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Low-Temperature and Additive-Free Synthesis of Spherical MIL-101(Cr) with Enhanced Dye Adsorption Performance

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Abstract: The chromium-benzenedicarboxylate metal–organic framework (MOF), MIL-101(Cr), is one of the most well-investigated and widely used prototypical MOFs. Regarding its synthesis, the use of a toxic modulator (usually HF) and high reaction temperature (220 °C) are the main factors hindering its further expansion of production and utilization. In fact, high quality MIL-101(Cr) crystals can be prepared at a much lower temperature (160 °C) with spherical morphology via an additive-free approach. Compared to traditional octahedral MIL-101(Cr), the spherical MIL-101(Cr) possesses higher adsorption performance toward dye molecules, including methyl orange (MO) and rhodamine B (RB). The results suggest that toxic additives and high reaction temperatures are not essential in the synthesis of MIL-101(Cr), and the fabrication of spherical MIL-101(Cr) may offer a facile and effective pathway for the large-scale industrial application of MIL-101(Cr).

Keywords: spherical MIL-101(Cr); morphology control; dye adsorption; industrial application

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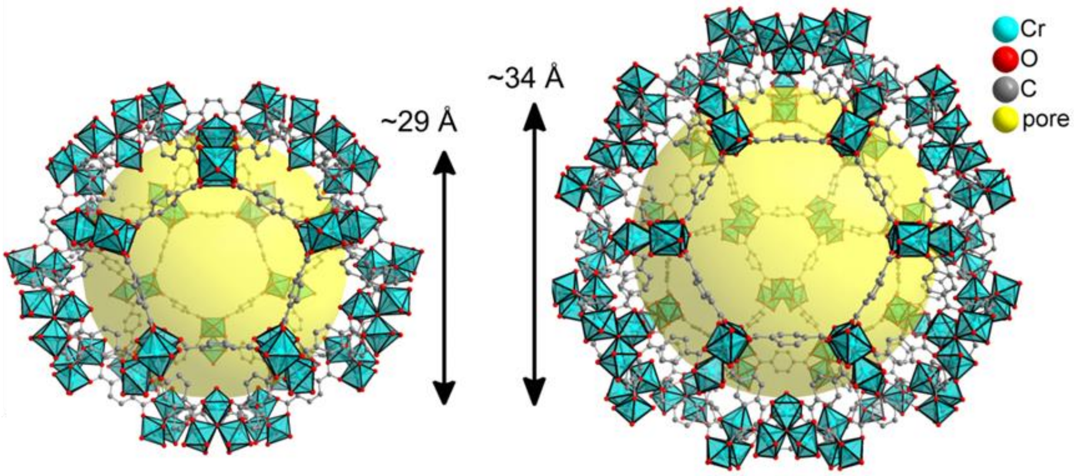

Benzene-1,4-dicarboxylate ligands bridge between trinuclear {Cr_3O} building units; small cage with pentagonal windows and large cage with pentagonal and hexagonal windows with pore diameters (yellow spheres); the yellow spheres in the mesoporous cages with diameter of 2.9 or 3.4 Å, respectively, taking into account the van der Waals radii of the framework walls; water-guest molecules are not shown (CSD-Refcode OCUNAK)

Figure S1. Building blocks for MIL-101(Cr).

Table S1. Price parameters of MIL-101(Cr) sold by various manufacturers.

Names and Specifications	Unit Price	Manufacturer
MIL-101(Cr) BET: 2800-3200 $m^2 g^{-1}$	237.1 $/g	Kaishu Chemical Technology Co., Ltd.
MIL-101(Cr) BET: NA*	221.3 $/g	Yanqu Information Technology Co., Ltd.
MIL-101(Cr) BET:NA	347.8 $/g	Ruixi Biological Technology Co., Ltd.
MIL-101(Cr) BET: 2800-3200 $m^2 g^{-1}$	237.1 $/g	Qiyue Biological Technology Co., Ltd.
MIL-101(Cr) BET: 2800-3200 $m^2 g^{-1}$	577.0 $/g	Yinuokai Technology Co., Ltd.
MIL-101(Cr) BET: 2800-3200 $m^2 g^{-1}$	474.3 $/g	Warwick Ruike Chemical Co., Ltd.
MIL-101(Cr) BET: 2800-3200 $m^2 g^{-1}$	316.2 $/g	Pusai Chemical Products Co., Ltd.
MIL-101(Cr) BET: 2800-3200 $m^2 g^{-1}$	284.6 $/g	Alpha Chemical Co., Ltd.
MIL-101(Cr) BET: 2800-3200 $m^2 g^{-1}$	237.1 $/g	Lavoisier Chemical Products Co., Ltd.
MIL-101(Cr) BET: 2800-3200 $m^2 g^{-1}$	579.6 $/g	Alfa Chemistry (USA)

*When no BET surface area were given (NA).

Table S2. BET specific surface area, pore volume and yield of MIL-101(Cr) synthesized by various additives.

Additive	S_{BET} /(m^2 g^{-1})	V_{pore} /(cm^3 g^{-1})	**Yield** /% [b]	**References**
Hydrofluoric Acid[a]	4100	2.02	~50	[19]
Hydrofluoric Acid	3609	1.55	46	[32]
Hydrofluoric Acid	2887	1.45	38	[33]
Hydrofluoric Acid	3498	1.72	49	[34]
Hydrofluoric Acid	2089	1.00	63	[35]
Acetic acid	3550	2.38	71.2	[37]
Nitric acid	3841	1.72	78	[34]
Hydrochloric acid	1720	0.87	NA	[38]
Sulfuric acid	838	0.77	NA	[39]
Sodium hydroxide	3223	1.57	37	[40]
Benzoic acid	3467	2.38	NA	[41]
Sodium acetate	3790	1.76	NA	[42]
Tetramethylammonium hydroxide	2939	1.55	51	[34]

[a]The preparation followed the original hydrothermal synthesis procedure by Férey et al [19]. [b]The yield is based on Cr and refers to the isolatedmaterial after the washing procedures. When no yields were given (NA) and the original procedure by Férey et al [19].

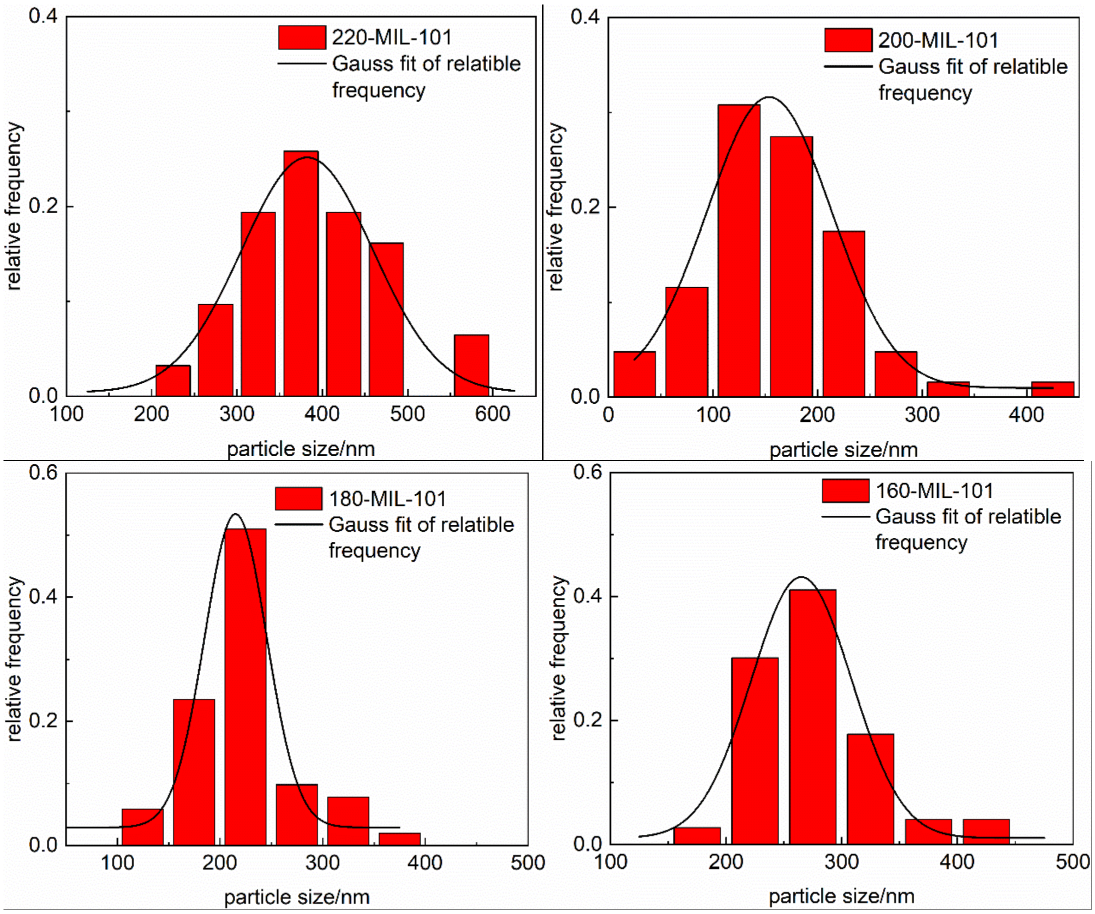

Figure S2. Particle size distribution of samples.

Table S3. Adsorption capacities (q_{max}) of MO on other MIL-101 and MIL-101 composite.

Adsorbents	q_{max} (mg g^{-1})	Ref.
MIL-101	140	[61]
MIL-101	87.5	[73]
150@MIL-101	420.2	[74]
MIL-101-Cr	196.1	[75]
Hierarchically mesostructured MIL-101	277.8	[76]
TiO_2/MIL-101(Cr)	240	[23]
MIL-101(Cr)/GA	331.5	[77]
GrO/MIL-101(Cr)	381	[78]
160-MIL-101	444.3	This work

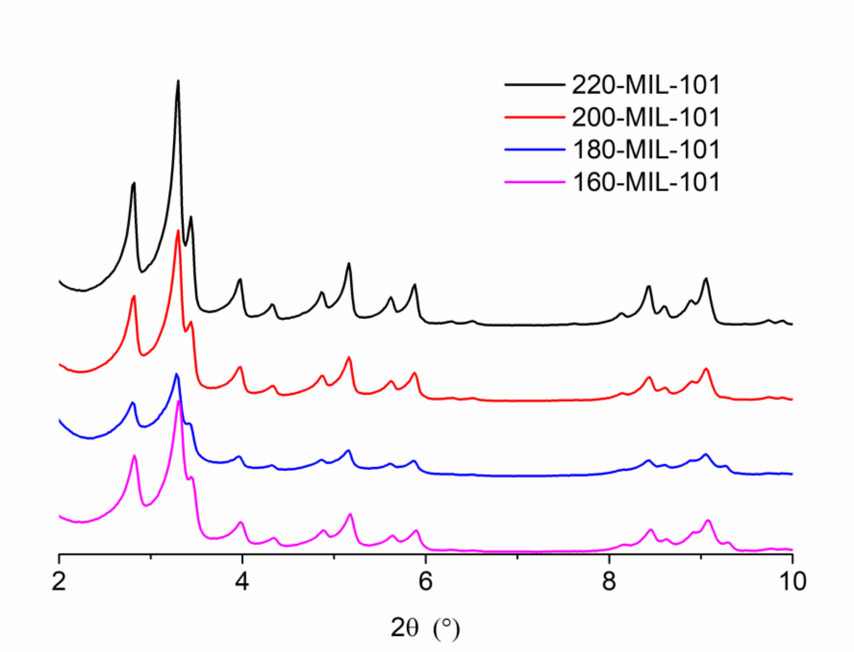

Figure S3. The low-angle region of the PXRD patterns of all MIL-101(Cr)s.

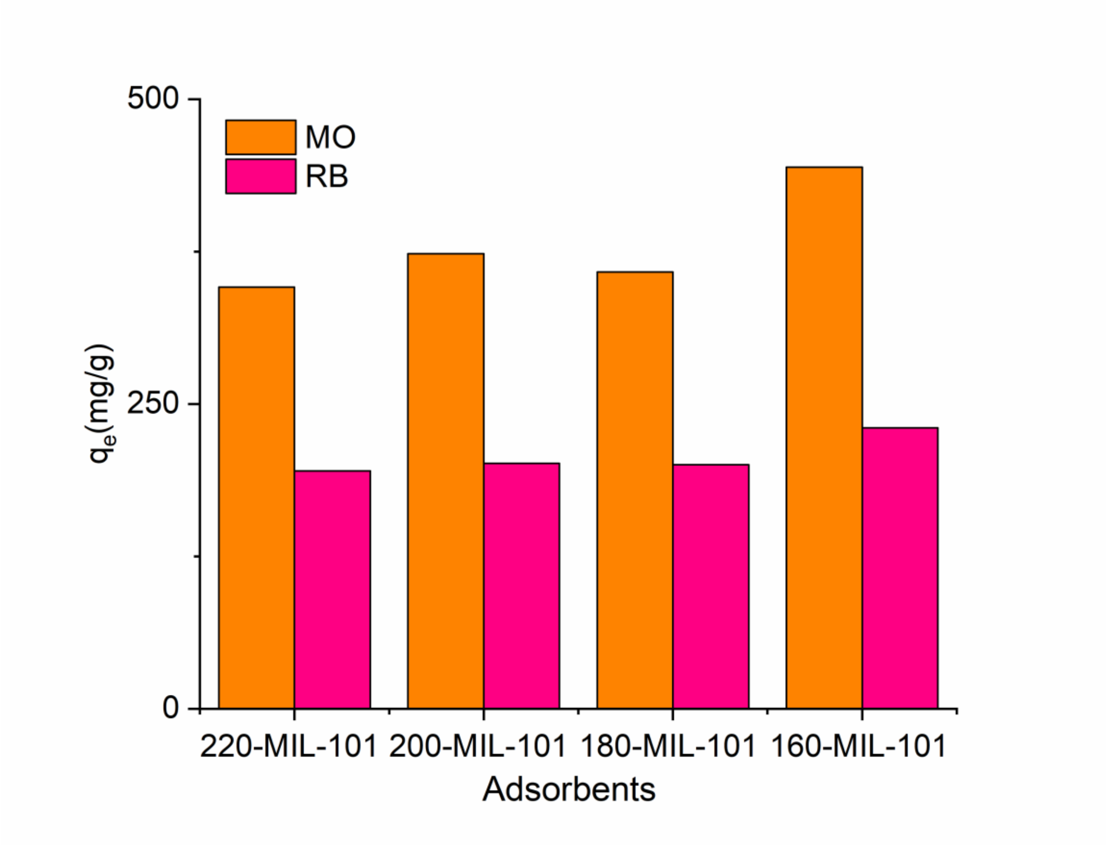

Figure S4. The adsorption capabilities of all MIL-101(Cr)s toward MO and RB.

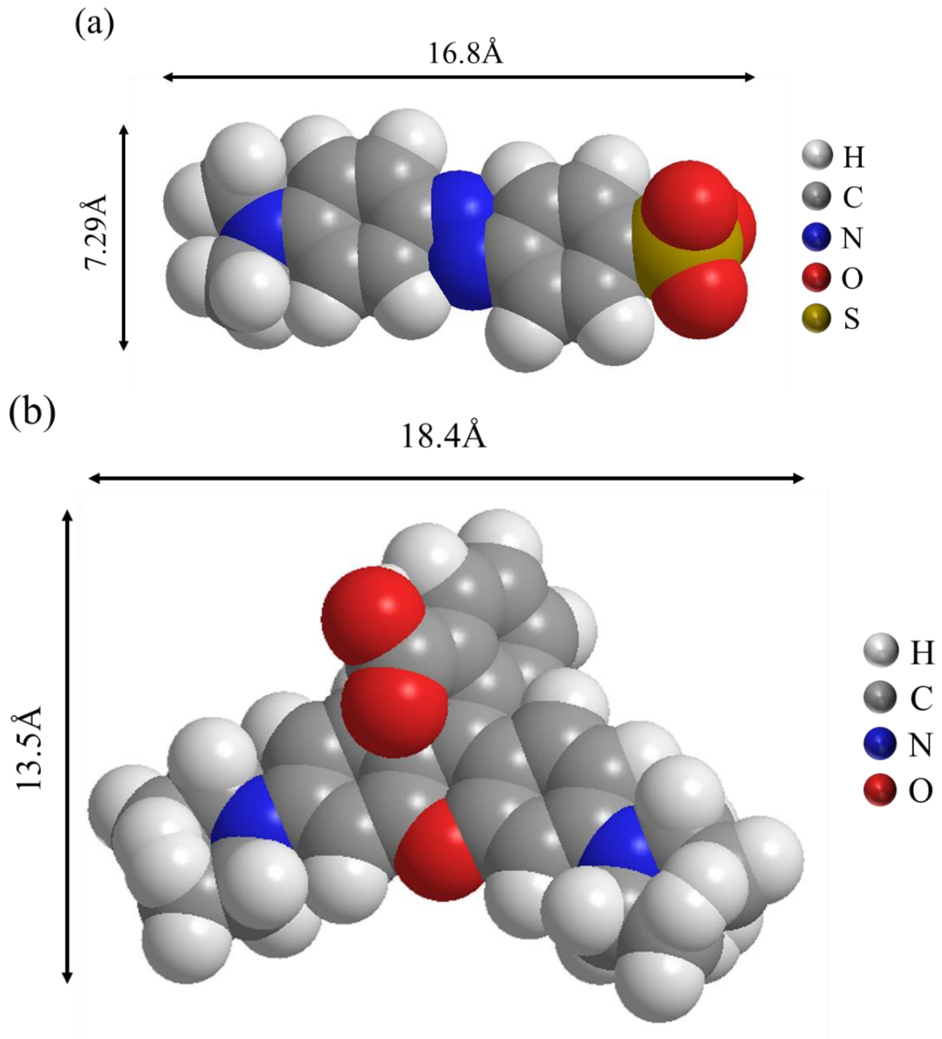

Figure S5. Dye molecule diagram, (**a**) MO and (**b**) RB.

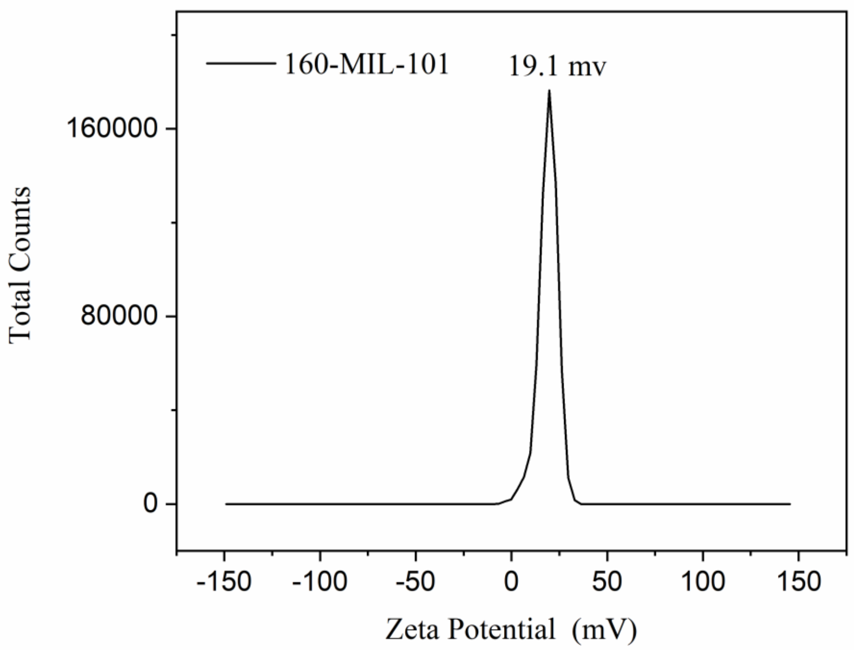

Figure S6. Zeta potential of 160-MIL-101 directly dispersed in water.

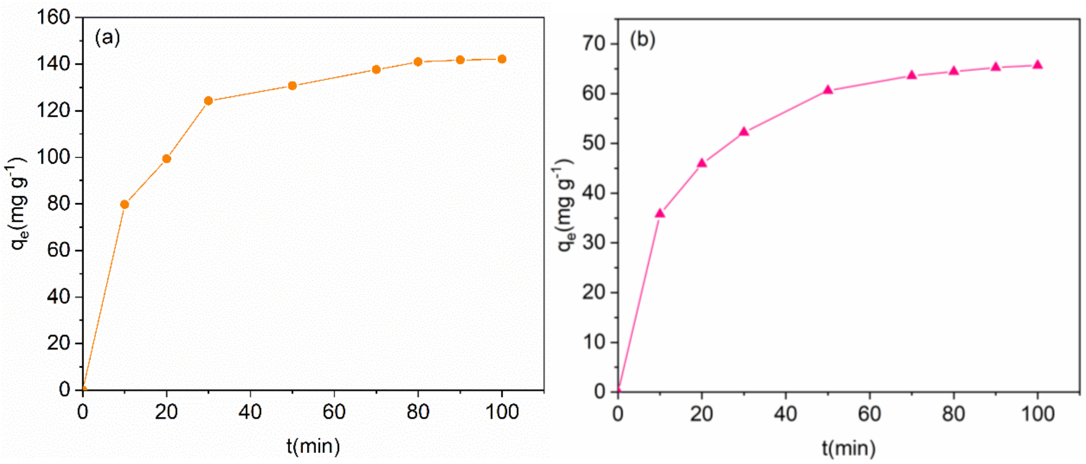

Figure S7. Impact of the time on the adsorption of (**a**) MO and (**b**) RB onto 160-MIL-101.

Table S4. Characteristic parameters of the adsorption of dyes on the 160-MIL-101.

		Parameter	MO	RB
Adsorption kinetics	Pseudo-first-order	$q_{e,Exp}$ (mg g^{-1})	164.7	74.5
		$q_{e,Cal}$ (mg g^{-1})	79.1	38.5
		k_1 (min^{-1})	0.0142	0.01632
		R^2	0.905	0.948
	Pseudo-second-order	$q_{e,Exp}$ (mg g^{-1})	164.7	74.5
		$q_{e,Cal}$ (mg g^{-1})	157.2	73.4
		k_2 (g mg^{-1} min^{-1})	6.5×10^{-4}	1.21×10^{-3}
		R^2	0.999	0.999
Adsorption isotherm	Tempkin	A (L g^{-1})	84.5	0.17
		B	46.7	66.5
		R^2	0.760	0.895
	Freundlich	n	6.7	2.2
		k_F (mg g^{-1} (L mg^{-1})$^{1/n}$)	209.1	21.6
		R^2	0.704	0.7960
	Langmuir	$q_{m,Exp}$ (mg g^{-1})	444.3	230.3
		$q_{m,Cal}$ (mg g^{-1})	446.4	291.6
		k_L (L mg^{-1})	0.431	0.018
		R^2	0.999	0.969

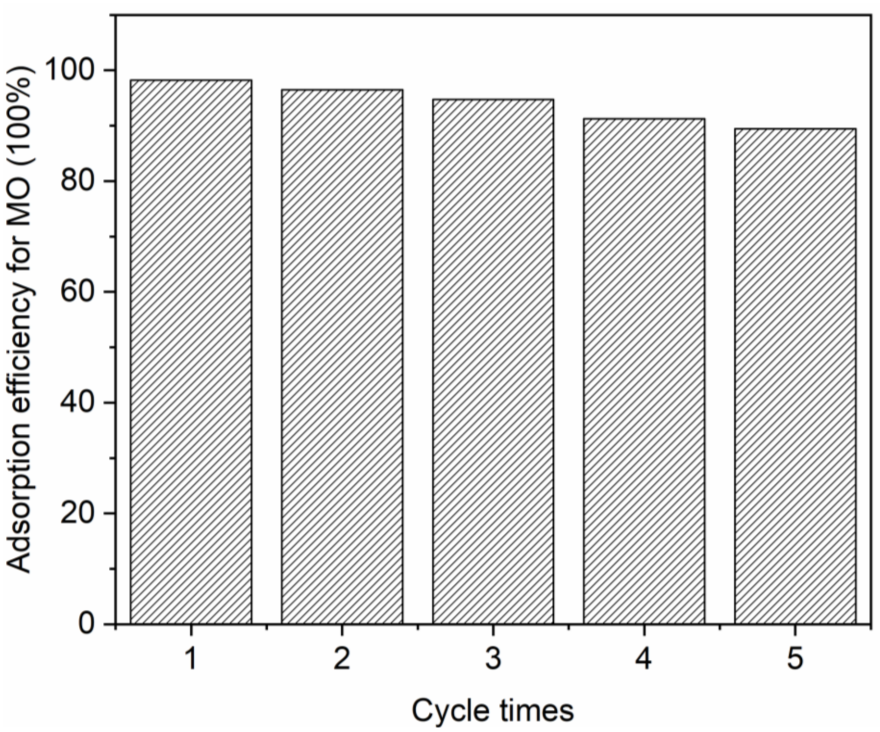

Figure S8. Recycle of the removal efficiency of 160-MIL-101 for MO.