Supporting information for

Highly Efficient Benzothiophene Capture with a Metal-Modified Cu-BTC Adsorbent

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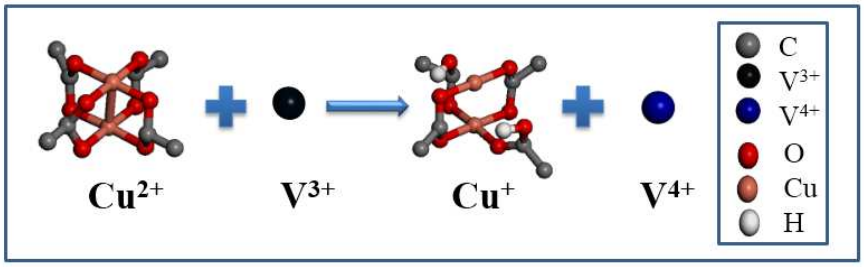
Part I:



Scheme S.I.1. Oxidation reduction mechanism.

Part II:

Table S.I. captions:

Table S.I.1 Textural properties of Cu-BTC and V/Cu-BTC.

Table S.I.2 Sulfur uptake capacity of different adsorbents.

Table S.I.3 Constants and correlation coefficients of different adsorption models in ALF.

Table S.I.4 Constants and correlation coefficients of different adsorption models in ARF.

Table S.I.5 Constants and correlation coefficients of different adsorption models in MIF.

Table S.I.6. Kinetic parameters in ALF for BT adsorption on Cu-BTC and V/Cu-BTC.

Table S.I.7. Kinetic parameters in ARF for BT adsorption on Cu-BTC and V/Cu-BTC.

Table S.I.8. Kinetic parameters in MIF for BT adsorption on Cu-BTC and V/Cu-BTC.

Table S.I.1 Textural properties of Cu-BTC and V/Cu-BTC.

Samples	BET surface area (m^2/g)	V_{total} (cm^3/g)	V_{mic} (cm^3/g, %)	V_{meso} (cm^3/g, %)
Cu-BTC	1243	0.68	0.54, 79	0.14, 11
V0.5/Cu-BTC	1094	0.58	0.48, 83	0.10, 17
V1.0/Cu-BTC	755	0.54	0.37, 69	0.18, 31
V1.5/Cu-BTC	683	0.49	0.33, 67	0.16, 33

Table S.I.2 Sulfur uptake capacity of different adsorbents.

Adsorbents	Solvents	q_{max} (mg/g)	References
Cu-BTC	ALF	45	this work
	ARF	60	
	MIF	55	
V1.0/Cu-BTC	ALF	60	this work
	ARF	75	
	MIF	68	
Cu(I)-Y zeolite	ALF	55	[18]
	ARF	6	
	MIF	7	
SBA-15	ALF	65	[22]
	ARF	11	
	MIF	10	
$CuCl_2$/V-BDC	ALF	66	[23]
	MIF	16	
Activated carbon	ALF	27	[27]
	ARF	11	
	MIF	16	
PTA@ (Zn, Ni, Cu)-BTC	ALF	17	[27]
	ARF	10	
	MIF	11	
Co-Y zeolite	ALF	29	[28]
Ce/Ni-Y zeolite	ALF	22	[29]
Activated Al_2O_3	n-hexane	21	[30]
CMK-3	n-hexane	11	[31]
ZIF-8-derived	n-hexane	27	[32]
ZIF-8-derived	MIF	22	[32]
Cu_2O/MIL-100(Fe)	ALF	35	[33]
MIL-101(V)	ALF	51	[34]

Table S.I.3 Constants and correlation coefficients of different adsorption models in ALF.

Samples	Langmuir			Freundlich			Temkin			D-R		
	q_L (mg/g)	K_L (L/mg)	R^2	K_f (L/g)	n	R^2	b_T (kJ/mol)	K_T (L/g)	R^2	q_s (mg/g)	K_D (mol^2/kJ^2)	R^2
Cu-BTC	48.10	0.082	0.995	21.19	8.25	0.530	510.52	23.21	0.524	48.53	6.36E-04	0.951
V0.5/Cu-BTC	56.65	0.035	0.999	22.89	7.61	0.687	412.18	11.73	0.719	54.93	4.38E-04	0.993
V1.0/Cu-BTC	59.48	0.055	0.993	20.24	6.17	0.606	325.69	3.15	0.615	59.23	5.03E-04	0.944
V1.5/Cu-BTC	50.20	0.038	0.994	18.49	6.88	0.519	423.77	5.34	0.526	50.23	1.04E-03	0.960

Table S.I.4 Constants and correlation coefficients of different adsorption models in ARF.

Samples	Langmuir			Freundlich			Temkin			D-R		
	q_L (mg/g)	K_L (L/mg)	R^2	K_f (L/g)	n	R^2	b_T (kJ/mol)	K_T (L/g)	R^2	q_s (mg/g)	K_D (mol^2/kJ^2)	R^2
Cu-BTC	61.23	0.042	0.997	21.74	6.63	0.681	337.32	4.19	0.686	60.20	3.90E-04	0.923
V0.5/Cu-BTC	73.21	0.022	0.998	21.94	5.66	0.738	244.38	1.41	0.773	71.08	6.37E-04	0.948
V1.0/Cu-BTC	81.37	0.022	0.994	20.38	4.95	0.708	201.30	0.72	0.716	76.52	6.37E-04	0.855
V1.5/Cu-BTC	72.62	0.019	0.998	18.25	5.04	0.754	230.80	0.74	0.786	68.36	7.49E-04	0.953

Table S.I.5 Constants and correlation coefficients of different adsorption models in MIF.

Samples	Langmuir			Freundlich			Temkin			D-R		
	q_L (mg/g)	K_L (L/mg)	R^2	K_f (L/g)	n	R^2	b_T (kJ/mol)	K_T (L/g)	R^2	q_s (mg/g)	K_D (mol^2/kJ^2)	R^2
Cu-BTC	53.24	0.041	0.990	16.88	5.91	0.539	343.77	1.78	0.533	53.89	1.26E-03	0.937
V0.5/Cu-BTC	64.22	0.015	0.997	14.19	4.65	0.771	243.46	0.43	0.804	59.50	9.95E-04	0.936
V1.0/Cu-BTC	70.22	0.021	0.996	16.88	4.80	0.804	229.33	0.64	0.834	65.19	4.79E-04	0.903
V1.5/Cu-BTC	60.20	0.019	0.999	17.14	5.69	0.760	306.17	1.32	0.797	56.57	7.43E-04	0.956

Table S.I.6. Kinetic parameters in ALF for BT adsorption on Cu-BTC and V/Cu-BTC.

Samples	Pseudo-first-order rate equation						Pseudo-second-order rate equation					Intra-particle diffusion model		
	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	K_1 (1/min)	R^2	Δq (mg/g)	Δq (%)	$q_{e,cal}$ (mg/g)	K_2 (g/mg.min)	R^2	Δq (mg/g)	Δq (%)	C (mg/g)	K_3 (mg/g.$min^{1/2}$)	R^2
Cu-BTC	45	6.3	-0.05	0.26	38.7	86.0	56.1	2.5E-03	0.990	-11.1	-24.7	15.1	5.2	0.71
V0.5/Cu-BTC	55	32.1	-0.10	0.92	22.9	41.7	59.1	6.3E-03	0.998	-4.1	-7.5	34.6	3.3	0.69
V1.0/Cu-BTC	60	21.2	-0.10	0.78	38.8	64.7	61.8	1.3E-02	0.998	-1.8	-3.1	44.6	2.5	0.54
V1.5/Cu-BTC	50	24.5	-0.07	0.53	25.5	51.0	55.1	5.2E-03	0.998	-5.1	-10.1	29.3	3.4	0.76

Table S.I.7. Kinetic parameters in ARF for BT adsorption on Cu-BTC and V/Cu-BTC.

Samples	Pseudo-first-order rate equation						Pseudo-second-order rate equation					Intra-particle diffusion model		
	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	K_1 (1/min)	R^2	Δq (mg/g)	Δq (%)	$q_{e,cal}$ (mg/g)	K_2 (g/mg.min)	R^2	Δq (mg/g)	Δq (%)	C (mg/g)	K_3 (mg/g.min$^{1/2}$)	R^2
Cu-BTC	60.0	39.75	-0.12	0.76	20.24	33.7	69.8	2.0E-03	0.990	-9.8	-16.4	19.7	6.3	0.63
V0.5/Cu-BTC	72.0	38.91	-0.12	0.70	33.09	45.9	77.5	3.3E-03	0.996	-5.6	-7.75	38.2	5.2	0.74
V1.0/Cu-BTC	79.5	45.26	-0.12	0.64	34.24	43.1	84.9	3.5E-03	0.998	-5.4	-6.78	44.3	5.5	0.71
V1.5/Cu-BTC	70.0	27.86	-0.08	0.64	42.14	60.2	76.4	3.0E-03	0.994	-6.5	-9.21	35.0	4.5	0.76

Table S.I.8. Kinetic parameters in MIF for BT adsorption on Cu-BTC and V/Cu-BTC.

Samples	Pseudo-first-order rate equation						Pseudo-second-order rate equation					Intra-particle diffusion model		
	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	K_1 (1/min)	R^2	Δq (mg/g)	Δq (%)	$q_{e,cal}$ (mg/g)	K_2 (g/mg.min)	R^2	Δq (mg/g)	Δq (%)	C (mg/g)	K_3 (mg/g.min$^{1/2}$)	R^2
Cu-BTC	55	16.4	-0.08	0.30	38.6	70.1	62.7	2.8E-03	0.991	-7.7	-14.0	21.1	5.6	0.56
V0.5/Cu-BTC	60	34.8	-0.10	0.74	25.2	42.0	64.2	5.3E-03	0.996	-4.2	-7.0	34.0	4.2	0.61
V1.0/Cu-BTC	66	15.5	-0.07	0.50	50.5	76.5	73.2	3.4E-03	0.997	-7.3	-11.0	34.9	5.1	0.74
V1.5/Cu-BTC	57	10.3	-0.07	0.21	46.7	82.0	62.1	4.7E-03	0.992	-5.1	-8.9	29.5	4.5	0.60

Part III:

Figure S.I. captions:

Figure S.I.1. IR spectra of Cu-BTC, V0.5/Cu-BTC, V1.0/Cu-BTC, and V1.5/Cu-BTC.

Figure S.I.2. Weber–Morris intra-particle diffusion plots for the adsorption of BT in the ALF, ARF and MIF over Cu-BTC, V0.5/Cu-BTC, V1.0/Cu-BTC, and V1.5/Cu-BTC. (A): ALF; (B): ARF; (C): MIF.

Fig. S.I.3. Effect of recycle times of V1.0/Cu-BTC on the regeneration.

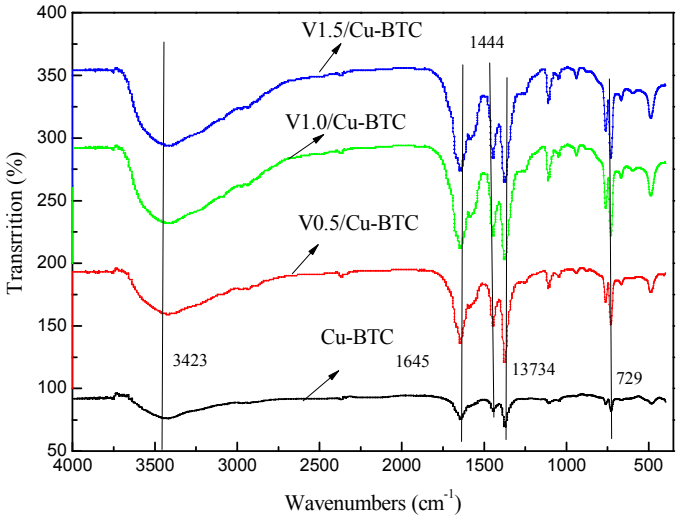
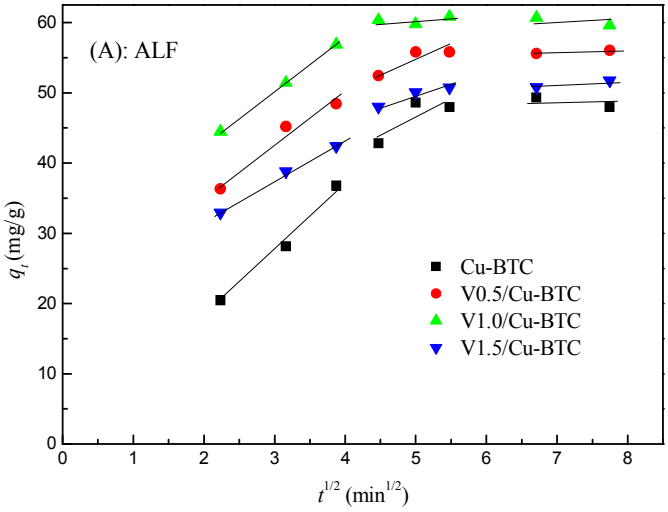
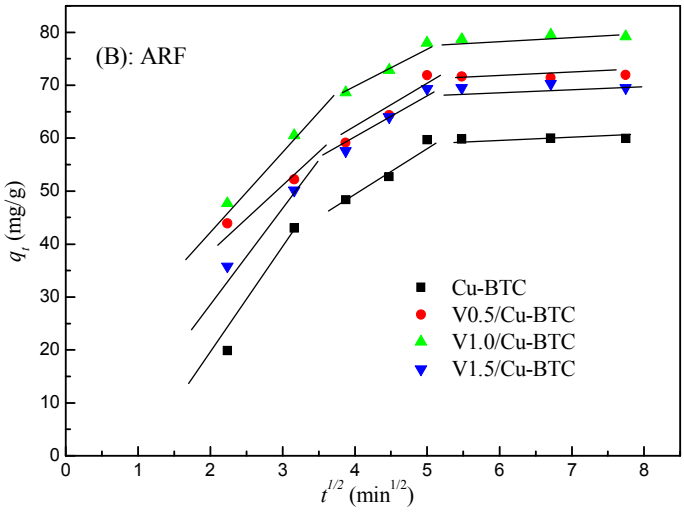


Figure S.I.1. IR spectra of Cu-BTC, V0.5/Cu-BTC, V1.0/Cu-BTC, and V1.5/Cu-BTC.


(A): ALF
q_t (mg/g)
$t^{1/2}$ (min$^{1/2}$)
Cu-BTC
V0.5/Cu-BTC
V1.0/Cu-BTC
V1.5/Cu-BTC


(B): ARF
q_t (mg/g)
$t^{1/2}$ (min$^{1/2}$)
Cu-BTC
V0.5/Cu-BTC
V1.0/Cu-BTC
V1.5/Cu-BTC

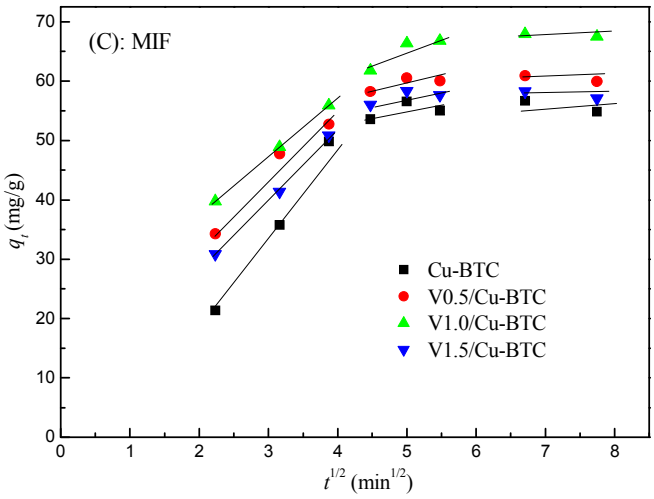


Figure S.I.2. Weber–Morris intra-particle diffusion plots for the adsorption of BT in the ALF, ARF and MIF over Cu-BTC, V0.5/Cu-BTC, V1.0/Cu-BTC, and V1.5/Cu-BTC. (A): ALF; (B): ARF; (C): MIF.

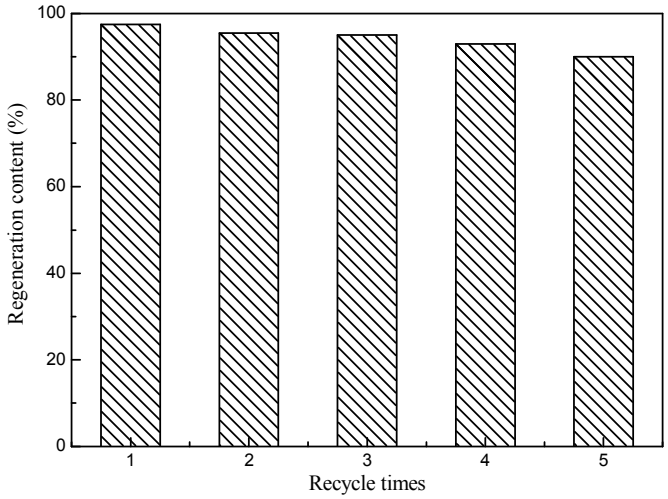


Fig. S.I.3. Effect of recycle times of V1.0/Cu-BTC on the regeneration.

Part IV:

(A) The sulfur uptake capacity was calculated by the formula (1):

$$q_e = \frac{W}{M}(C_o - C_e) \qquad (1)$$

where q_e is the uptake capacity of sulfur (mg/g), W is the mass of model fuel (g), M is the mass of the sorbent (g), and C_o and C_e are the initial and final S-concentrations (mg/g).

(B): Adsorption isotherm models used in this study and their linear forms.

Isotherm	Nonlinear form	Linear form	Plot	Eqs
Langmuir-I	$q_e = \frac{K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_L \cdot K_L} + (\frac{1}{q_L}) \cdot C_e$	$\frac{C_e}{q_e}$ versus C_e	(2)
Freundlich	$q_e = K_f C_e^{\frac{1}{n}}$	$\ln q_e = \ln K_f + (\frac{1}{n}) \cdot \ln C_e$	$\ln q_e$ versus $\ln C_e$	(3)
Temkin	$e^{qe} = (K_T C_e)^{\frac{RT}{b_T}}$	$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e$	q_e versus $\ln C_e$	(4)
D–R	$q_e = q_s e^{(-K_D \varepsilon^2)}$	$\ln q_e = \ln q_s - K_D \varepsilon^2$	$\ln q_e$ versus ε^2	(5)

Where q_e is the maximum capacity of adsorption in mg/g; K_L is a constant related to the affinity of the binding sites in L/mg; 'K_f' and 'n' are the measures of adsorption capacity and intensity of adsorption; R is the universal gas constant; b_T is related to the heat of adsorption in kJ/mol. T is the absolute temperature in K; R is the universal gas constant; K_T is the Temkin constant about the capacity of adsorption in L/g; q_s is the D-R isotherm constant in mg/g; K_D stands for the constant that is relevant with the adsorption energy in mol^2/kJ^2; ε represents the Polanyi potential constant in kJ/mol;

(C): Adsorption kinetic equations:

Pseudo-first order model: $\ln(q_e - q_t) = \ln(q_e) - K_1 t \qquad (6)$

Pseudo-second order model: $\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{t}{q_e} \qquad (7)$

Intra-particle diffusion model: $q_t = K_3 t^{1/2}$ (8)

where q_e and q_t (mg/g) are the BT uptake at equilibrium and at time t (min), respectively, K_1 (1/min) is the adsorption rate constant, K_2 (g/mg.min) is the rate constant of second-order equation, K_3 (mg/g.min$^{1/2}$) is the intra-particle diffusion rate constant.