## Supporting information

### Materials and instrumentation

All reagents were purchased from Sigma-Aldrich and Merck chemical companies and used without further purification. FT-IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrophotometer using KBr pellets over the range of 4000–400 cm$^{-1}$. The X-ray powder diffraction (XRD) data were recorded on a Siefert XRD 3003 PTS diffractometer, using Cu K$_{\alpha 1}$ radiation (k = 1.5406 Å). UV-Vis spectra were obtained with a shimadzu UV-260 spectrophotometer. Scanning electron microscopy (SEM) images were obtained on a Philips XL-30ESEM equipped with an X-ray energy dispersive detector. Thermogravimetric analysis (TGA) was performed using a Mettler Toledo TGA/DSC instrument with heating rate of 10 °C/min in an air atmosphere. Nitrogen sorption isotherms were recorded on a Belsorp Mini–II instrument at 77K. The amount of sulfur was determined using an ELTRA carbon-sulfur analyzer.

### Adsorption kinetics

The pseudo-first-order is based on the following equation:

$$log\left(q_e - q_t\right) = log\, q_e - \frac{k_1}{2.303}t \qquad (1)$$

Where $q_e$ and $q_t$ (mg/g) are the amounts of dye adsorbed at equilibrium and contact time (t), respectively and $K_1$ (min$^{-1}$) represents the rate constant of pseudo-first-order kinetics.

The pseudo-second-order model is generally represented as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (2)$$

Where $K_2$ (g.mg$^{-1}$ min$^{-1}$) denotes the adsorption constant of pseudo-second-order kinetics.

**Adsorption isotherms**

The Langmuir isotherm is expressed by the following equation:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}} + \frac{1}{k_L Q_{max}}$$  (3)

Where $C_e$ is the equilibrium concentration of the dye in the solution (mg.g$^{-1}$), $Q_e$ represents the amount of the adsorbed dye at equilibrium (mg/g), $Q_{max}$ denotes the maximum adsorption capacity (mg/g), and $K_L$ is the Langmuir constant (L/g) which is related to the adsorption binding energy. The Freundlich model is represented as:

$$ln\ Q_e - Lnk_F = \frac{1}{n} ln\ C_e$$  (4)

Where $K_F$ and n are Freundlich adsorption constants which are attributed to the heterogeneous surface of the adsorbent and the desirability of the adsorption, respectively. If n is greater than 1, the adsorption is favorable and in the case of n<1, the adsorption is unfavorable.

**Adsorption thermodynamics**

The values of thermodynamic parameters including the changes in enthalpy ($\Delta H°$; kJ/mol), entropy ($\Delta S°$; kJ/mol), and Gibbs free energy ($\Delta G°$; kJ/mol) were computed by the following equations:

$$LnK_0 = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT}$$  (5)

$$-RT\ LnK_0 = \Delta H° - T\ \Delta S°$$  (6)

$$\Delta G° = \Delta H° - T\ \Delta S°$$  (7)

Where $K_0$ is the thermodynamic equilibrium constant, T is the solution temperature (K), and R is the universal gas constant (8.314 J/mol.K) and the plots of $LnK_0$ vs. 1/T are shown in Fig. S14.
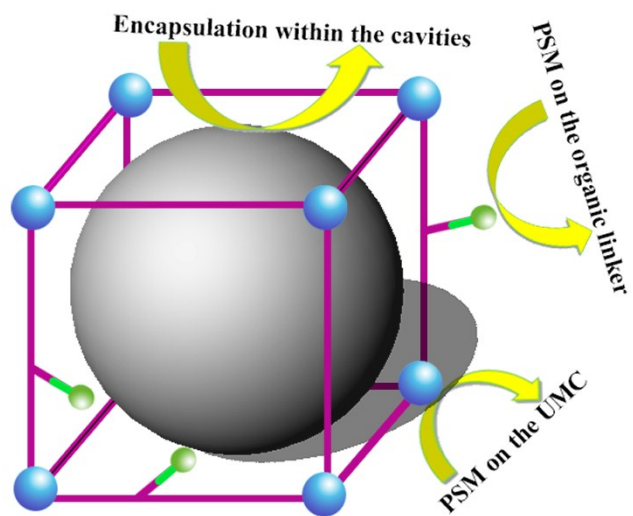
**Scheme S1**. Various situation for post synthetic modification of MOFs.
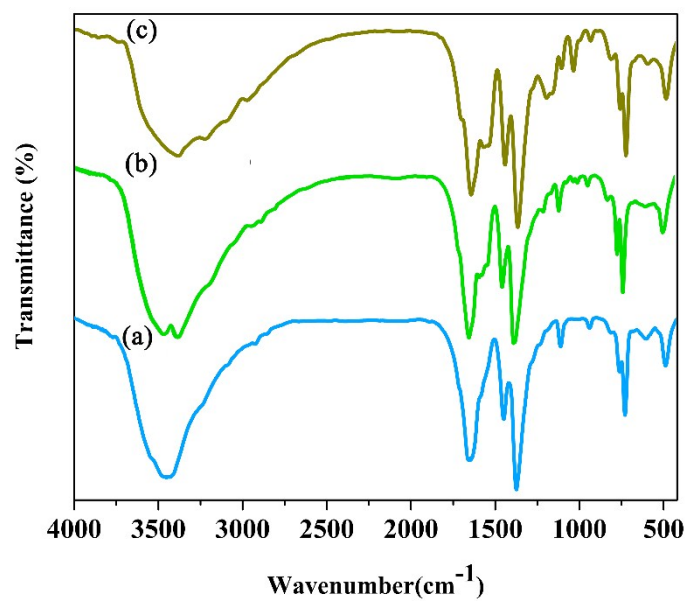


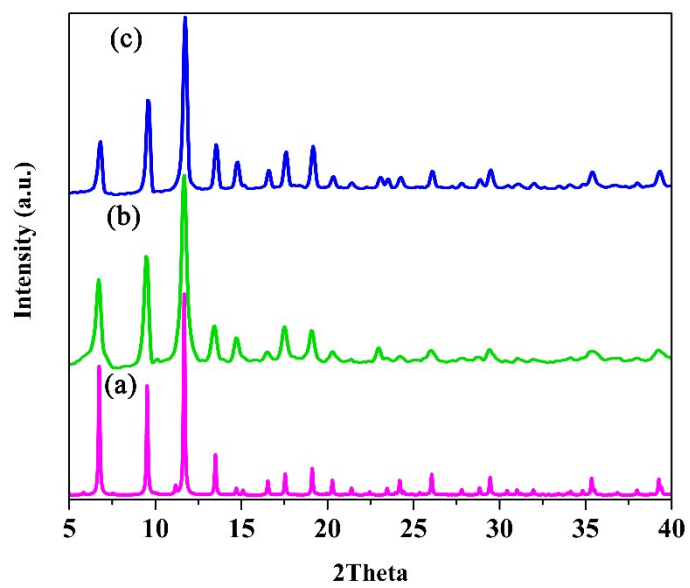**Fig. S1**. FT-IR spectra of (a) HKUST (b) HKUST-AMP (c) HKUST-AMP-SO$_3$H.

**Fig. S2**. XRD patterns of HKUST (a) simulated (b) as-synthesized, and (c) HKUST-AMP-SO$_3$H.
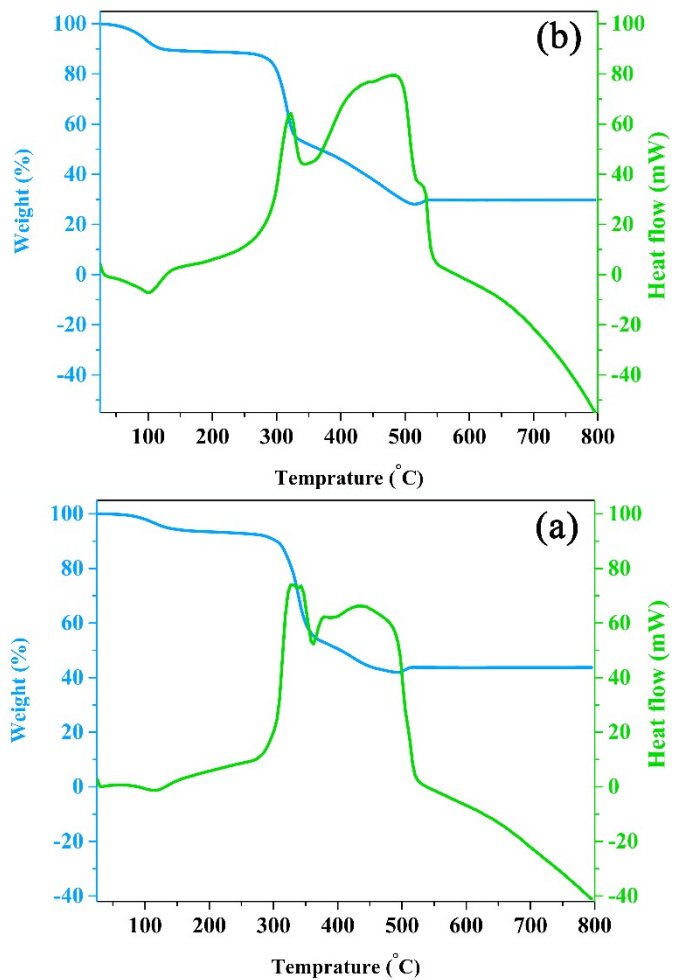
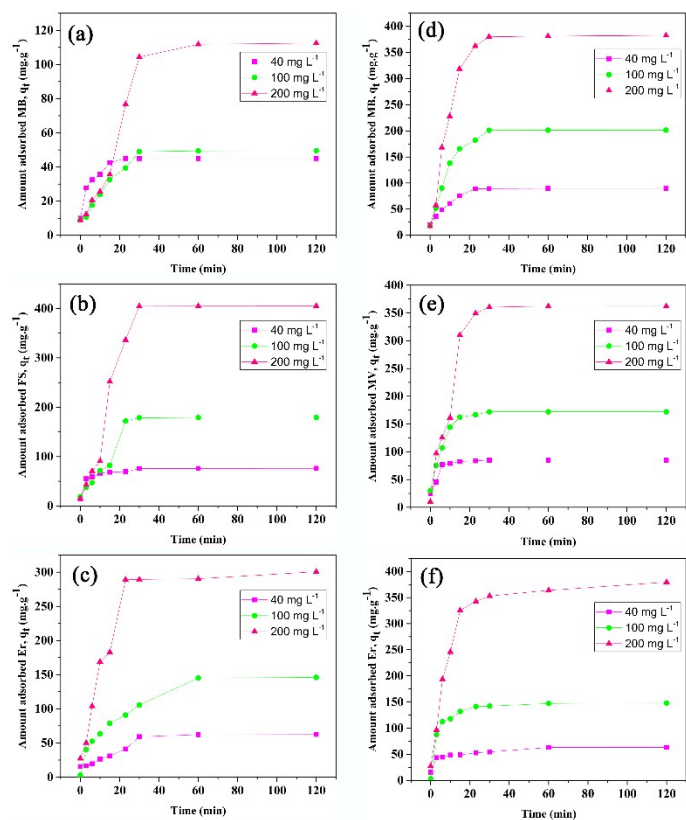**Fig. S3**. TGA-DSC curves of (a) HKUST (b) HKUST-AMP-SO$_3$H.

**Fig. S4**. Adsorption Capacity over HKUST for a) MB, b) FS, and c) Er. Adsorption capacity over HKUST-AMP-SO$_3$H for d) MB, e) MV, and f) Er.

**Table S1.** The dye removal percentage of dyes using HKUST and HKUST-AMP-SO$_3$H in different concentration of dye molecules.

| $C_0$(mg L$^{-1}$) | Dye removal (%) | | | | | |
| --- | --- | --- | --- | --- | --- | --- |
| | HKUST | | | HKUST-AMP-SO$_3$H | | |
| | MB | FS | Er | MB | MV | Er |
| 20 | 64 | 81 | 46 | 97 | 85 | 72 |
| 40 | 60 | 80 | 42 | 95 | 84 | 71 |
| 60 | 55 | 79 | 39 | 90 | 83 | 70 |
| 80 | 51 | 76 | 36 | 87 | 82 | 68 |
| 100 | 49 | 75 | 31 | 86 | 80 | 65 |
| 200 | 45 | 73 | 20 | 86 | 78 | 60 |
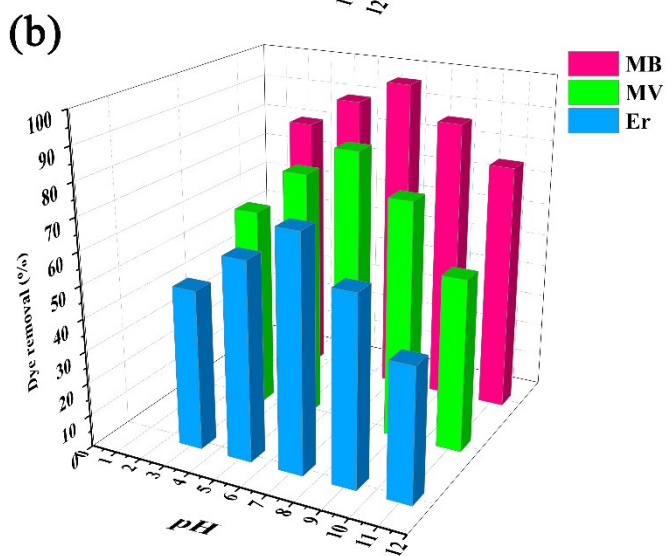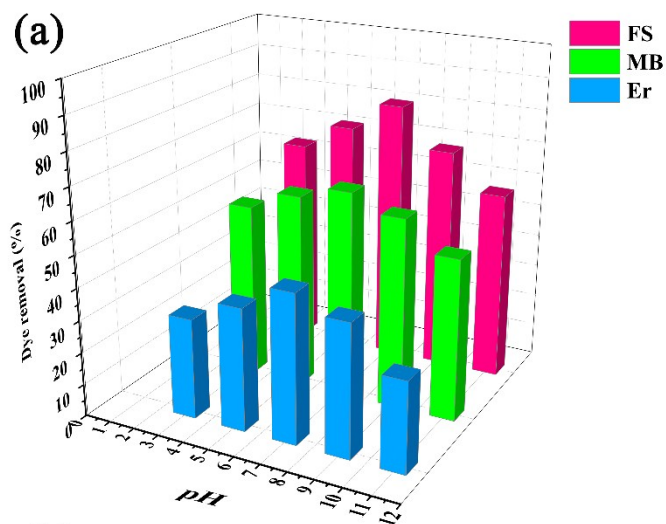
**Fig. S5**. Effect of pH on dye removal using (a) HKUST (b) HKUST-AMP-SO$_3$H.

**Table S2.** The effect of temperature on dye adsorption of MB, FS, Er, and MV over HKUST and HKUST-AMP-SO$_3$H.

| Temperature (K) | Dye removal (%) | | | | | |
| --- | --- | --- | --- | --- | --- | --- |
| | HKUST | | | HKUST-AMP-SO$_3$H | | |
| | MB | FS | Er | MB | MV | Er |
| 298 | 64 | 81 | 46 | 97 | 85 | 72 |
| 308 | 50 | 61 | 32 | 72 | 69 | 61 |
| 323 | 23 | 45 | 17 | 54 | 48 | 43 |

**Table S3.** The effect of adsorbent dosage on dye adsorption of MB, FS, Er, and MV.

| Dose (mg) | Dye removal (%) | | | | | |
| --- | --- | --- | --- | --- | --- | --- |
| | HKUST | | | HKUST–AMP–SO$_3$H | | |
| | MB | FS | Er | MB | MV | Er |
| 3 | 19 | 43 | 20 | 41 | 61 | 39 |
| 5 | 39 | 66 | 32 | 68 | 76 | 45 |
| 10 | 64 | 81 | 46 | 97 | 85 | 72 |
| 15 | 64 | 82 | 48 | 97 | 88 | 74 |
| 20 | 65 | 84 | 49 | 99 | 89 | 77 |



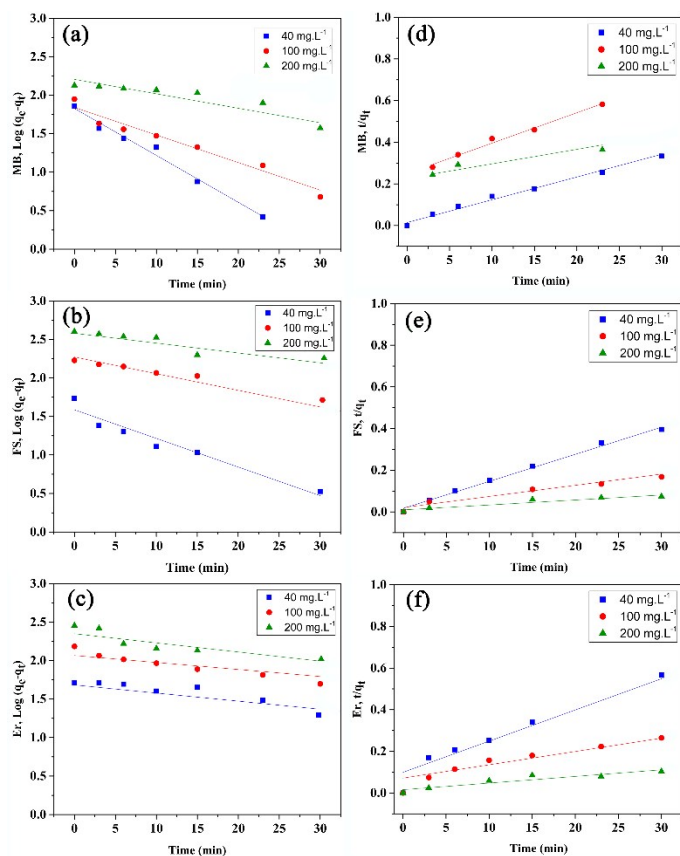**Fig. S6**. Plots of pseudo-first-order kinetics over HKUST for a) MB, b) FS, and c) Er. Plots of pseudo-second-order kinetics over HKUST-AMP-SO$_3$H for d) MB, e) FS, and f) Er.
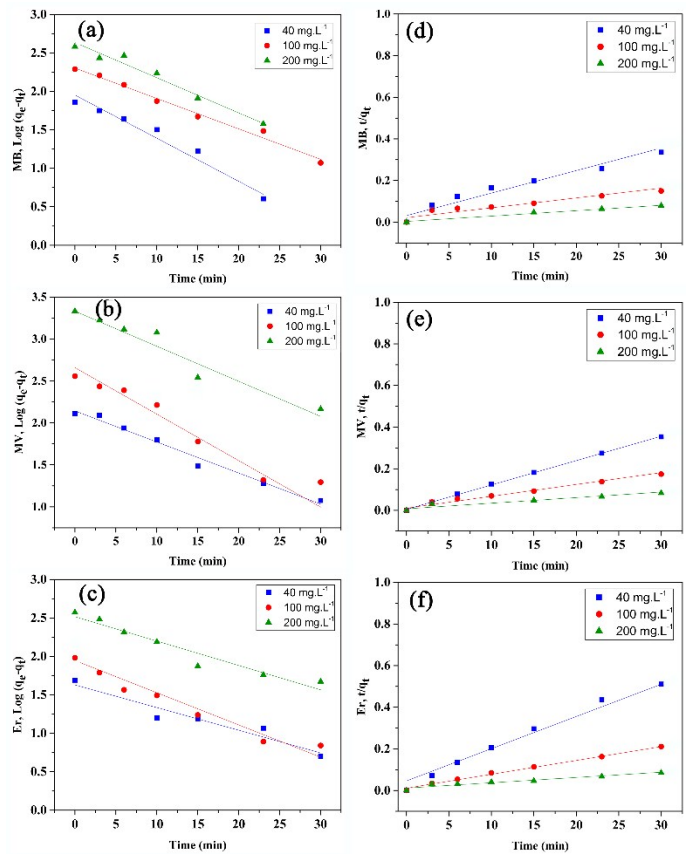
**Fig. S7**. Plots of pseudo-first-order kinetics over HKUST-AMP-SO$_3$H for a) MB, b) MV, and c) Er. Plots of pseudo-second-order kinetics over HKUST-AMP-SO$_3$H for d) MB, e) MV, and f) Er.

**Table S4.** Adsorption kinetics parameters of MB, FS, and Er using HKUST as adsorbent.

| Dye | $C_0$(mg L$^{-1}$) | pseudo-first-order | | | pseudo-second-order | | |
|-----|------|-----------------|-----------------|-------|-------------------------|-------------------|-------|
| | | $K_1$(min$^{-1}$) | $q_e$(mg g$^{-1}$) | $R_2$ | $K_2$(g mg$^{-1}$ min$^{-1}$) | qe(mg g$^{-1}$) | $R_2$ |
| MB | 40 | 0.140 | 67.28 | 0.9849 | 0.021 | 91.74 | 0.9994 |
| | 100 | 0.070 | 54.18 | 0.9357 | 0.011 | 53.76 | 0.9893 |
| | 200 | 0.012 | 128.20 | 0.973 | 0.001 | 142.85 | 0.9975 |
| FS | 40 | 0.085 | 38.69 | 0.9219 | $2.1\times10^{-3}$ | 59.17 | 0.9996 |
| | 100 | 0.027 | 125.89 | 0.849 | $1\times10^{-3}$ | 188.67 | 0.9911 |
| | 200 | 0.029 | 380.18 | 0.9791 | $0.6\times10^{-3}$ | 416.66 | 0.9930 |
| Er | 40 | 0.024 | 47.86 | 0.8626 | 0.002 | 66.66 | 0.9885 |
| | 100 | 0.020 | 114.81 | 0.9704 | $0.5\times10^{-3}$ | 156.25 | 0.9816 |
| | 200 | 0.027 | 218.77 | 0.9233 | $0.6\times10^{-3}$ | 312.5 | 0.990 |

**Table S5.** Adsorption kinetics parameters of MB, MV, and Er using HKUST-AMP-SO$_3$H as adsorbent.

| Dye | $C_0$(mg L$^{-1}$) | pseudo-first-order | | | pseudo-second-order | | |
|-----|------|-----------------|-----------------|-------|-------------------------|-------------------|-------|
| | | $K_1$(min$^{-1}$) | $q_e$(mg g$^{-1}$) | $R_2$ | $K_2$(g mg$^{-1}$ min$^{-1}$) | qe(mg g$^{-1}$) | $R_2$ |
| MB | 40 | 0.129 | 89.61 | 0.9566 | $3\times10^{-3}$ | 92.59 | 0.9973 |
| | 100 | 0.091 | 201.37 | 0.9874 | $1\times10^{-3}$ | 212.76 | 0.9942 |
| | 200 | 0.105 | 425.99 | 0.988 | $0.1\times10^{-3}$ | 400 | 0.9993 |
| MV | 40 | 0.002 | 129.12 | 0.9434 | $2\times10^{-3}$ | 204.08 | 0.9999 |
| | 100 | 0.003 | 153.12 | 0.9451 | $3\times10^{-3}$ | 175.43 | 0.9987 |
| | 200 | 0.1275 | 398.10 | 0.969 | $0.3\times10^{-3}$ | 370.37 | 0.9956 |
| Er | 40 | 0.025 | 24.54 | 0.9261 | 0.005 | 64.51 | 0.9976 |
| | 100 | 0.096 | 25.02 | 0.9235 | 0.006 | 149.25 | 0.9996 |
| | 200 | 0.073 | 323.59 | 0.938 | $0.5\times10^{-3}$ | 400 | 0.9956 |
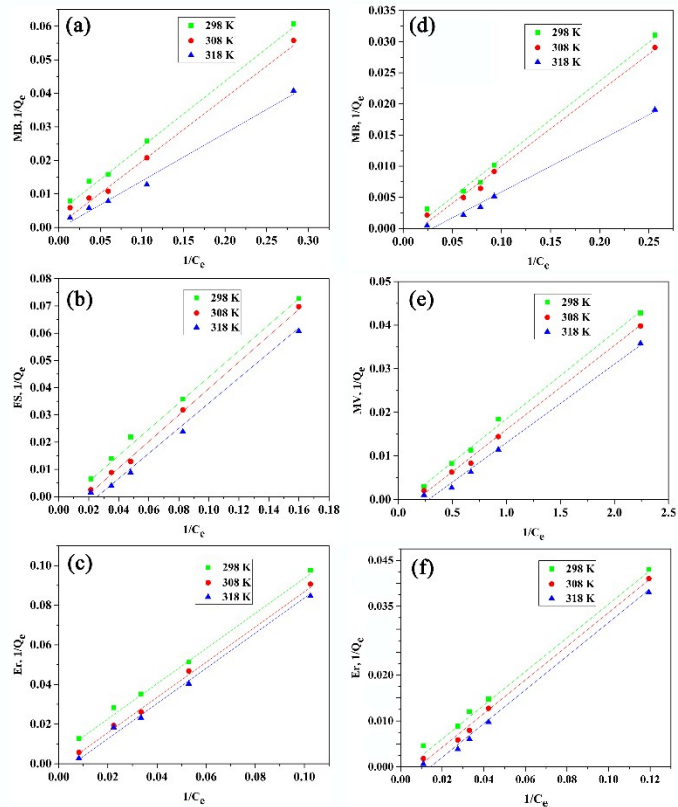
**Fig. S8**. Langmuir isotherm of adsorption over HKUST for a) MB, b) FS, and c) Er. Langmuir isotherm of adsorption over HKUST-AMP-SO$_3$H for d) MB, e) MV, and f) Er at 298, 308,318 $^0$K.
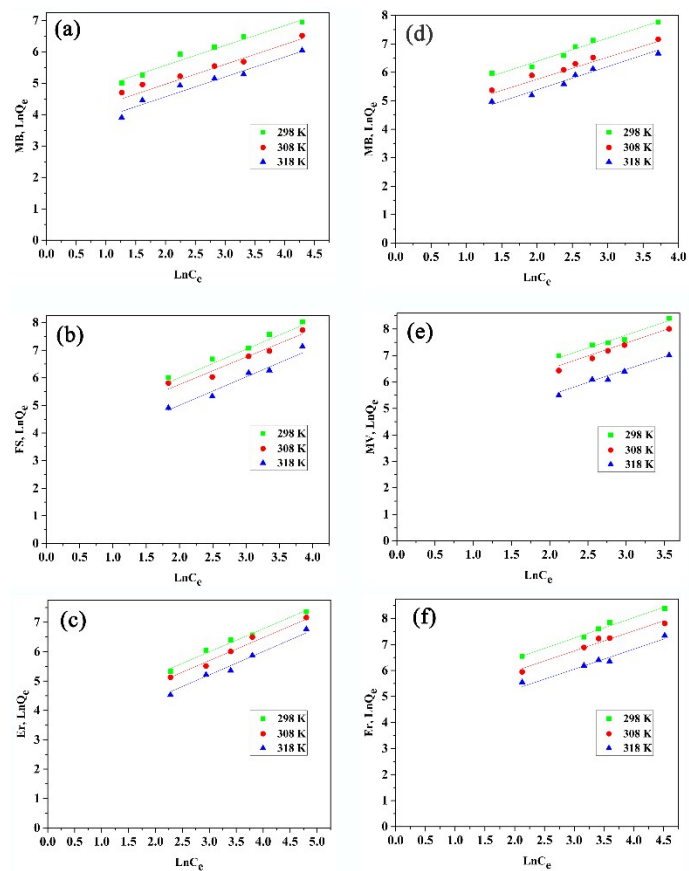
**Fig. S9**. Freundlich isotherm of adsorption over HKUST for a) MB, b) FS, and c) Er. Freundlich isotherm of adsorption over HKUST-AMP-SO$_3$H for d) MB, e) MV, and f) Er at 298, 308,318 $^0$K.

**Table S6.** Isotherm parameters of MB, FS, and Er over HKUST.

| Dye | T(K) | Langmuir | | | | | Freundlich | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Q(mg/g) | $K_L$(L mg$^{-1}$) | $R_L$ | $R_2$ | | $n_F$ | $K_F$ | $R_2$ |
| MB | 298 | 238.09 | 0.0214 | 0.423 | 0.980 | | 1.620 | 81.10 | 0.921 |
| | 308 | 224.65 | 0.0192 | 0.389 | 0.991 | | 1.425 | 80.34 | 0.932 |
| | 318 | 204.21 | 0.0142 | 0.354 | 0.987 | | 1.372 | 78.12 | 0.968 |
| FS | 298 | 243.90 | 0.0082 | 0.627 | 0.998 | | 0.991 | 54.99 | 0.962 |
| | 308 | 234.02 | 0.0072 | 0.605 | 0.994 | | 0.990 | 52.76 | 0.942 |
| | 318 | 210.54 | 0.0055 | 0.586 | 0.991 | | 0.859 | 50.12 | 0.957 |
| Er | 298 | 200 | 0.0056 | 0.709 | 0.991 | | 1.282 | 57.64 | 0.983 |
| | 308 | 183.21 | 0.0045 | 0.692 | 0.984 | | 1.204 | 54.98 | 0.964 |
| | 318 | 176.09 | 0.0023 | 0.675 | 0.995 | | 1.145 | 52.56 | 0.978 |

**Table S7.** Isotherm parameters of MB, MV, and Er over HKUST-AMP-SO$_3$H.

| Dye | T(K) | Langmuir | | | | | Freundlich | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Q(mg/g) | $K_L$(L mg$^{-1}$) | $R_L$ | $R_2$ | | $n_F$ | $K_F$ | $R_2$ |
| MB | 298 | 833.33 | 0.0096 | 0.598 | 0.993 | | 1.240 | 119.02 | 0.974 |
| | 308 | 810.98 | 0.0084 | 0.431 | 0.986 | | 1.178 | 110.56 | 0.962 |
| | 318 | 797.45 | 0.0071 | 0.367 | 0.991 | | 1.023 | 105.98 | 0.979 |
| MV | 298 | 714.28 | 0.0706 | 0.201 | 0997 | | 1.049 | 135.74 | 0.959 |
| | 308 | 706.23 | 0.0695 | 0.187 | 0.988 | | 1.023 | 123.68 | 0.969 |
| | 318 | 695.87 | 0.0618 | 0.145 | 0.992 | | 1.001 | 109.06 | 0.973 |
| Er | 298 | 833.33 | 0.0033 | 0.801 | 0.994 | | 1.275 | 133.79 | 0.967 |
| | 308 | 813.98 | 0.0029 | 0.765 | 0.991 | | 1.165 | 126.25 | 0.952 |
| | 318 | 798.23 | 0.0021 | 0.632 | 0.989 | | 1.078 | 117.04 | 0.975 |

**Table S8.** Thermodynamic parameters of MB, FS, and Er adsorption over HKUST.

| Dye | T(K) | $LnK_0$ | $\Delta G°(kJ\ mol^{-1})$ | $\Delta H°\ (kJ\ mol^{-1})$ | $\Delta S°\ (J\ mol^{-1}\ K^{-1})$ |
|-----|------|---------|---------------------------|------------------------------|-------------------------------------|
| MB | 298 | 1.43 | -3.30 | | |
| | 308 | 1.40 | -2.91 | -5.08 | -5.09 |
| | 318 | 1.30 | -2.73 | | |
| FS | 298 | 1.04 | -2.52 | | |
| | 308 | 0.91 | -2.14 | -13.35 | -36.04 |
| | 318 | 0.70 | -1.74 | | |
| Er | 298 | 0.65 | -1.45 | | |
| | 308 | 0.5 | -1.19 | -12.98 | -38.10 |
| | 318 | 0.32 | -0.81 | | |

**Table S9.** Thermodynamic parameters of MB, MV, and Er adsorption over HKUST-AMP-SO$_3$H.

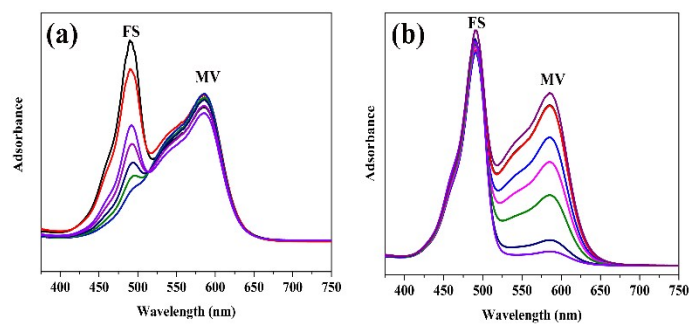| Dye | T(K) | $LnK_0$ | $\Delta G°(kJ\ mol^{-1})$ | $\Delta H°\ (kJ\ mol^{-1})$ | $\Delta S°\ (J\ mol^{-1}\ K^{-1})$ |
|-----|------|---------|---------------------------|------------------------------|-------------------------------------|
| MB | 298 | 2.22 | -5.40 | | |
| | 308 | 1.87 | -4.73 | -22.56 | -57.58 |
| | 318 | 1.80 | -4.14 | | |
| MV | 298 | 6.12 | -4.29 | | |
| | 308 | 6.01 | -4.13 | -10.61 | -15.35 |
| | 318 | 5.85 | -3.96 | | |
| Er | 298 | 1.01 | -2.42 | | |
| | 308 | 0.89 | -2.21 | -10.23 | -25.89 |
| | 318 | 0.75 | -1.89 | | |

**Fig. S10**. The reverse performance of (a) HKUST and (b) HKUST-AMP-SO$_3$H for FS-MV mixture.
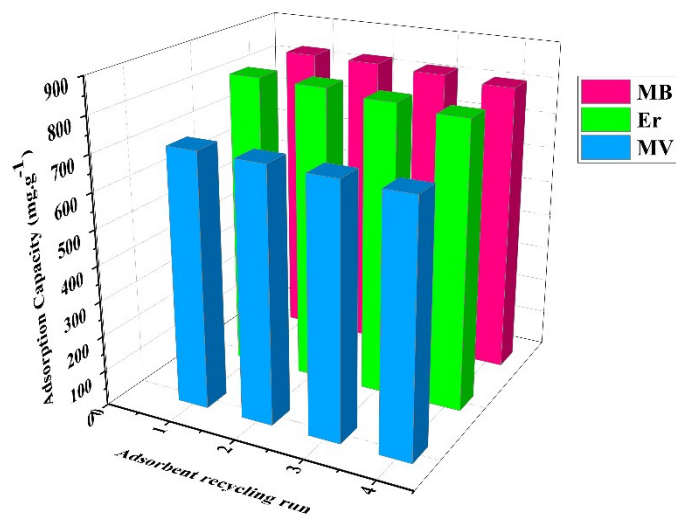


**Fig. S11**. The effect of recycling run on adsorption of MB, Er, and MV over HKUST-AMP-SO$_3$H.
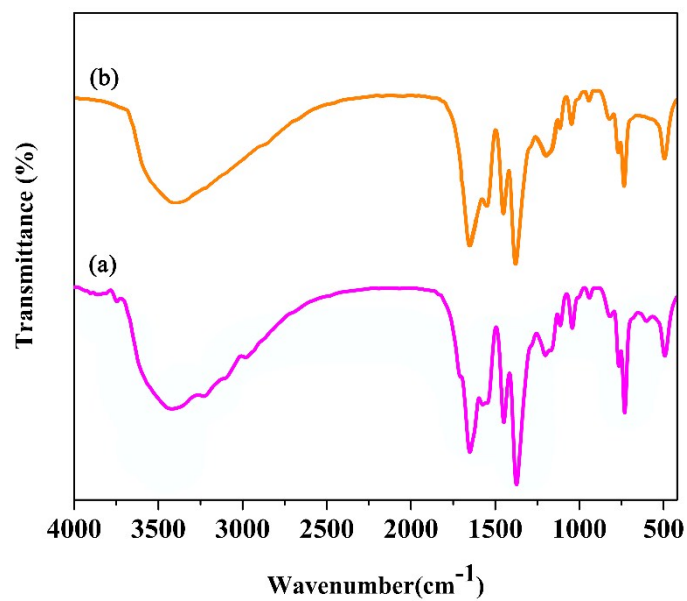
**Fig. S12**. FT-IR spectra of HKUST-AMP-SO$_3$H (a) before and (b) after using as an adsorbent.
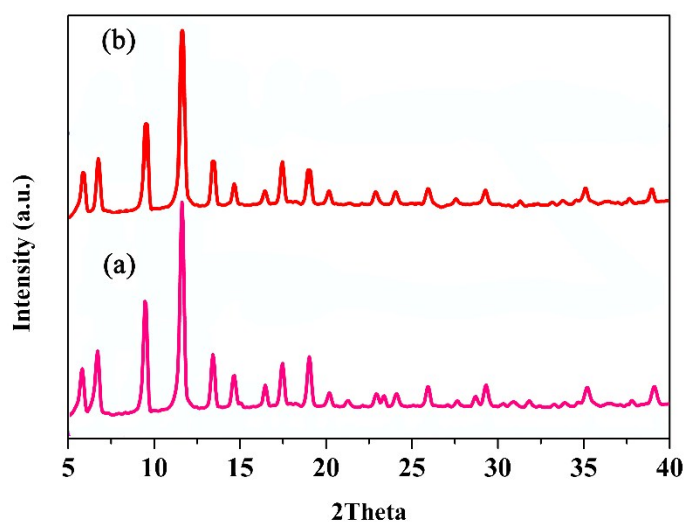


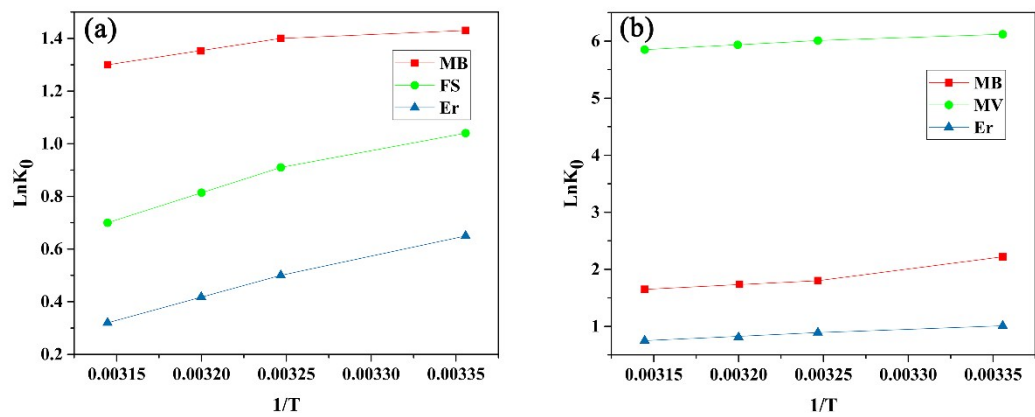**Fig. S13**. XRD patterns of HKUST-AMP-SO$_3$H (a) before and (b) after using as an adsorbent.

**Fig. S14**. Van't Hoff plots of used dye molecule over a) HKUST b) HKUST-AMP-SO$_3$H.