

## Supporting Information

# Highly efficient simultaneous ultrasonic-assisted adsorption of Methylene Blue and Rhodamine B onto Metal Organic Framework MIL-68(Al): Central composite design optimization

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## Results and discussion; Characterization of MIL-68(Al)

According to the Fig.S1, a peak at  $3438\text{ cm}^{-1}$  can be assigned to the absorption of  $\text{H}_2\text{O}$  on the sample. The most intense signals at  $1598\text{ cm}^{-1}$  and  $1390\text{ cm}^{-1}$  clearly ascribe the presence of the vibrational bands characteristic of the carboxylates groups ( $\nu\text{C}=\text{O}$ ) within MIL-68(Al). The signal at  $863\text{ cm}^{-1}$  is due to the bending mode related to the  $\text{U}_2$ -hydroxo groups of the corner-sharing octahedral  $\text{AlO}_4(\text{OH})_2$ .

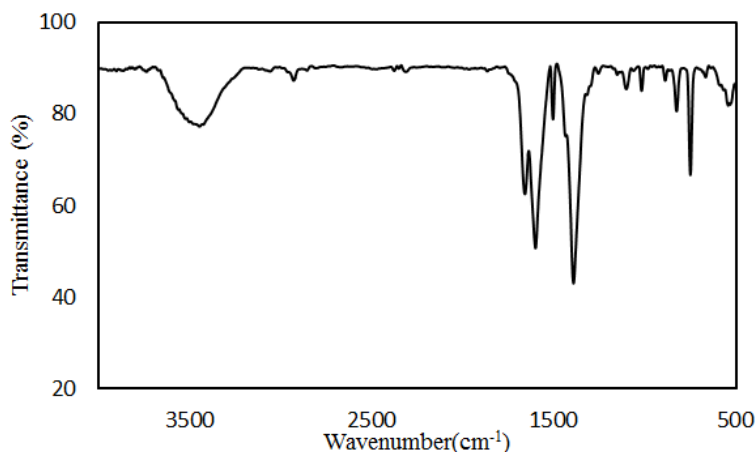


Fig.S1. FT- IR spectra of MIL-68(Al) sample

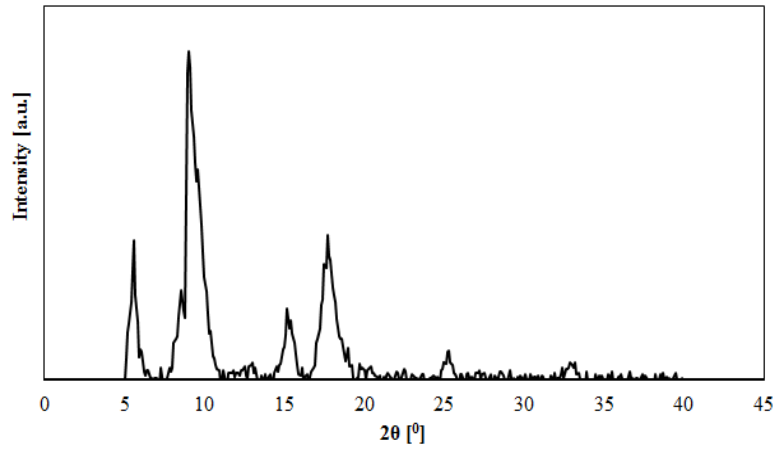


Fig.S2. XRD diffraction pattern of synthesized MIL-68(Al)

According to the N<sub>2</sub> adsorption-desorption analysis, desorption average pore width obtained by BET and BJH desorption average pore diameter was evaluated about 2.90 and 5.36 nm respectively.

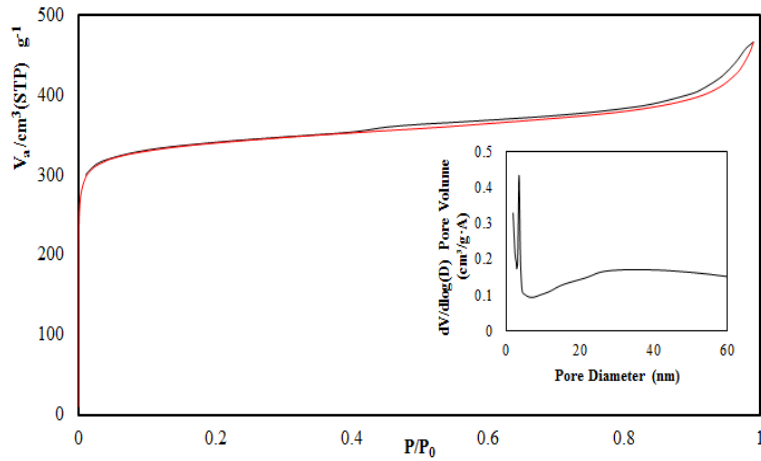


Fig.S3. N<sub>2</sub> adsorption/desorption isotherm at 77 K and BJH pore size distributions (inset) for synthesized MIL-68(Al)

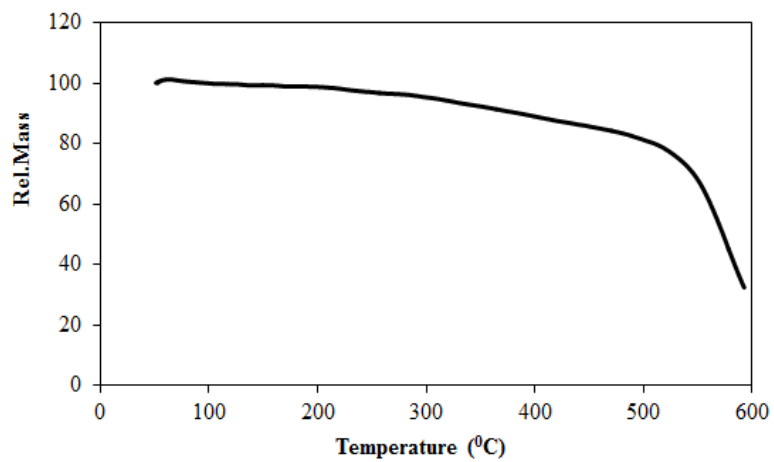


Fig. S4. TGA curve of the as-prepared MIL-68(Al) under air (heating rate of 5 K per minute, 10 mg of solid).

**Central composite design (CCD); Experimental design for single and binary dye solutions**

Table S1- Experimental factors and levels with responses for binary dye solutions according to the central composite design.

Factors	Levels			Star point	
	Low (-1)	Central (0)	High (+1)	- $\alpha$	+ $\alpha$
(A) Time	8	10	12	6	14
(B) pH	4	6	8	2	10
(C) Adsorbent dosage	6	10	14	2	18
(D) MB Concentration	60	80	100	40	120
(E) RhB Concentration	15	20	25	10	30

Runs	A	B	C	D	E	(R <sub>3</sub> )	(R <sub>4</sub> )
1	10	6	2	80	20	45.5	23.4
2	8	4	6	100	15	46.1	15.0
3	10	6	10	120	20	69.5	16.2
4	8	4	14	100	25	86.9	32.1
5	8	8	6	60	15	88.6	36.8
6	10	6	10	80	20	92.4	33.8
7	10	6	10	80	10	92.4	42.9
8	10	6	10	80	20	93.5	32.3
9	12	8	14	100	25	97.3	35.9
10	10	6	10	80	20	91.3	33.1
11	10	6	18	80	20	99.7	80.5
12	10	6	10	80	20	92.5	34.1
13	8	8	14	60	25	97.7	50.7
14	8	4	6	60	25	63.7	26.6
15	10	6	10	80	20	92.8	32.0
16	12	8	14	60	15	100	66.7
17	6	6	10	80	20	91.9	27.2
18	10	2	10	80	20	61.0	20.6
19	10	6	10	40	20	97.7	55.8
20	12	8	6	60	25	89.1	21.4
21	10	6	10	80	30	90.3	25.0
22	12	8	6	100	15	67.8	10.0
23	12	4	14	100	15	85.7	35.8
24	12	4	14	60	25	96.8	58.9
25	14	6	10	80	20	96.1	37.6
26	10	6	10	80	20	91.3	37.0
27	12	4	6	100	25	45.6	11.0
28	8	8	6	100	25	76.7	10.7
29	12	4	6	60	15	70.6	28.0
30	8	8	14	100	15	97.3	45.2
31	10	10	10	80	20	93.0	22.5
32	8	4	14	60	15	97.6	66.4

R<sub>3</sub>: MB removal% in binary solution, R<sub>4</sub>: RhB removal% in binary solution

Table S2. Experimental factors and levels with responses for single dye solution (MB) according to the central composite design

Factors	Levels			Star point	
	Low (-1)	Central (0)	High (+1)	- $\alpha$	+ $\alpha$
(A) Time (min)	8	10	12	6	14
(B) pH	4	6	8	2	10
(C) Adsorbent dosage (mg)	6	10	14	2	18
(D) MB Concentration (mg/L)	60	80	100	40	120

Runs	A	B	C	D	(R <sub>1</sub> )
1	12.00	4.00	6.00	60.00	63.51
2	8.00	8.00	6.00	60.00	90.81
3	12.00	8.00	14.00	60.00	100
4	8.00	4.00	6.00	100.00	47.04
5	8.00	8.00	14.00	100.00	97.25
6(C)	10.00	6.00	10.00	80.00	94.24
7	12.00	4.00	14.00	100.00	89.12
8	12.00	8.00	6.00	100.00	80.92
9	8.00	4.00	14.00	60.00	99.07
10(C)	10.00	6.00	10.00	80.00	94.28
11	12.00	8.00	6.00	60.00	93.47
12	12.00	8.00	14.00	100.00	98.22
13	8.00	8.00	6.00	100.00	77.03
14	8.00	8.00	14.00	60.00	99.76
15	8.00	4.00	6.00	60.00	64.29
16(C)	10.00	6.00	10.00	80.00	93.31
17	12.00	4.00	6.00	100.00	49.11
18(C)	10.00	6.00	10.00	80.00	94.86
19	12.00	4.00	14.00	60.00	100
20	8.00	4.00	14.00	100.00	87.02
21	10.00	2.00	10.00	80.00	61.1
22(C)	10.00	6.00	10.00	80.00	94.21
23	14.00	6.00	10.00	80.00	95.99
24	10.00	6.00	10.00	40.00	98.59
25	10.00	6.00	10.00	120.00	74.33
26	6.00	6.00	10.00	80.00	91.5
27	10.00	6.00	2.00	80.00	42.05
28	10.00	10.00	10.00	80.00	95
29	10.00	6.00	18.00	80.00	100
30(C)	10.00	6.00	10.00	80.00	93.18

R<sub>1</sub>: MB removal % in single solution

C: Center point

Table S3. Experimental factors and levels with responses for single dye solution (RhB) according to the central composite design

Factors	Levels			Star point	
	Low (-1)	Central (0)	High (+1)	- $\alpha$	+ $\alpha$
(A) Time (min)	8	10	12	6	14
(B) pH	4	6	8	2	10
(C) Adsorbent dosage (mg)	6	10	14	2	18
(D) RhB Concentration (mg/L)	15	20	25	10	30

Runs	A	B	C	D	(R <sub>2</sub> )
1(C)	10.00	6.00	10.00	20.00	89.24
2	8.00	4.00	14.00	15.00	95.00
3	12.00	4.00	14.00	25.00	83.15
4	12.00	8.00	14.00	15.00	68.02
5	8.00	8.00	14.00	25.00	55.85
6	8.00	8.00	6.00	15.00	50.66
7	8.00	4.00	6.00	25.00	61.70
8	12.00	4.00	6.00	15.00	76.74
9	12.00	8.00	6.00	25.00	49.10
10(C)	10.00	6.00	10.00	20.00	88.83
11	12.00	4.00	14.00	15.00	97.03
12	8.00	8.00	6.00	25.00	44.91
13	12.00	8.00	14.00	25.00	49.87
14	8.00	8.00	14.00	15.00	61.90
15	8.00	4.00	14.00	25.00	79.69
16	8.00	4.00	6.00	15.00	63.02
17	12.00	4.00	6.00	25.00	71.16
18	12.00	8.00	6.00	15.00	61.99
19(C)	10.00	6.00	10.00	20.00	88.03
20(C)	10.00	6.00	10.00	20.00	90.02
21	14.00	6.00	10.00	20.00	92.86
22	10.00	6.00	10.00	30.00	73.27
23	10.00	2.00	10.00	20.00	59.52
24(C)	10.00	6.00	10.00	20.00	91.27
25	6.00	6.00	10.00	20.00	77.58
26(C)	10.00	6.00	10.00	20.00	88.14
27	10.00	6.00	18.00	20.00	93.31
28	10.00	10.0	10.00	20.00	20.07
29	10.00	6.00	2.00	20.00	63.03
30	10.00	6.00	10.00	10.00	95.04

R<sub>2</sub>: RhB removal % in single solution  
 C: Center point

## The results of ANOVA and P-values

Table S4. ANOVA for response surface quadratic model for MB in single solution

Source	Sum of Squares	df	Mean Square	F-value	Prob > F
Block	7.67	2	3.84		
Model	8661.83	14	618.70	218.68	<0.0001
A-Time	18.48	1	18.48	6.53	0.0239
B-pH	1769.88	1	1769.8	625.58	<0.0001
C-Dosage	4270.93	1	4270.9	1509.5	<0.0001
D-MB concentration	745.04	1	745.04	263.34	<0.0001
AB	0.74	1	0.74	0.26	0.6177
AC	0.81	1	0.81	0.29	0.6016
AD	2.24	1	2.24	0.79	0.3903
BC	603.44	1	603.44	213.29	<0.0001
BD	35.88	1	35.88	12.68	0.0035
CD	59.14	1	59.14	20.90	0.0005
A <sup>2</sup>	0.51	1	0.51	0.18	0.6788
B <sup>2</sup>	393.51	1	393.51	139.09	<0.0001
C <sup>2</sup>	843.03	1	843.03	297.97	<0.0001
D <sup>2</sup>	77.90	1	77.90	27.53	0.0002
Residual	36.78	13	2.83		
Lack of Fit	35.05	10	3.50	6.07	0.0823 not significant
Pure Error	1.73	3	0.58		
Cor total	8706.28	29			

$R^2 = 0.996$ , adjusted  $R^2 = 0.991$ , predicted  $R^2 = 0.967$

Table S5. ANOVA for response surface quadratic model for RhB in single solution

Source	Sum of Squares	df	Mean Square	F-value	Prob > F
Block	118.43	2	59.21		
Model	10188.41	14	727.74	107.90	<0.0001
A-Time	233.38	1	233.38	34.60	<0.0001
B-pH	2905.76	1	2905.76	430.83	<0.0001
C-Dosage	1228.94	1	1228.94	182.21	<0.0001
D-RhB concentration	623.63	1	623.63	92.46	<0.0001
AB	10.56	1	10.56	1.57	0.2328
AC	68.56	1	68.56	10.17	0.0071
AD	30.31	1	30.31	4.49	0.0538
BC	177.29	1	177.29	26.29	0.0002
BD	2.86	1	2.86	0.42	0.5265
CD	48.30	1	48.30	7.16	0.0190
A <sup>2</sup>	92.59	1	92.59	13.73	0.0026
B <sup>2</sup>	4774.48	1	4774.48	707.90	<0.0001
C <sup>2</sup>	355.43	1	355.43	52.70	<0.0001
D <sup>2</sup>	121.95	1	121.95	18.08	0.0009
Residual	87.86	13	6.74		
Lack of Fit	80.72	10	8.07	3.48	0.1666 not significant
Pure Error	6.69	3	2.32		
Cor total	10394.51	29			

$R^2 = 0.992$ , adjusted  $R^2 = 0.982$ , predicted  $R^2 = 0.945$



Table S6. ANOVA for response surface quadratic model for MB in binary solution

Source	Sum of Squares	df	Mean Square	F-value	Prob > F
Model	8447.92	20	422.40	286.73	<0.0001
A-Time	1.74	1	1.74	1.18	0.3003
B-pH	1430.72	1	1430.72	971.19	<0.0001
C-Dosage	4208.28	1	4208.28	2856.64	<0.0001
D- MB concentration	1029.70	1	1029.70	698.97	<0.0001
E- RhB concentration	0.66	1	0.66	0.45	0.5174
AB	6.69	1	6.69	4.54	0.0565
AC	0.33	1	0.33	0.22	0.6454
AD	23.42	1	23.45	15.90	0.0021
AE	5.57	1	5.57	3.78	0.0779
BC	314.38	1	314.38	213.41	<0.0001
BD	49.36	1	49.36	33.51	0.0001
BE	12.78	1	12.78	8.67	0.0133
CD	163.48	1	163.48	110.97	<0.0001
CE	0.93	1	0.93	0.63	0.4430
DE	22.76	1	22.76	15.45	0.0023
A <sup>2</sup>	6.57	1	6.57	4.46	0.0583
B <sup>2</sup>	419.76	1	419.76	284.94	<0.0001
C <sup>2</sup>	724.30	1	724.30	494.67	<0.0001
D <sup>2</sup>	133.44	1	133.44	90.58	<0.0001
E <sup>2</sup>	1.08	1	1.08	0.73	0.4107
Residual	16.20	11	1.47		
Lack of Fit	12.54	6	2.09	2.85	0.1352
					not significant
Pure Error	3.67	5	0.73		
Cor total	8464.13	31			

$R^2 = 0.998$ , adjusted  $R^2 = 0.995$ , predicted  $R^2 = 0.959$

Table S7. ANOVA for response surface quadratic model for RhB in binary solution

Source	Sum of Squares	df	Mean Square	F-value	Prob > F
Model	8931.76	20	446.59	48.37	<0.0001
A-Time	0.97	1	0.97	0.11	0.7517
B-pH	2.35	1	2.35	0.25	0.6238
C-Dosage	5008.66	1	5008.66	542.53	<0.0001
D- MB concentration	2374.67	1	2374.67	257.22	<0.0001
E- RhB concentration	355.20	1	355.20	38.48	<0.0001
AB	0.58	1	0.58	0.063	0.8065
AC	29.19	1	29.19	3.16	0.1030
AD	1.37	1	1.37	0.15	0.7069
AE	55.84	1	55.84	6.05	0.0317
BC	3.11	1	3.11	0.34	0.5736
BD	9.23	1	9.23	1.0	0.3389
BE	33.84	1	33.84	3.67	0.0819
CD	47.58	1	47.58	5.15	0.0443
CE	17.00	1	17.00	1.84	0.2020
DE	36.27	1	36.27	3.93	0.0730
A <sup>2</sup>	9.17	1	9.17	0.99	0.3403
B <sup>2</sup>	313.03	1	313.03	33.91	0.0001
C <sup>2</sup>	550.49	1	550.49	59.63	<0.0001
D <sup>2</sup>	3.61	1	3.61	0.39	0.5445
E <sup>2</sup>	0.83	1	0.83	0.090	0.7702
Residual	101.55	11	9.23		0.1235
Lack of Fit	79.53	6	13.26	3.01	not significant
Pure Error	22.02	5	4.40		
Cor total	9033.31	31			

$R^2 = 0.989$ , adjusted  $R^2 = 0.968$ , predicted  $R^2 = 0.762$

## Equations S1-4

$$R1 = +94.01 + 0.88A + 8.59B + 13.34C - 5.5D + 0.22AB - 0.22AC + 0.37AD - 6.14BC + 1.50BD + 1.92CD + 0.14A^2 - 3.79B^2 - 5.54C^2 - 1.69D^2 \quad (1)$$

$$R2 = +89.26 + 3.12A - 11.00B + 7.16C - 5.10D - 3.33AB + 0.81AC - 0.42AD - 2.07BC - 1.74BD - 1.38CD - 13.19A^2 - 3.60B^2 - 1.84C^2 - 2.11D^2 \quad (2)$$

$$R3 = +92.30 + 0.27A + 7.72B + 13.24C - 6.55D - 0.17E - 0.65AB + 0.14AC - 1.21AD + 0.59AE + 4.43BC + 1.76BD + 0.89BE + 3.20CD - 0.24CE + 1.19DE + 0.47A^2 - 3.78B^2 - 4.97C^2 - 2.13D^2 - 0.19E^2 \quad (3)$$

$$R4 = +34.08 + 0.20A + 0.31B + 14.45C - 9.95D - 3.85E - 0.19AB + 1.35AC - 0.29AD + 1.87AE + 0.44BC + 0.76BD - 1.45BE - 1.72CD - 1.03CE + 1.5DE - 0.56A^2 - 3.27B^2 + 4.33C^2 + 0.35D^2 - 0.17E^2 \quad (4)$$