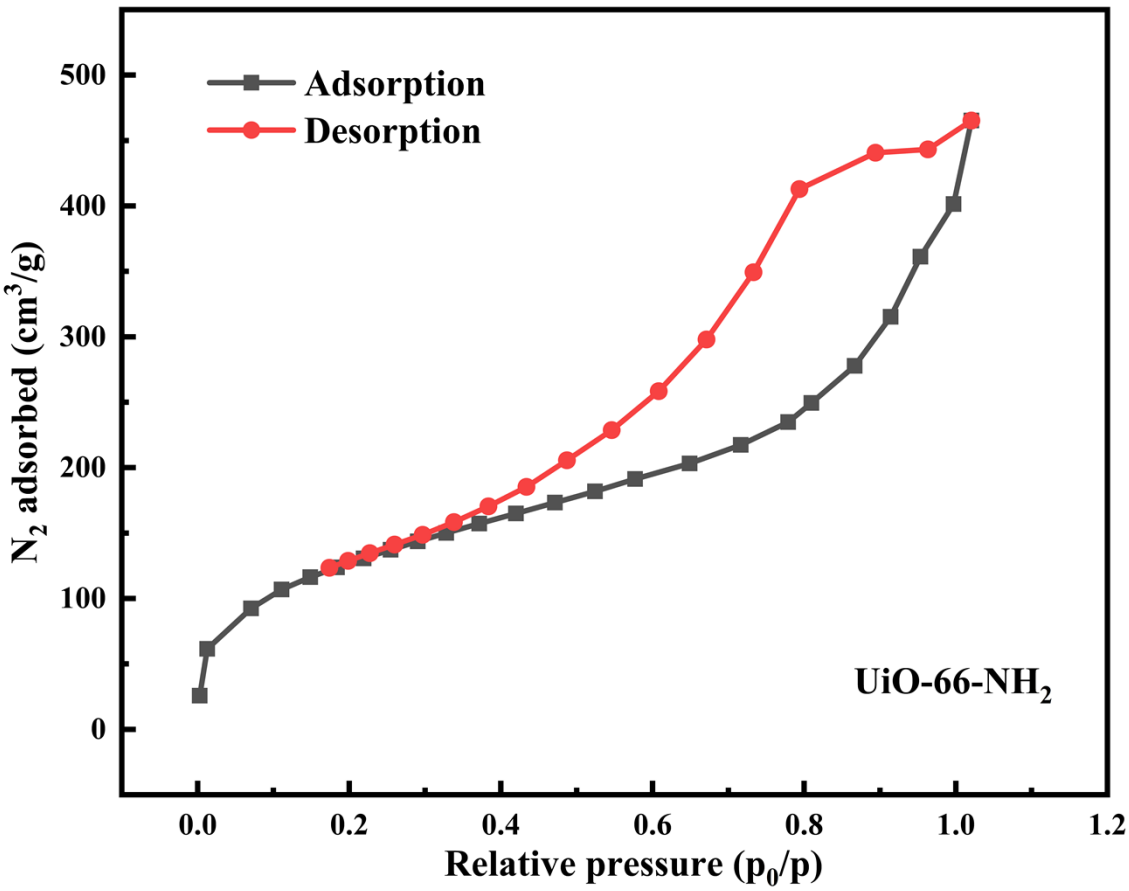


Fig. S3 N_2 adsorption-desorption isotherm at 77 K for UiO-66-NH_2

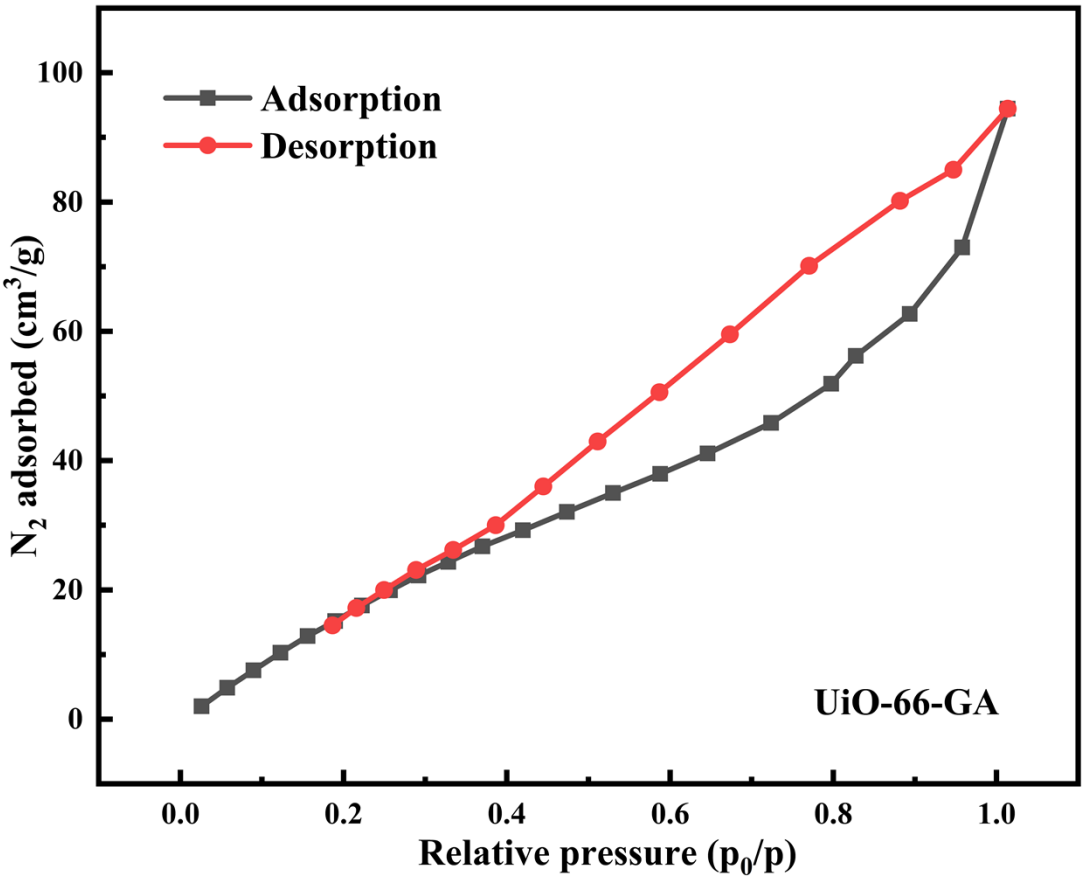


Fig. S4 N_2 adsorption-desorption isotherm at 77 K for UiO-66-GA

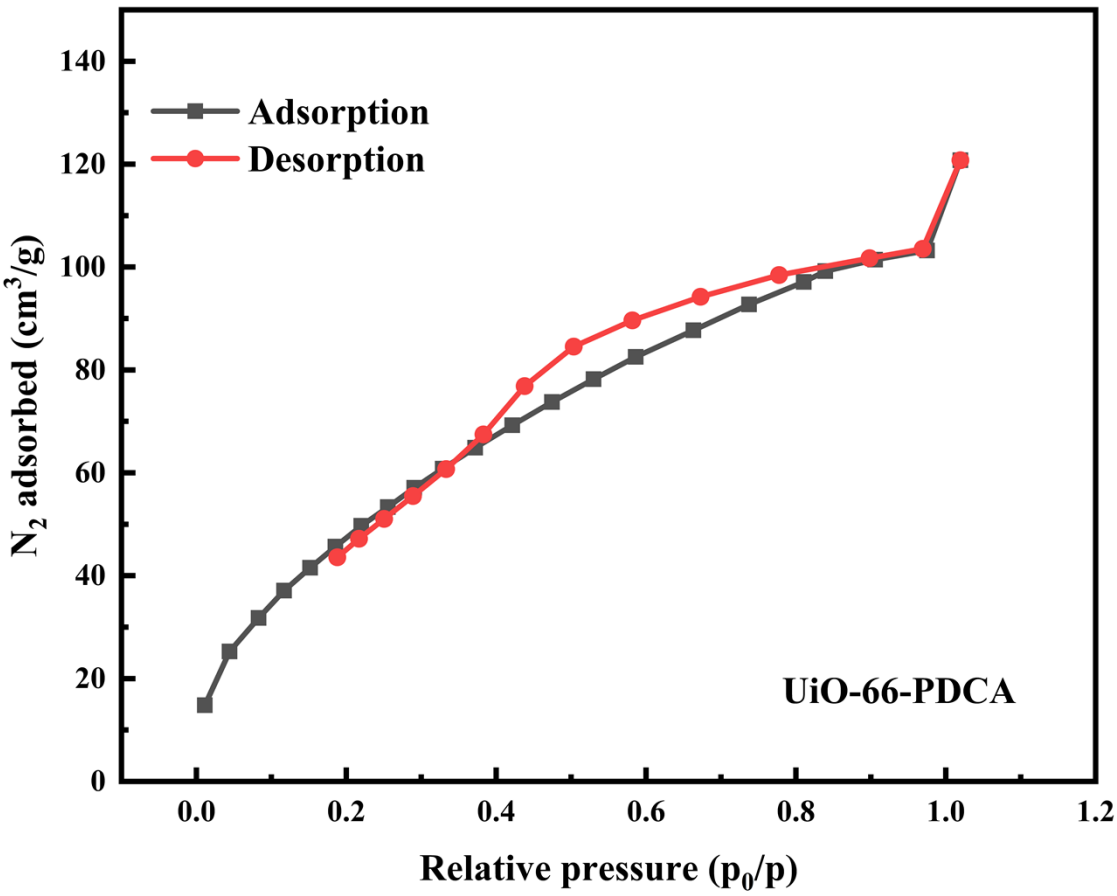


Fig. S5 N_2 adsorption-desorption isotherm at 77 K for UiO-66-PDCA

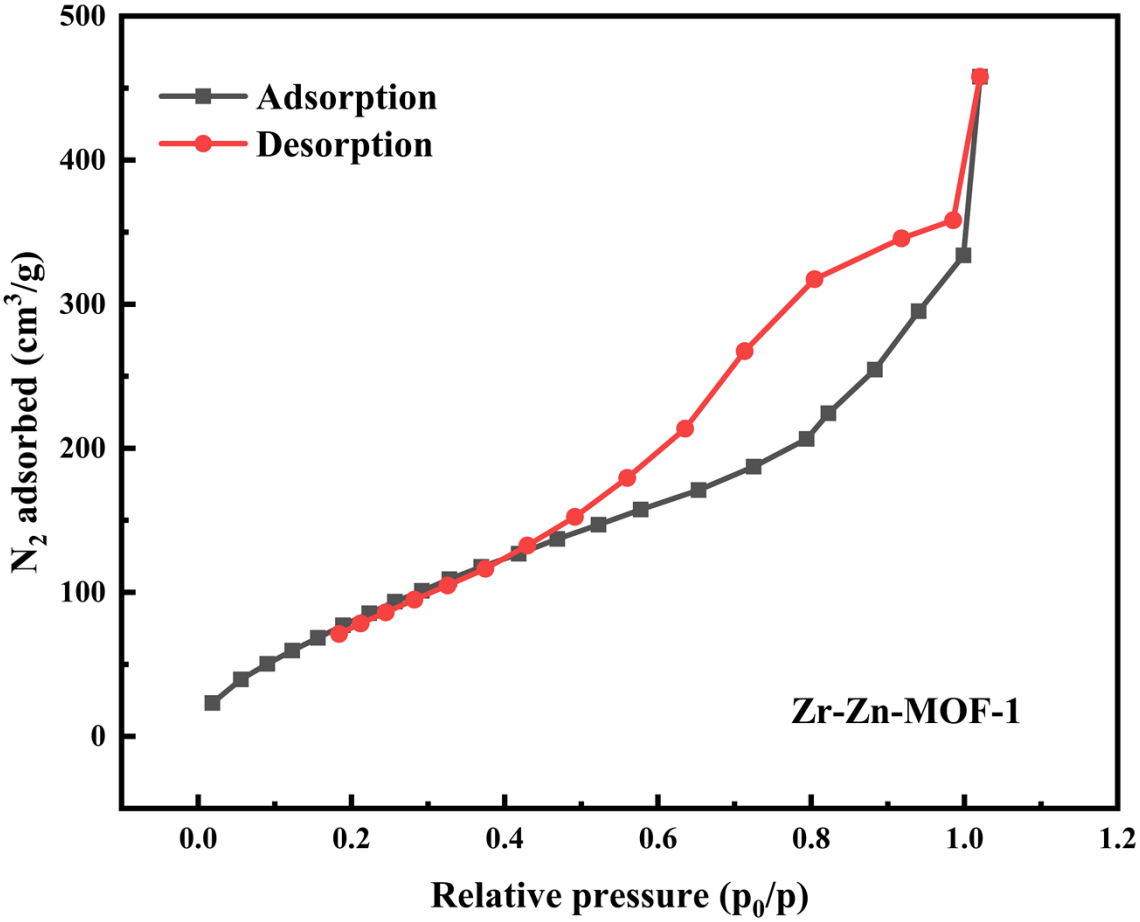


Fig. S6 N_2 adsorption-desorption isotherm at 77 K for Zr-Zn-MOF-1

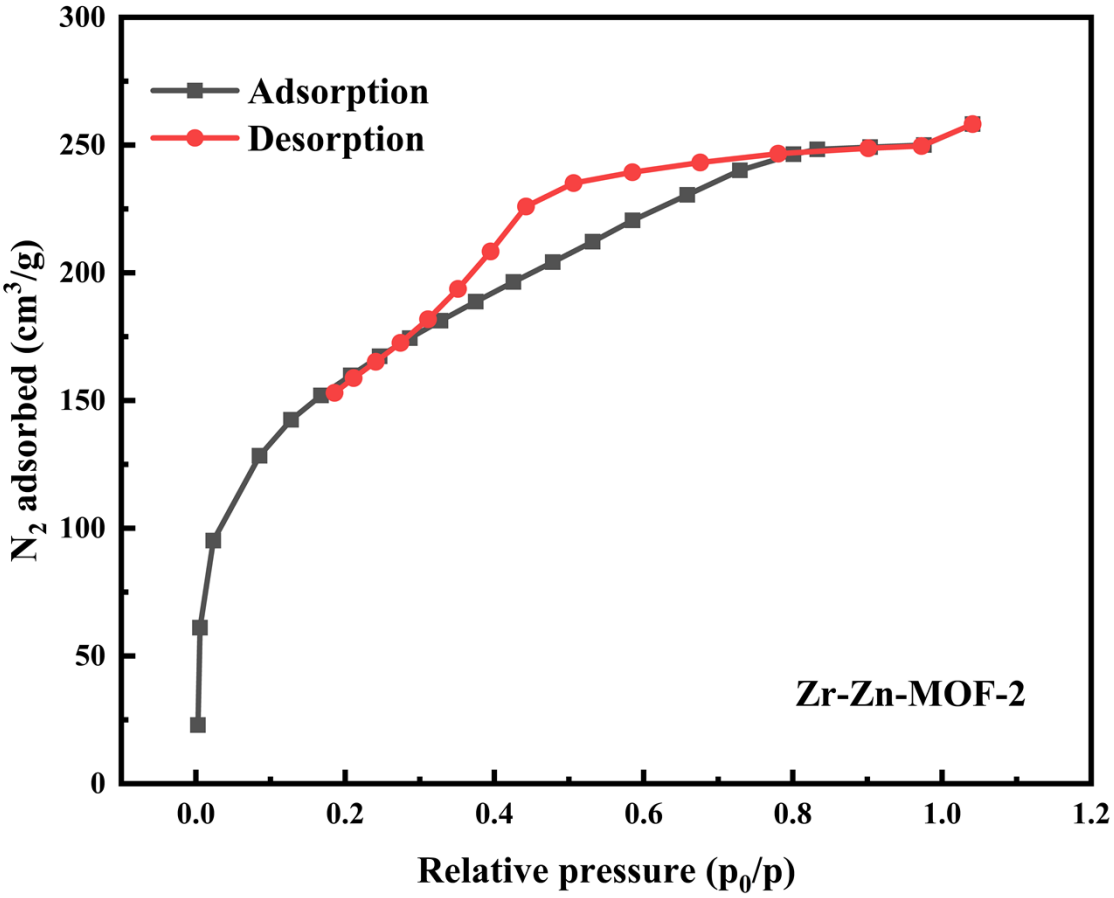


Fig. S7 N_2 adsorption-desorption isotherm at 77 K for Zr-Zn-MOF-2

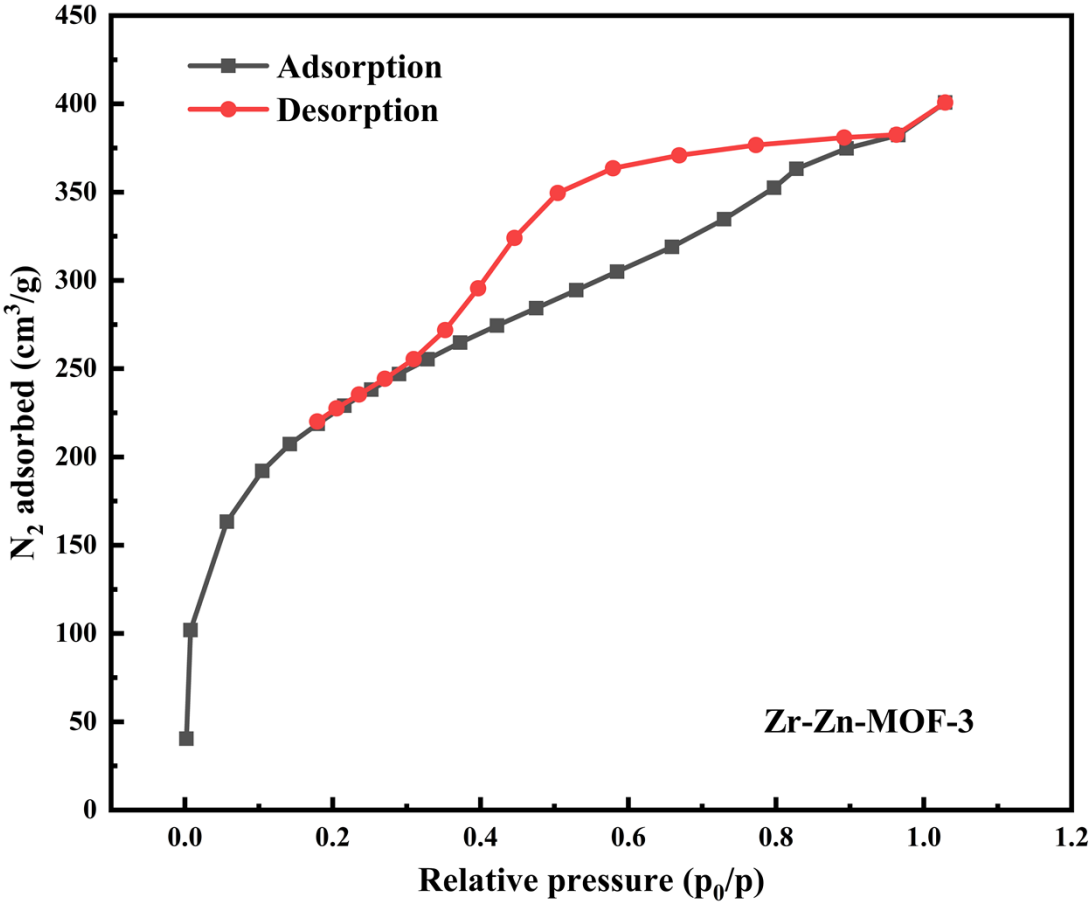
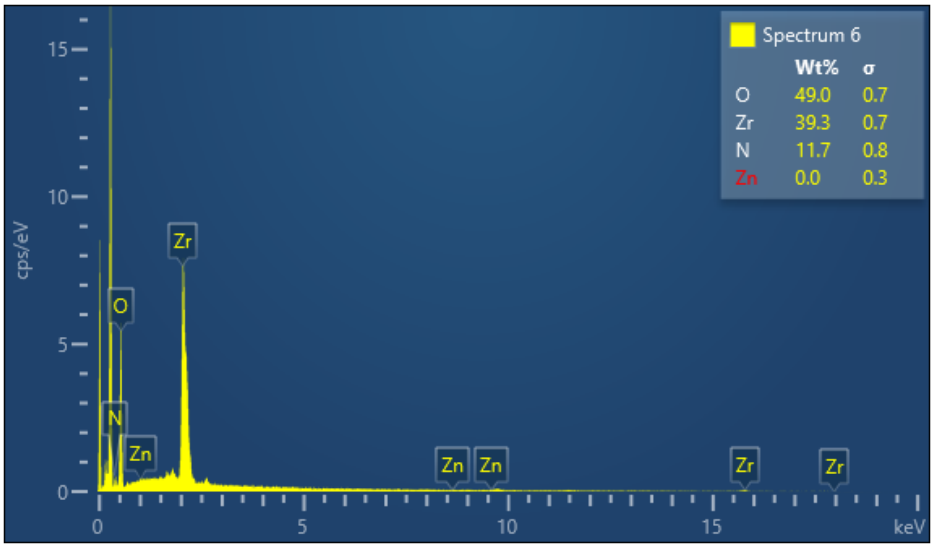
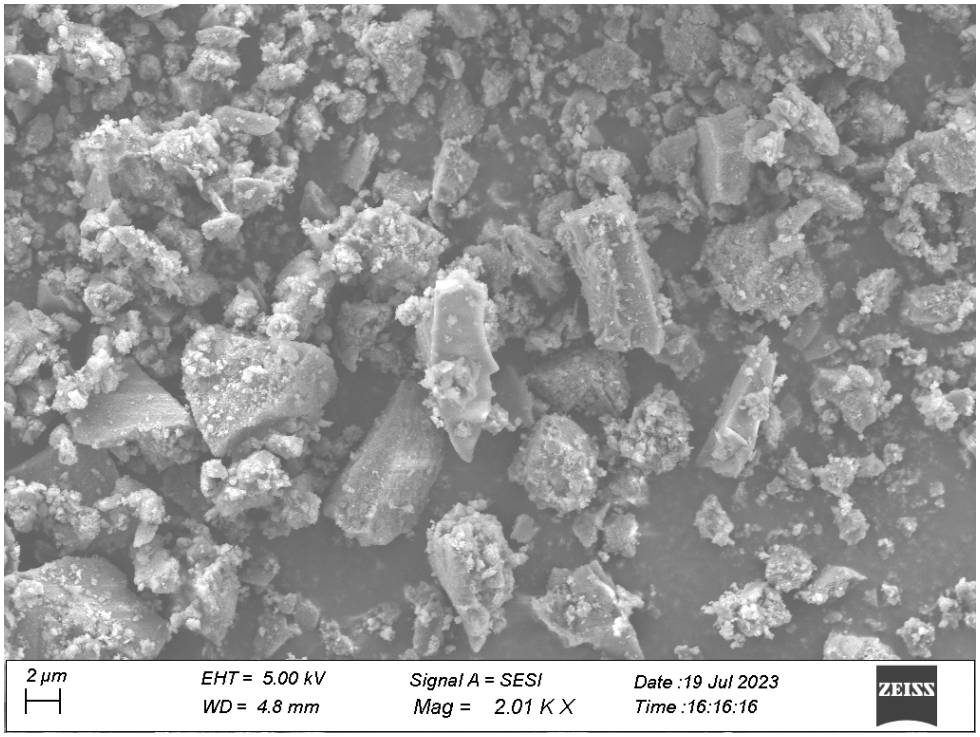


Fig. S8 N_2 adsorption-desorption isotherm at 77 K for Zr-Zn-MOF-3

SEM-EDX Analysis

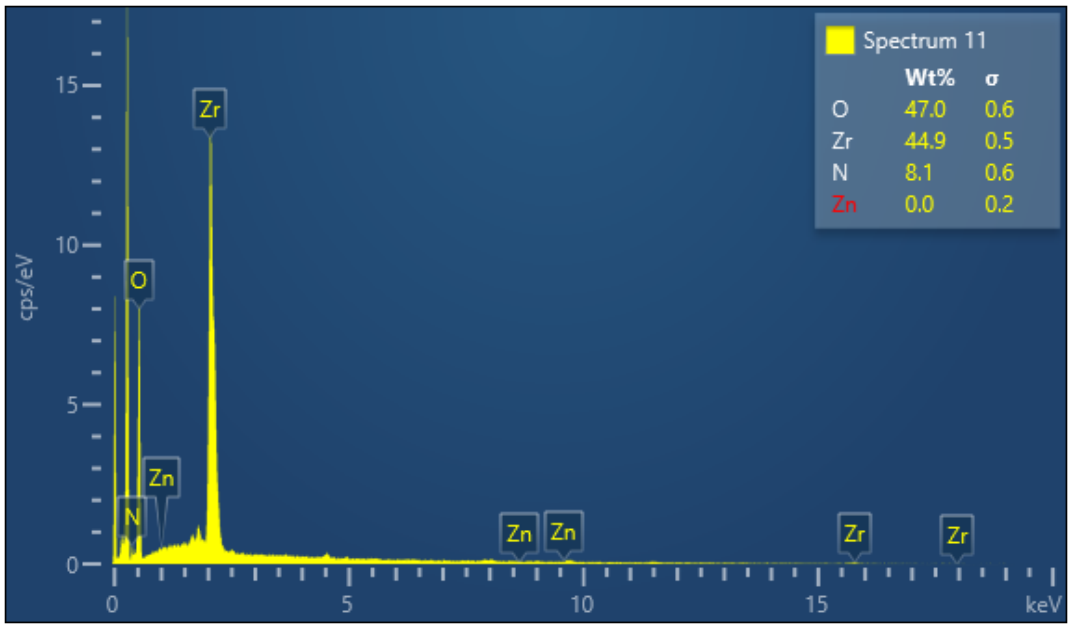


(a)

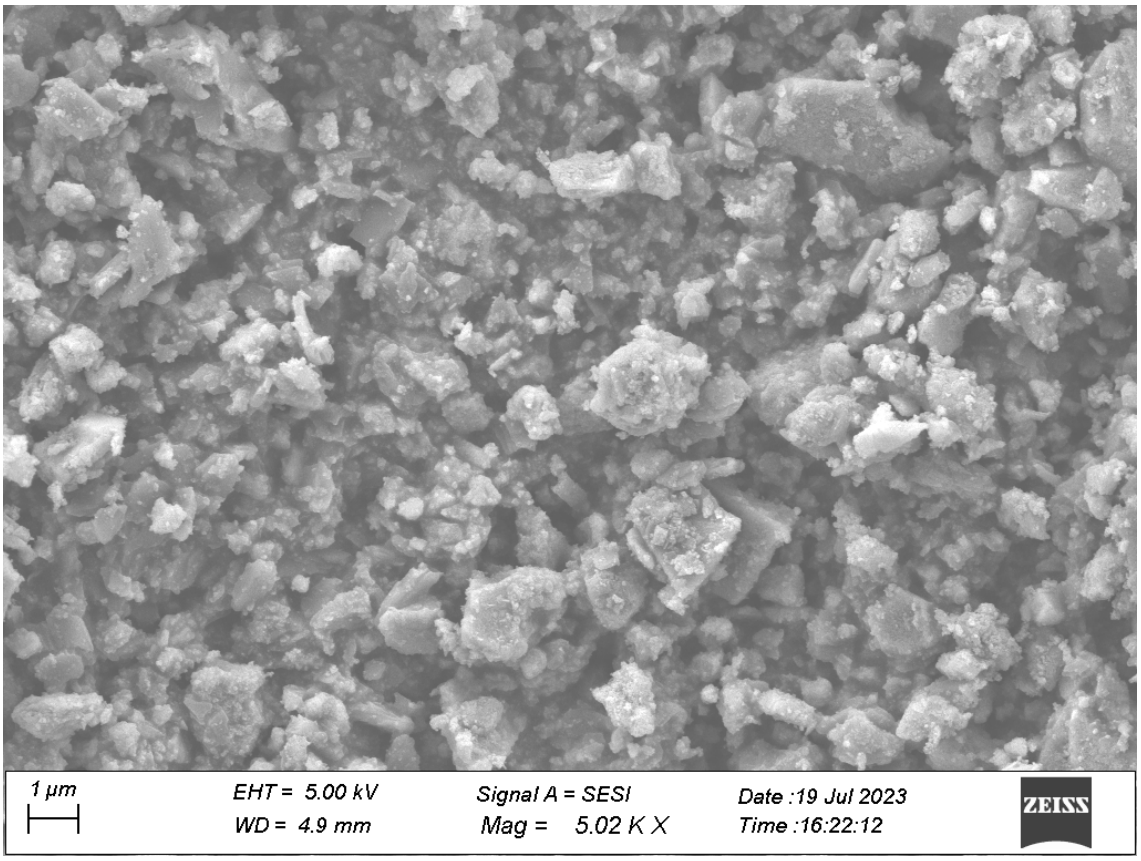


(b)

Fig. S9(a) EDX spectra and (b) SEM image of UiO-66-NH_2.

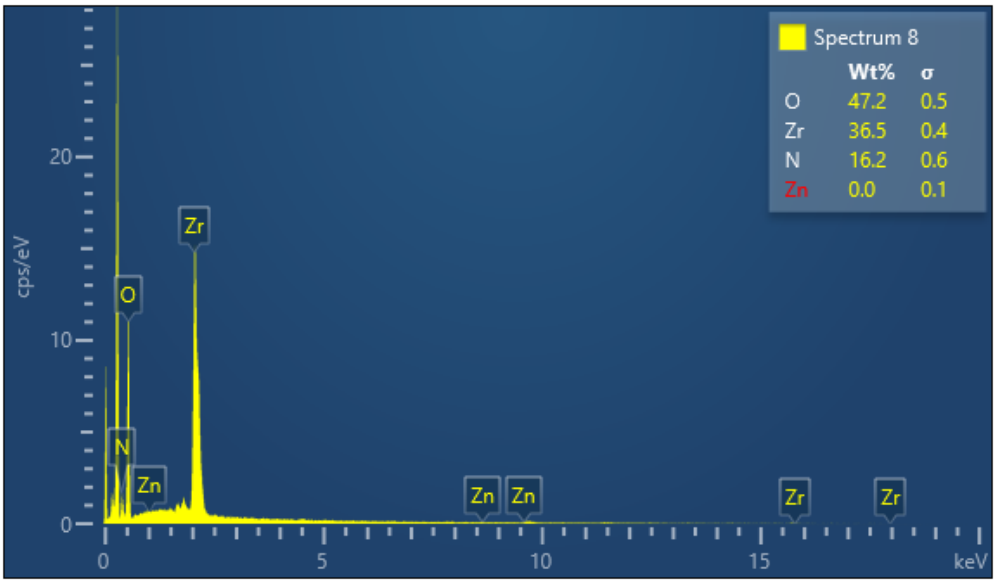


(a)

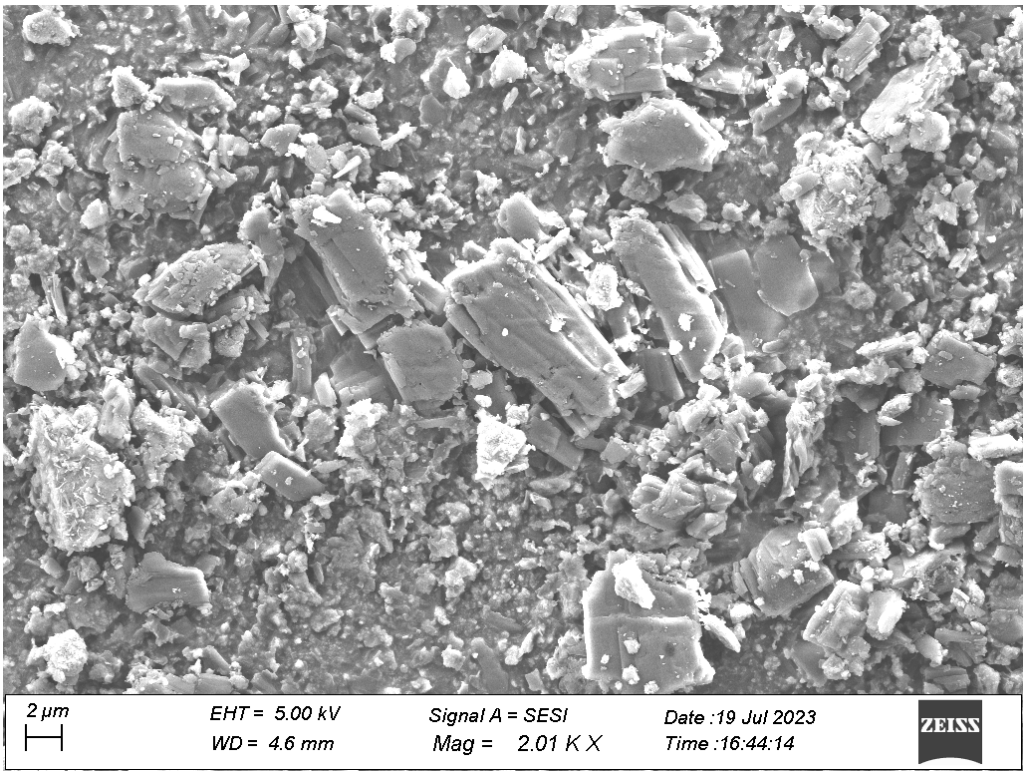


(b)

Fig. S10(a) EDX spectra and (b) SEM image of UiO-66-GA.

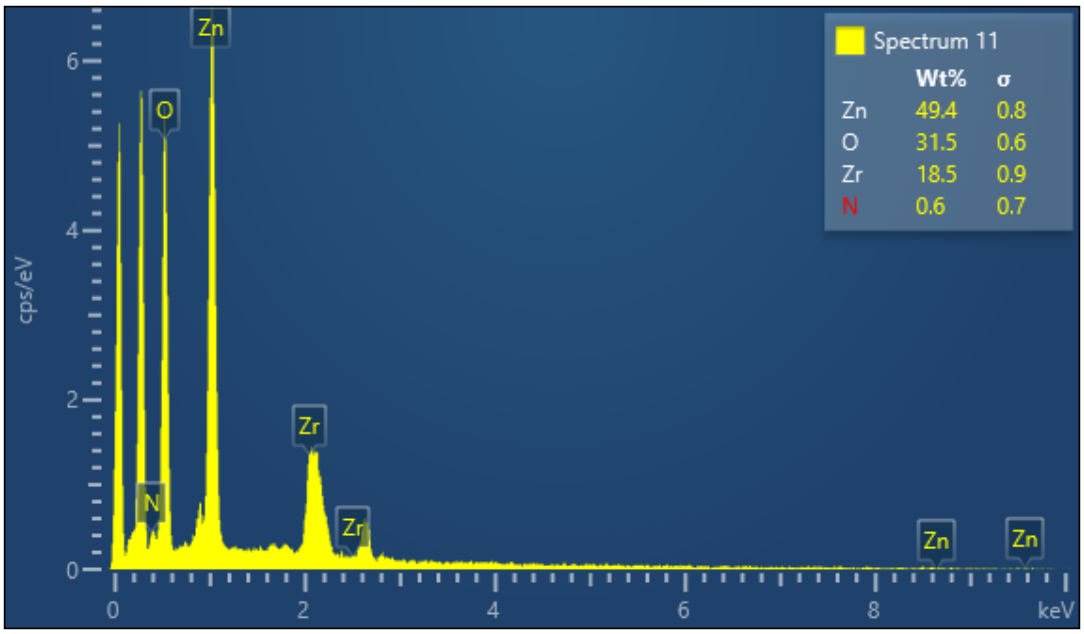


(a)

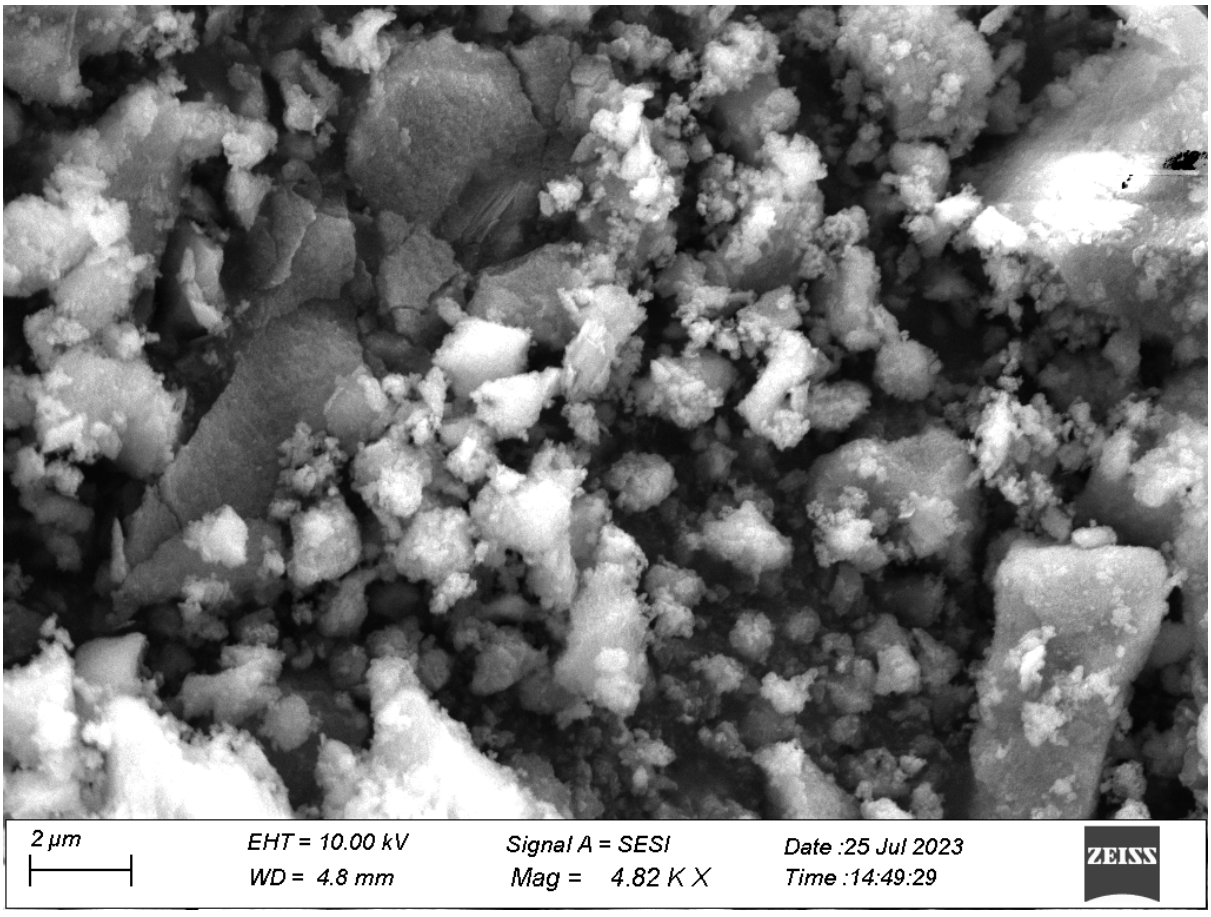


(b)

Fig. S11(a) EDX spectra and (b) SEM image of UiO-66-PDCA.

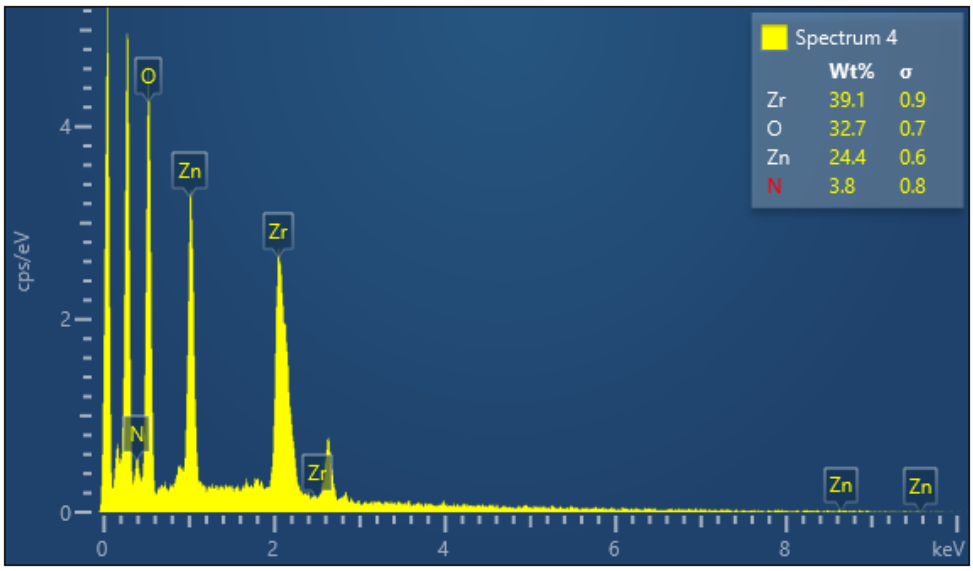


(a)

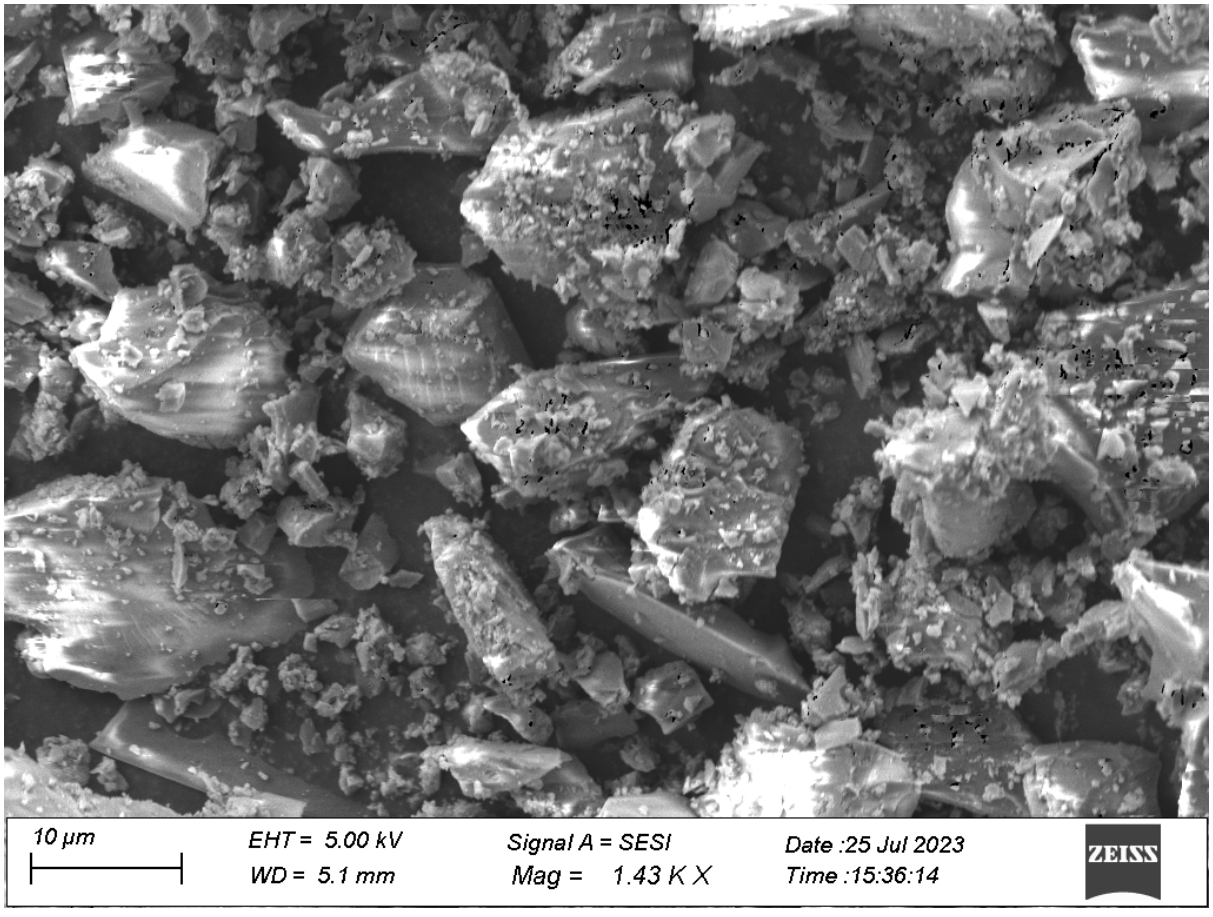


(b)

Fig. S12(a) EDX spectra and (b) SEM image of Zr-Zn-MOF-1.

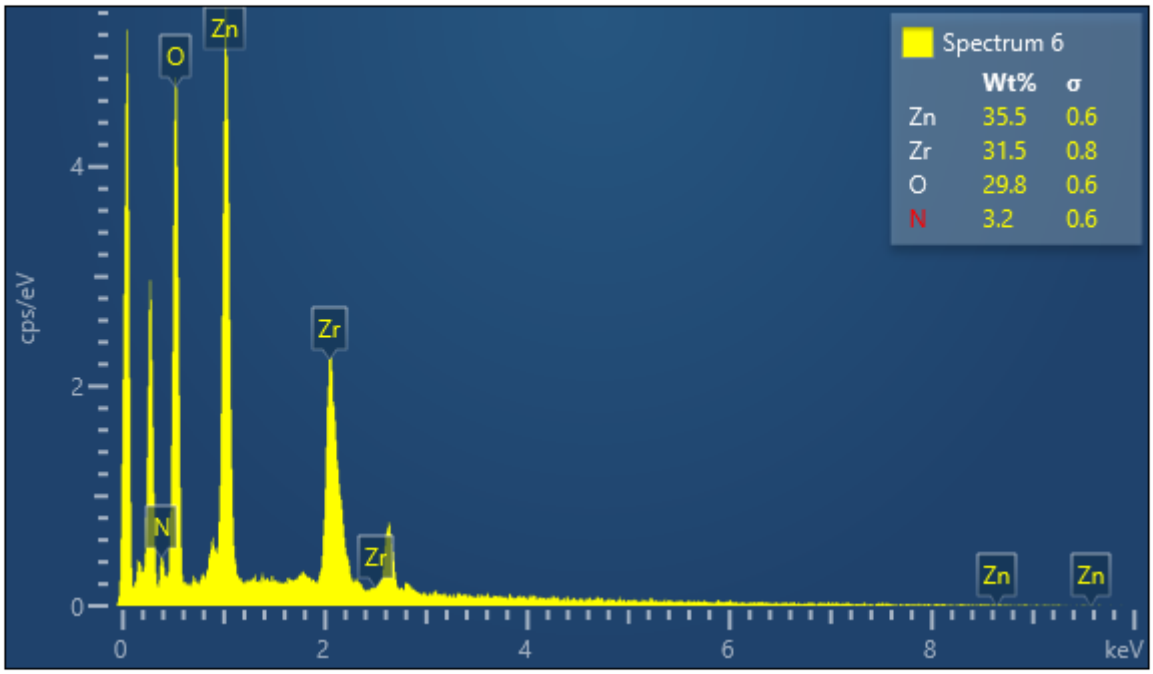

Spectrum 4
Wt% σ
Zr 39.1 0.9
O 32.7 0.7
Zn 24.4 0.6
N 3.8 0.8
O
Zn
Zr
N
Zr
Zn
Zn
cps/eV
0
2
4
0
2
4
6
8
keV

(a)

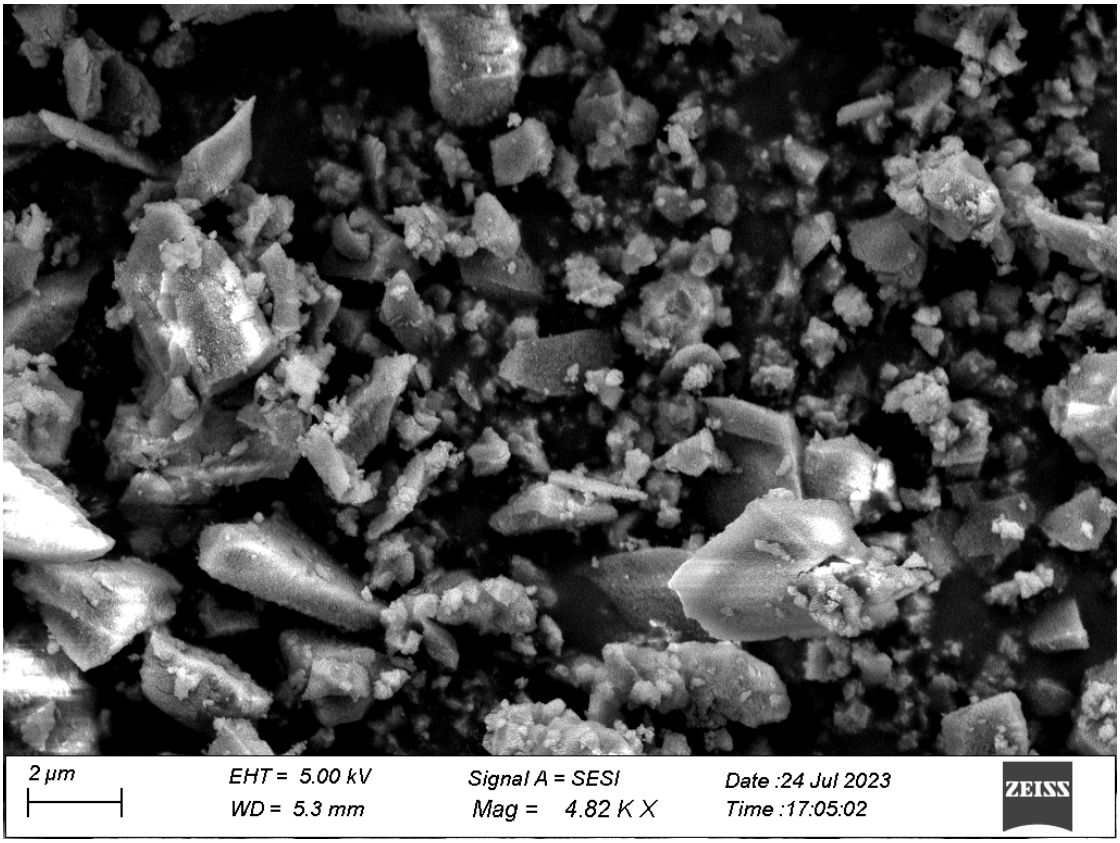

10 µm
EHT = 5.00 kV
WD = 5.1 mm
Signal A = SESI
Mag = 1.43 K X
Date :25 Jul 2023
Time :15:36:14
ZEISS

(b)

Fig. S13(a) EDX spectra and (b) SEM image of Zr-Zn-MOF-2.



(a)



(b)

Fig. S14(a) EDX spectra and (b) SEM image of Zr-Zn-MOF-3.

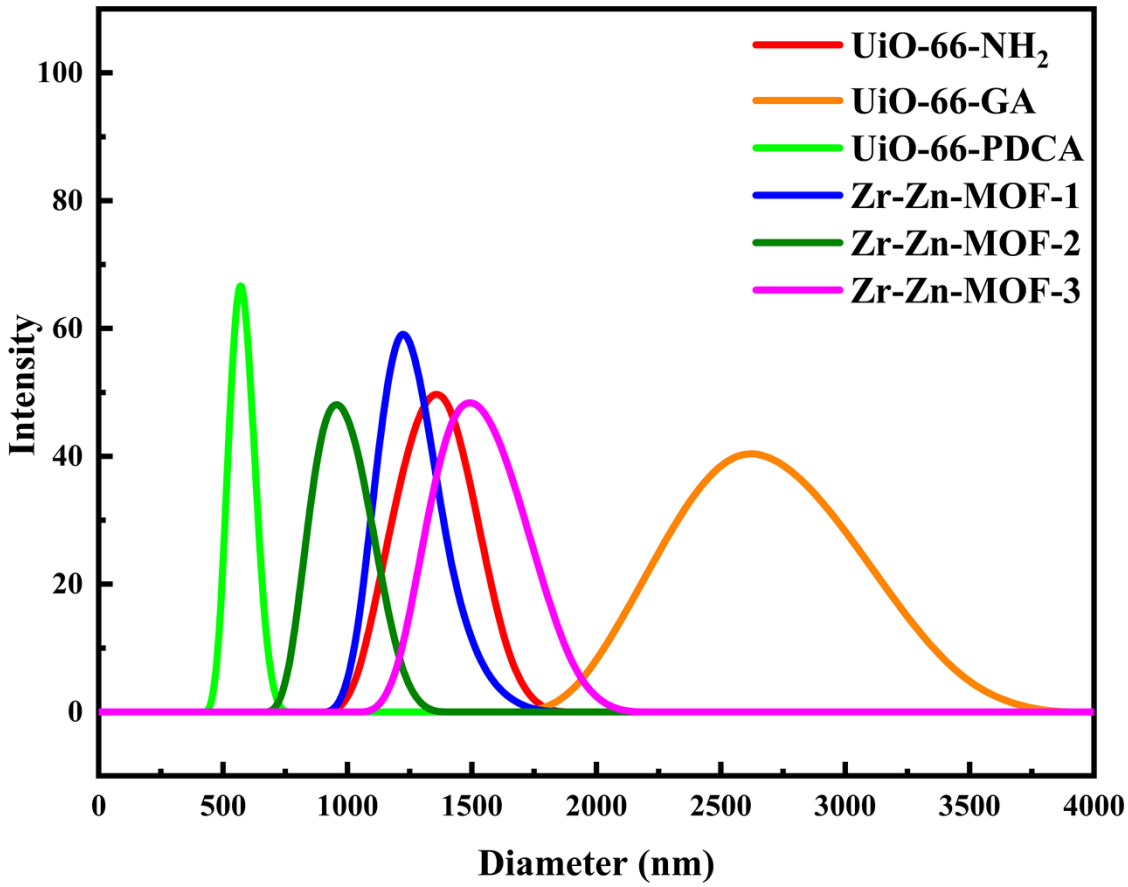
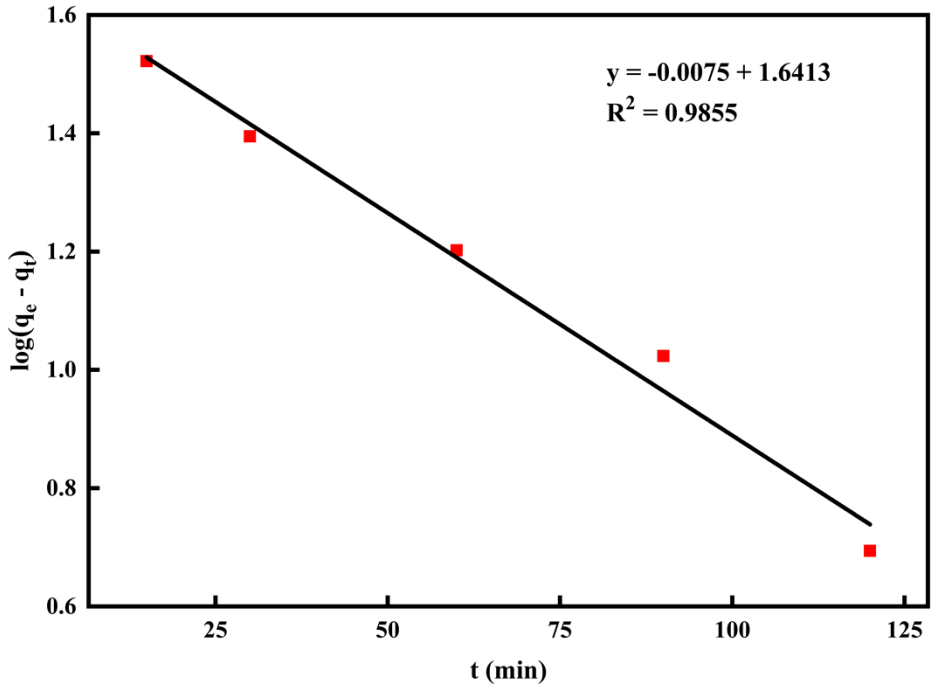
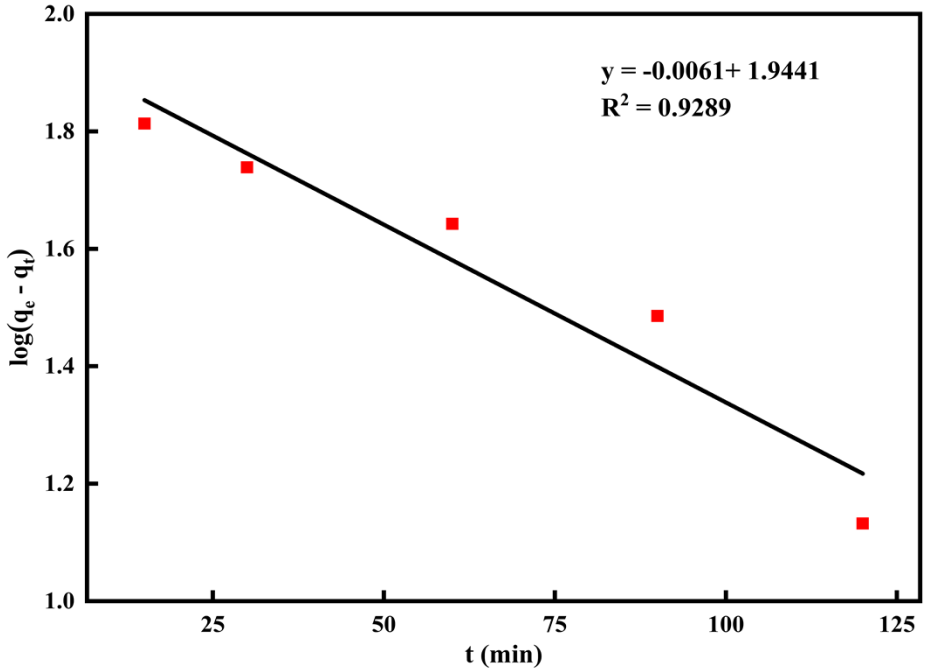


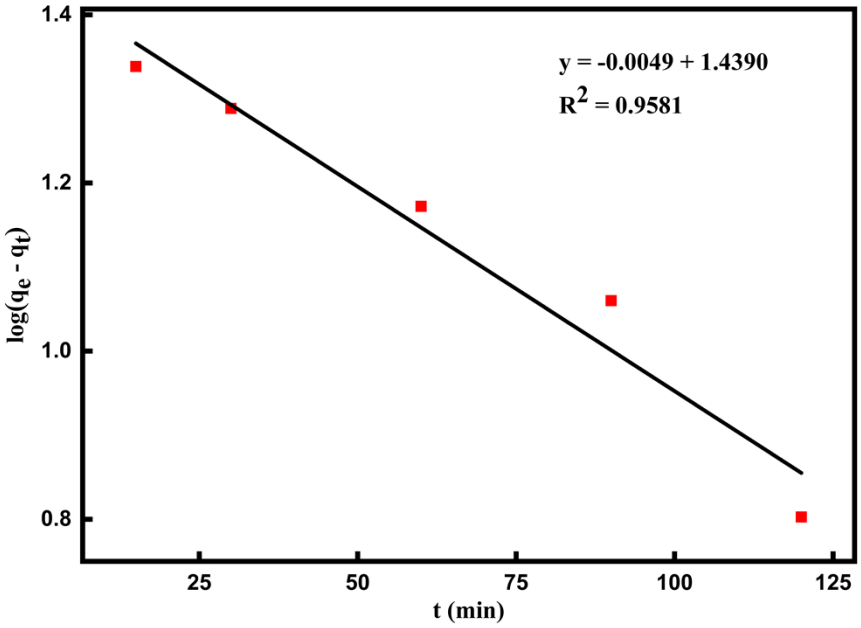
Fig. S15 Dynamic light scattering (DLS) particle size distributions for the MOF samples dispersed in aqueous solution.


y = -0.0075 + 1.6413
R2 = 0.9855
log(qe - qt)
t (min)
1.6
1.4
1.2
1.0
0.8
0.6
25
50
75
100
125

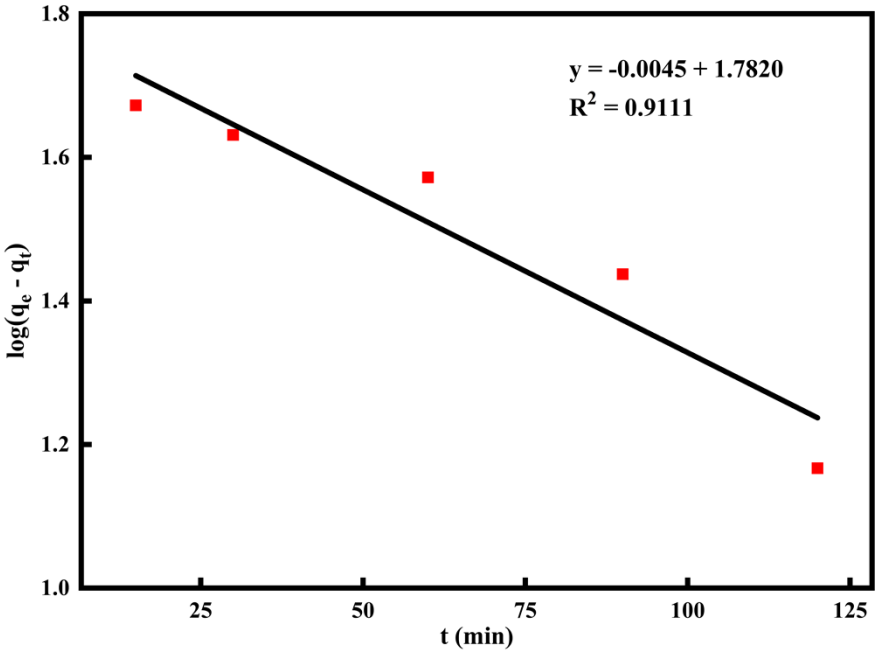
(a)


y = -0.0061+ 1.9441
R2 = 0.9289
log(qe - qt)
t (min)
2.0
1.8
1.6
1.4
1.2
1.0
25
50
75
100
125

(b)

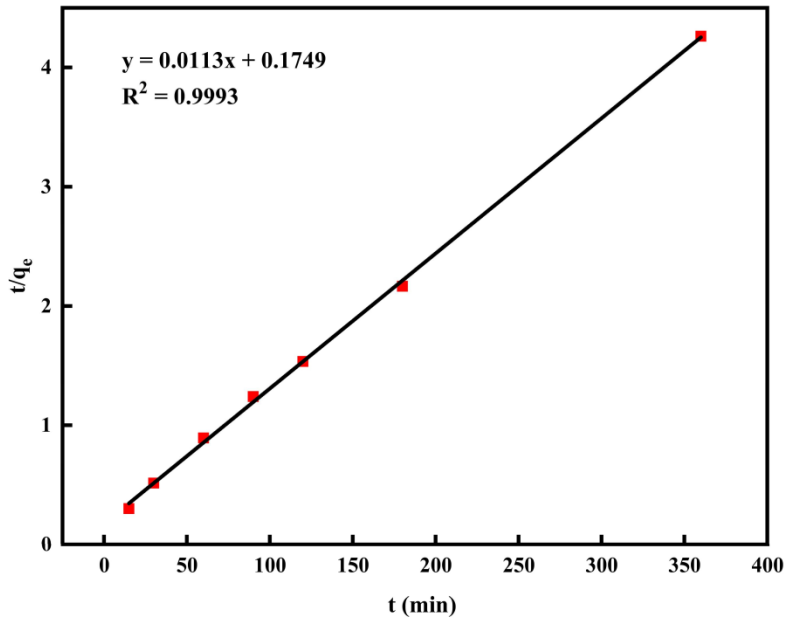


(c)

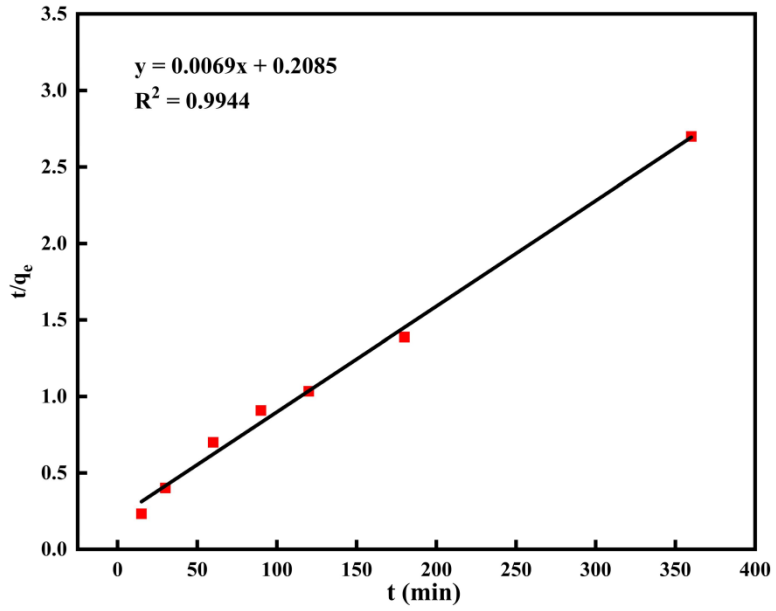


(d)

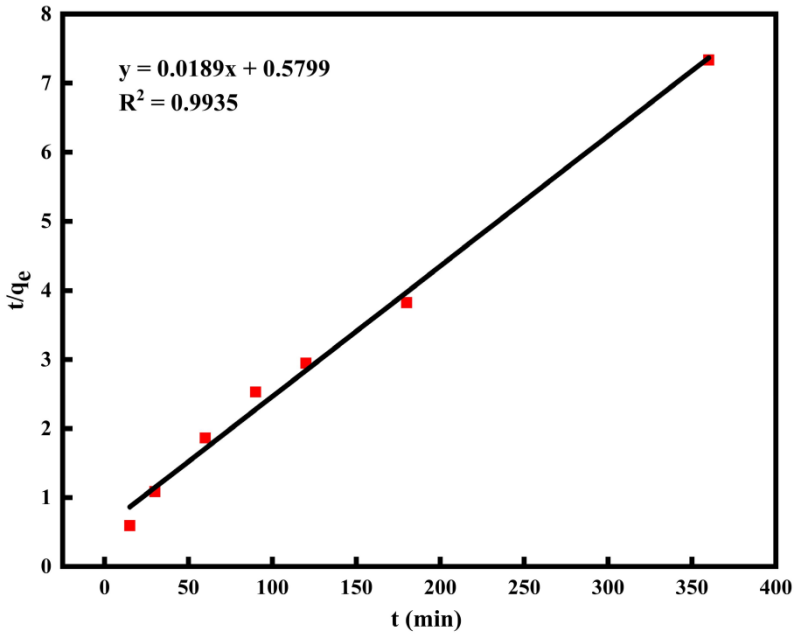
Fig. S16 Linear plots for pseudo-first order kinetics for the adsorption of palladium(II) on different MOFs (a) UiO-66-NH_2 (b) Zr-Zn-MOF-1 (c) Zr-Zn-MOF-2 (d) Zr-Zn-MOF-3


y = 0.0113x + 0.1749
R2 = 0.9993
t/qe
t (min)
0
1
2
3
4
0
50
100
150
200
250
300
350
400

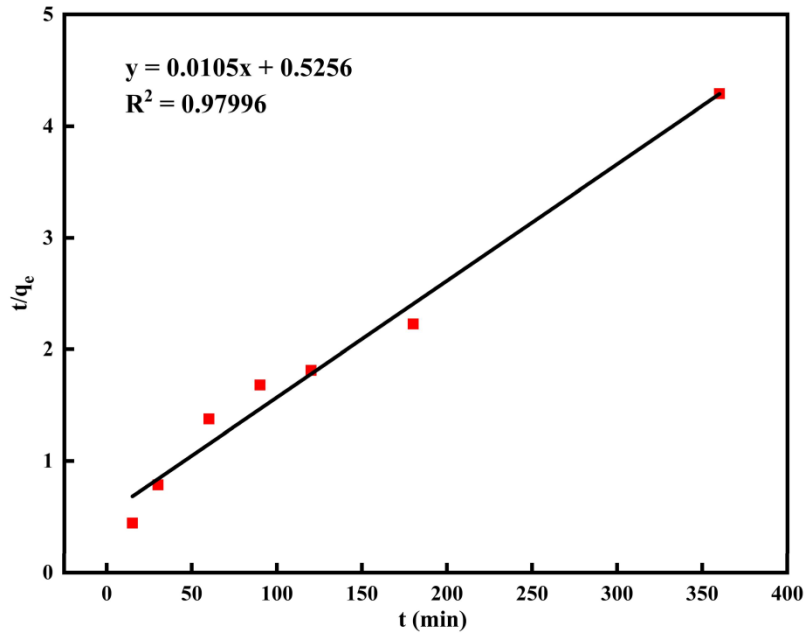
(a)


y = 0.0069x + 0.2085
R2 = 0.9944
t/qe
t (min)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
0
50
100
150
200
250
300
350
400

(b)

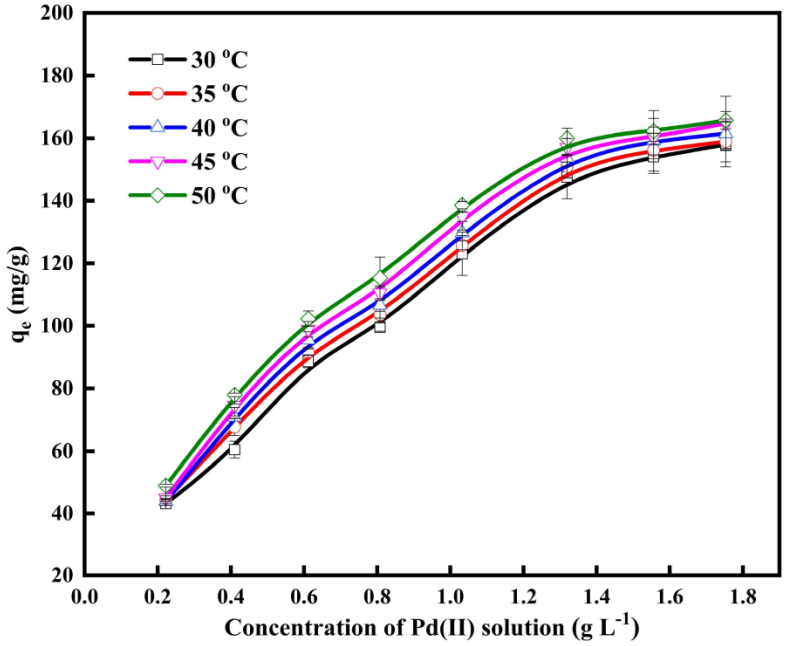


(c)

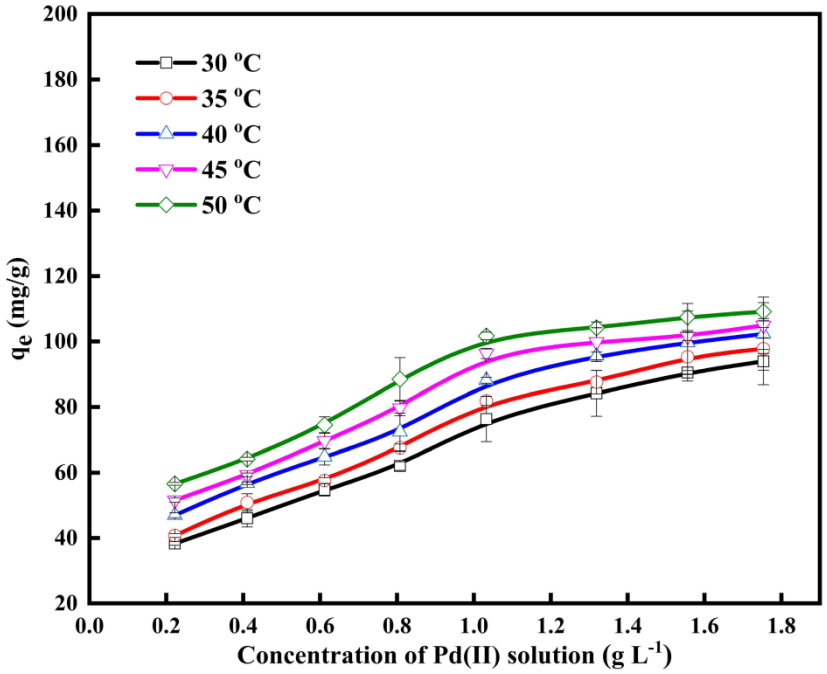


(d)

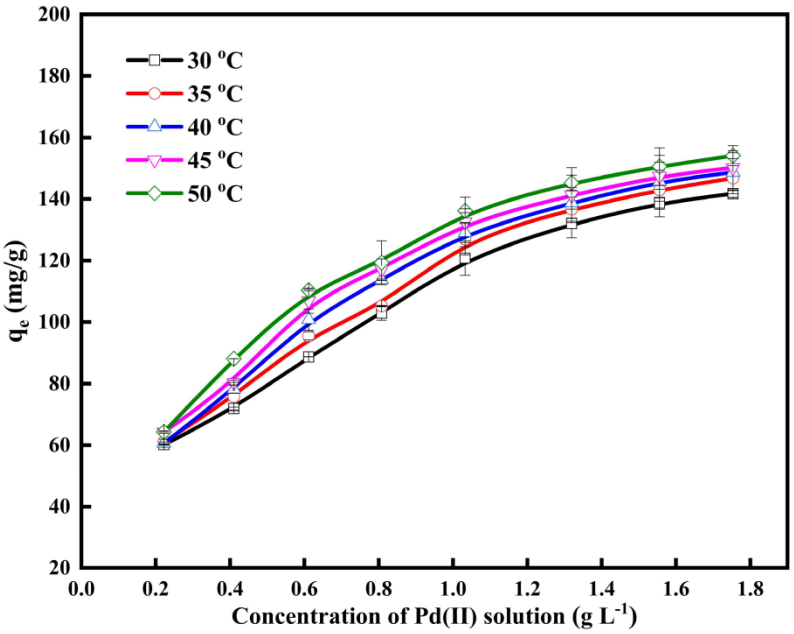
Fig. S17 Linear plots for pseudo-second order kinetics for the adsorption of palladium (II) on different MOFs (a) UiO-66-NH_2 (b) Zr-Zn-MOF-1 (c) Zr-Zn-MOF-2 (d) Zr-Zn-MOF-3


30 °C
35 °C
40 °C
45 °C
50 °C
q_e (mg/g)
Concentration of Pd(II) solution (g L^{-1})

(a)

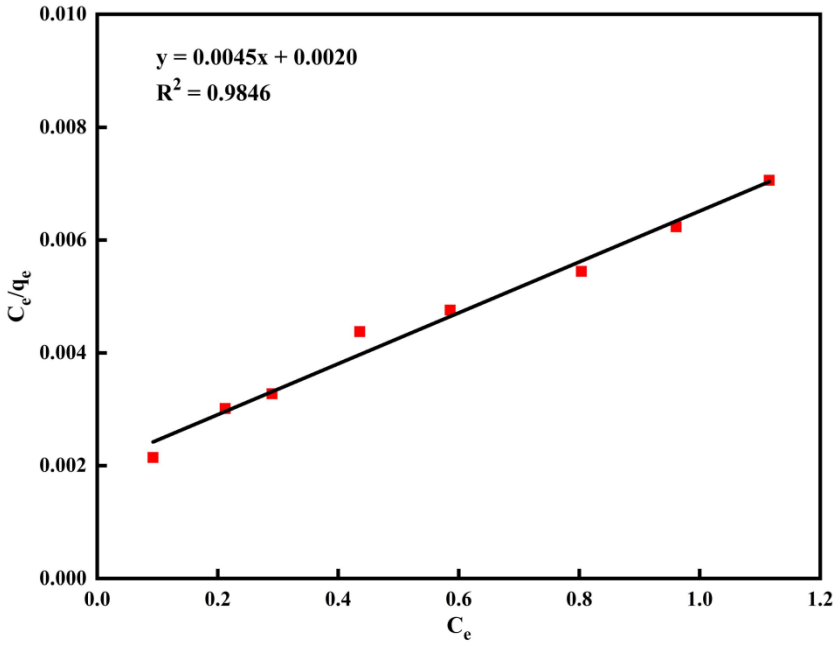


(b)

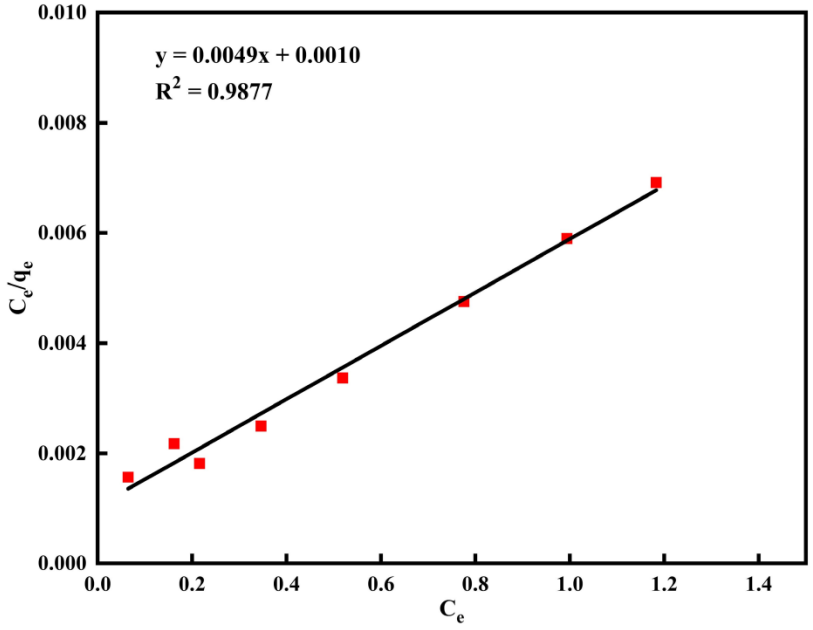


(c)

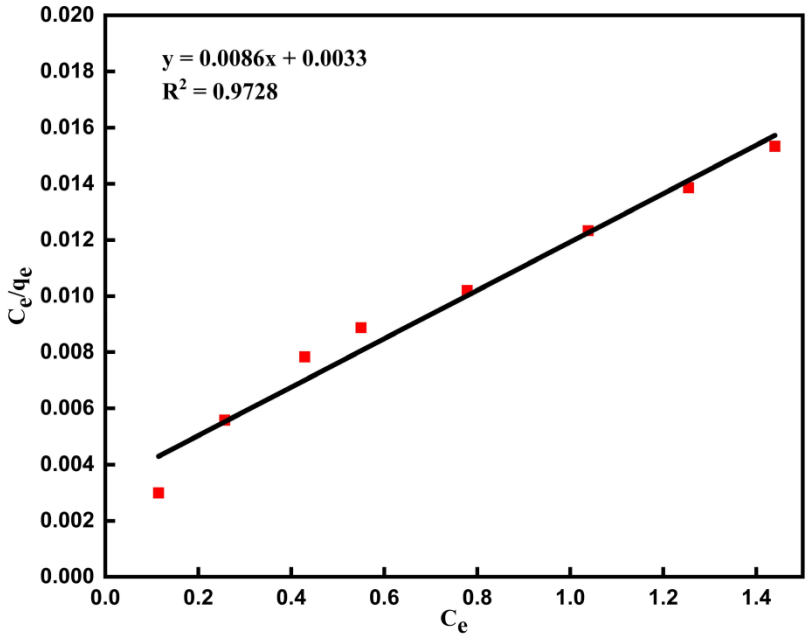
Fig. S18 Effect of palladium(II) concentration and temperature on the adsorption by (a) UiO-66-NH_2 (b) Zr-Zn-MOF-2 (c) Zr-Zn-MOF-3


y = 0.0045x + 0.0020
R2 = 0.9846
0.010
0.008
0.006
0.004
0.002
0.000
Ce/qe
0.0
0.2
0.4
0.6
0.8
1.0
1.2
Ce

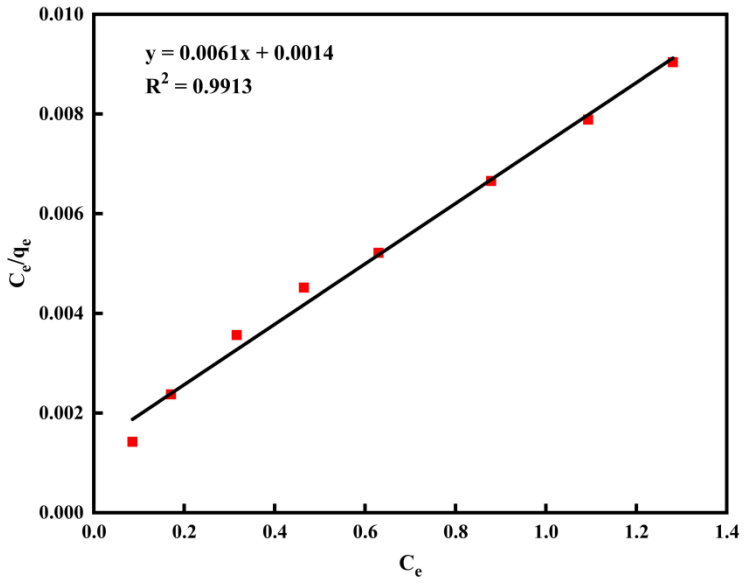
(a)


y = 0.0049x + 0.0010
R2 = 0.9877
Ce/qe
Ce
0.000
0.002
0.004
0.006
0.008
0.010
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4

(b)

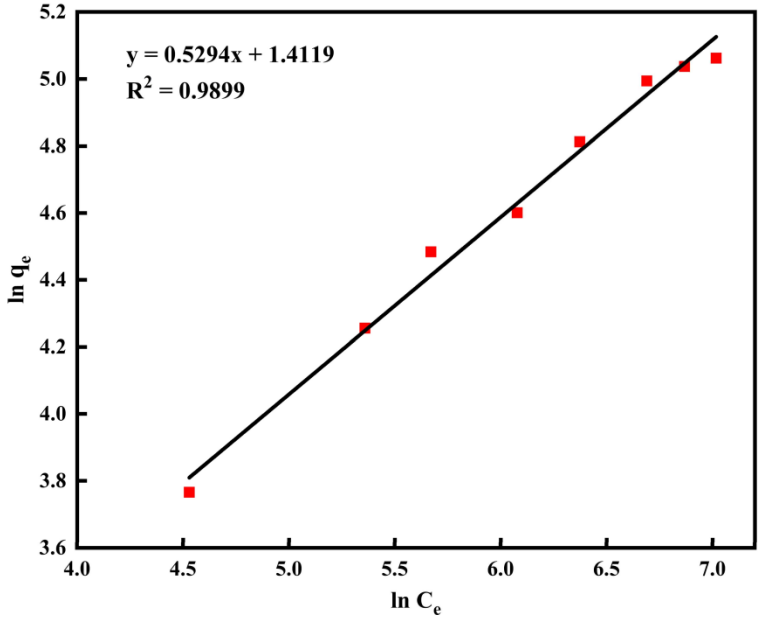

y = 0.0086x + 0.0033
R2 = 0.9728
Ce/qe
Ce
0.000
0.002
0.004
0.006
0.008
0.010
0.012
0.014
0.016
0.018
0.020
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4

(c)

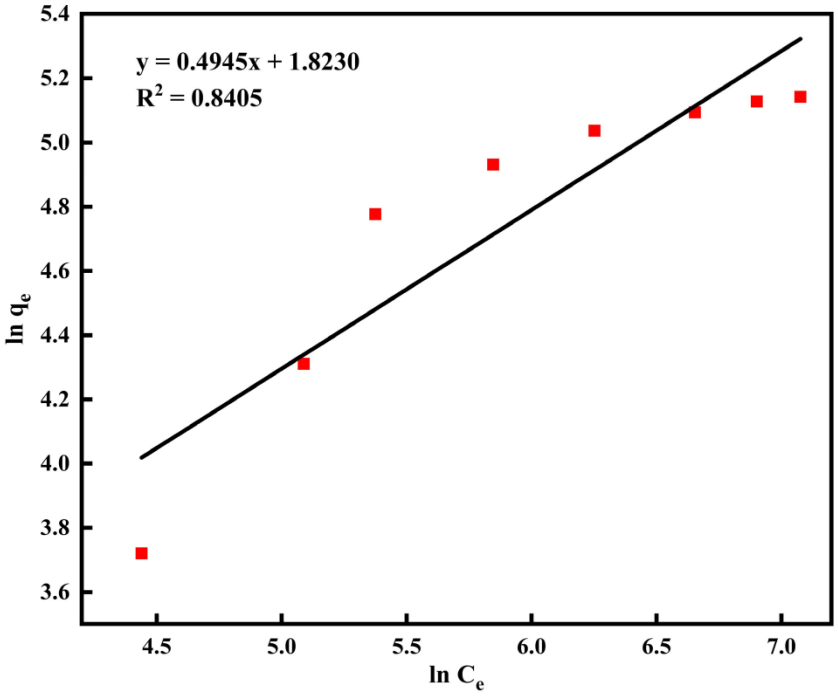


(d)

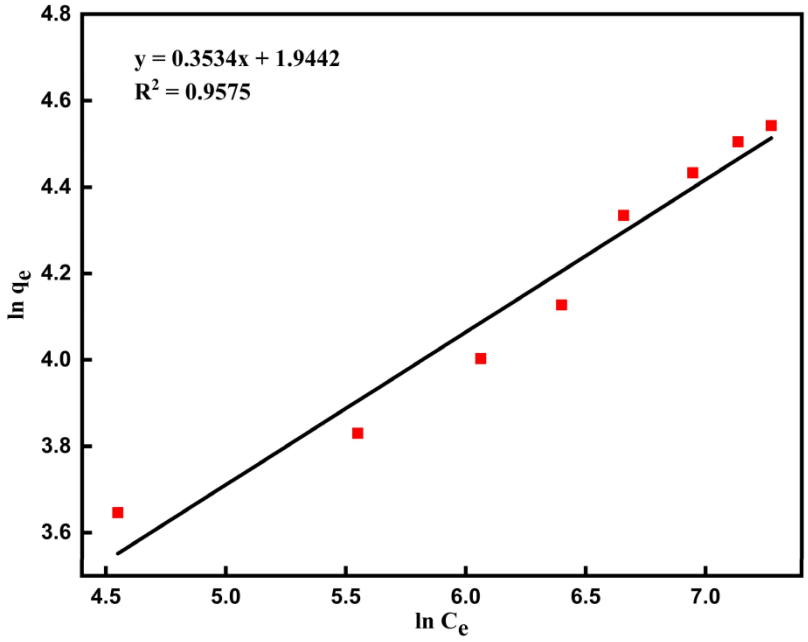
Fig S19. Linear Langmuir isotherm for the adsorption of palladium(II) on different MOFs (a) UiO-66-NH_2 (b) Zr-Zn-MOF-1 (c) Zr-Zn-MOF-2 (d) Zr-Zn-MOF-3



(a)


y = 0.4945x + 1.8230
R2 = 0.8405
ln qe
ln Ce
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
4.5
5.0
5.5
6.0
6.5
7.0

(b)


y = 0.3534x + 1.9442
R2 = 0.9575
ln qe
ln Ce
4.8
4.6
4.4
4.2
4.0
3.8
3.6
4.5
5.0
5.5
6.0
6.5
7.0

(c)

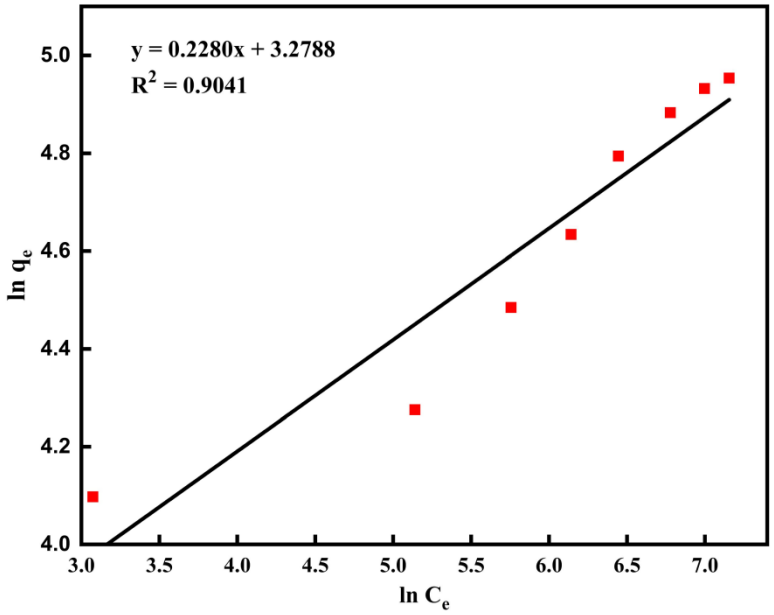
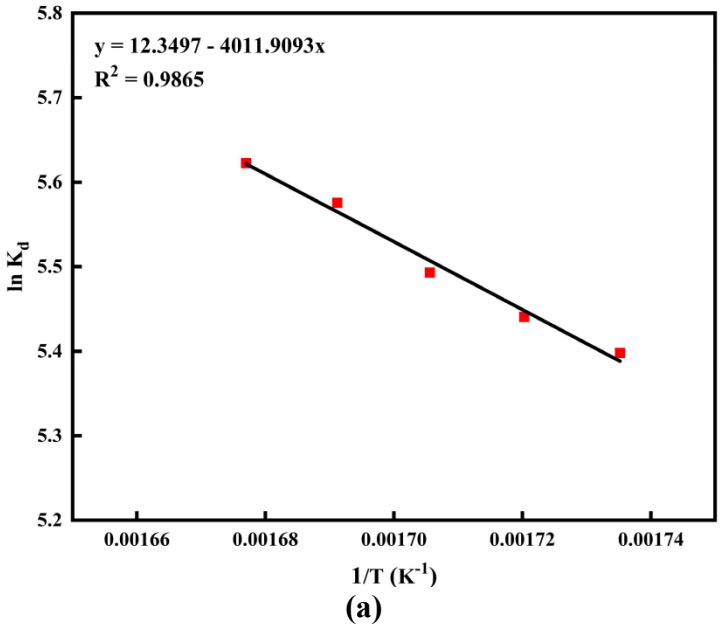
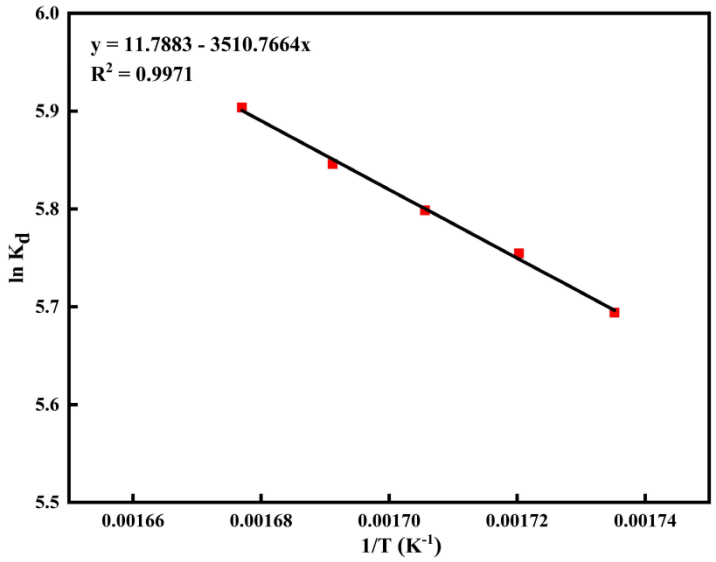
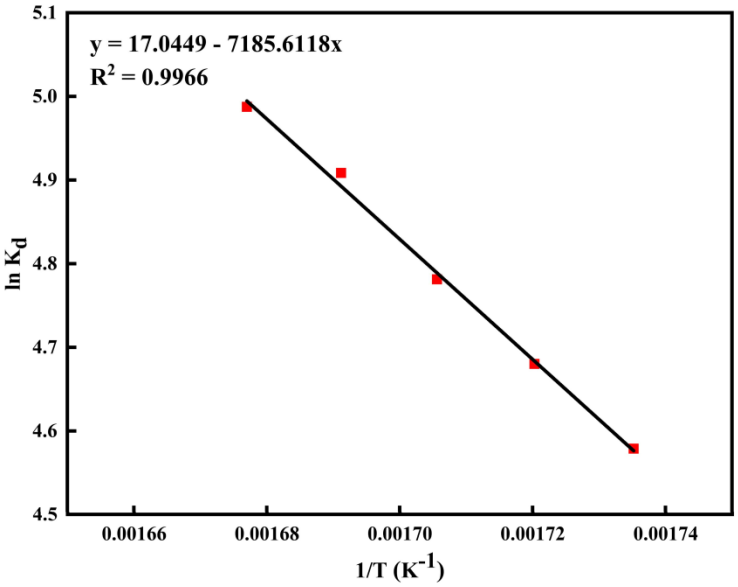


Fig S20. Linear Freundlich isotherm for the adsorption of palladium(II) on different MOFs (a) UiO-66-NH_2 (b) Zr-Zn-MOF-1 (c) Zr-Zn-MOF-2 (d) Zr-Zn-MOF-3

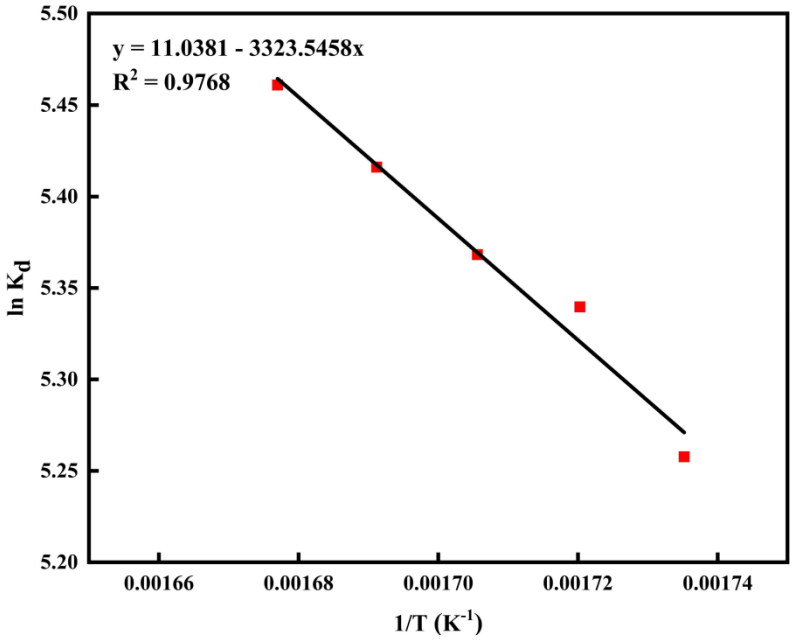



y = 11.7883 - 3510.7664x
R2 = 0.9971
6.0
5.9
5.8
5.7
5.6
5.5
ln Kd
0.00166
0.00168
0.00170
0.00172
0.00174
1/T (K-1)

(b)



(c)



(d)

Fig. S21 ln $K_d$versus 1/T (a) UiO-66-NH_2 (b) Zr-Zn-MOF-1 (c) Zr-Zn-MOF-2 (d) Zr-Zn-MOF-3

References:

1. S. P. Sangal and A. K. Dey, Microdetermination of palladium (II) using 1-(o-arsonophenylazo)-2-naphthol-3, 6-disulfonate (thoron) as a colorimetric reagent, *Microchemical Journal*, 1963, **7**, 257-262.