Electronic Supplementary Information (ESI)

Superior adsorptive removal of anionic dyes by MIL-101 analogues: Effect of free carboxylic acid groups in the pore channel

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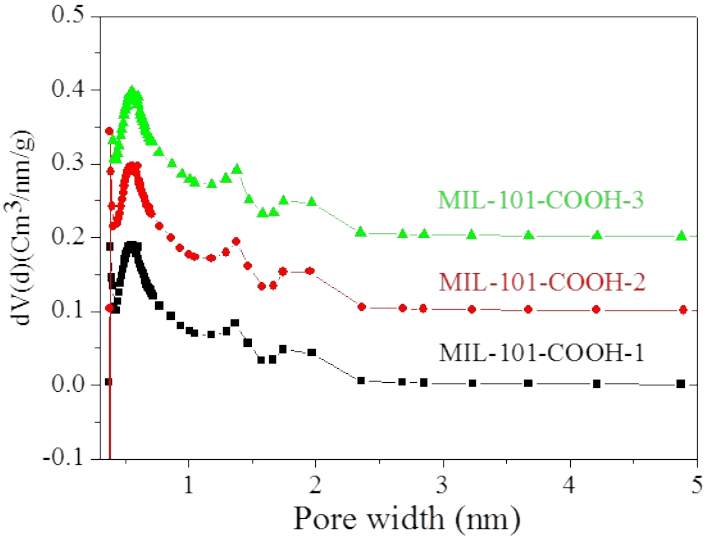

Fig. S1 The pore size distributions of MIL-101-COOH microcrystals.

Table S1 Summary of CR maximum adsorption capacities (q) on various adsorbents.

Type of adsorbent	q (mg g^{-1})	Reference
MIL-101-COOH-1	2835.7	This work
MIL-101(Cr)-2	1367.1	3
MIL-68(In)	1204	17
Ce(III)-doped UiO-66	1033.2	33
Ni-Cu-BTC	999.2	34
Mesoporous alumina fibers	781.3	35
$[Co(L_2)(Htp)(tp)_{0.5}]_n$	629.6	36
Hierarchical hollow NiO	440	37
a-FeOOH	275	38
Activated carbon	200	39

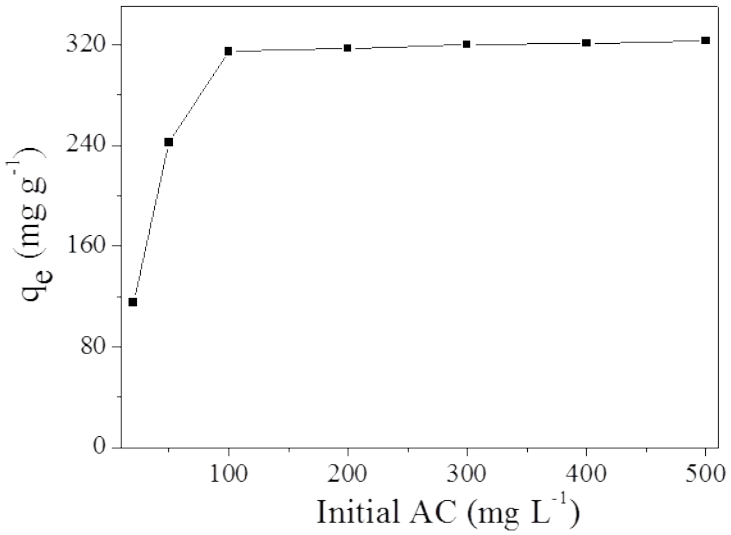

Fig. S2 Adsorption uptake of AC by MIL-101-COOH after 24 h, as determined by dispersing 5 mg of MIL-101-COOH in solutions of the organic dyes (50 mL) at room temperature.

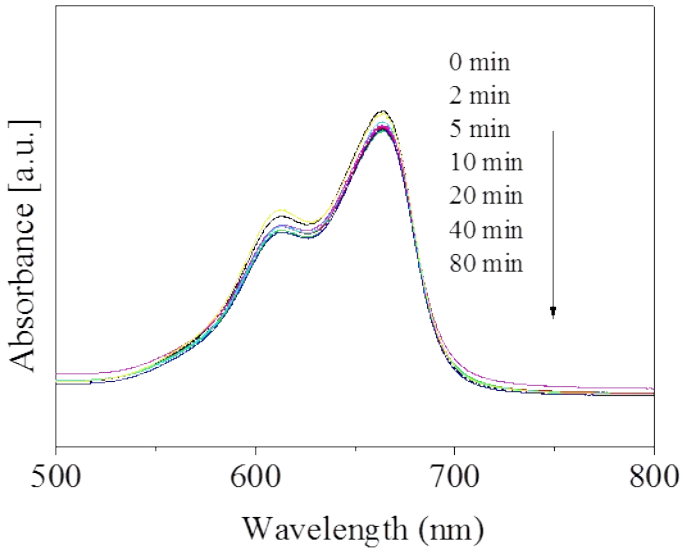

Fig. S3 UV-vis absorption spectra of a solution of MB (20 mg L^{-1}, 50 mL) in the presence of MIL-101-COOH-1 (10 mg) at different time intervals.

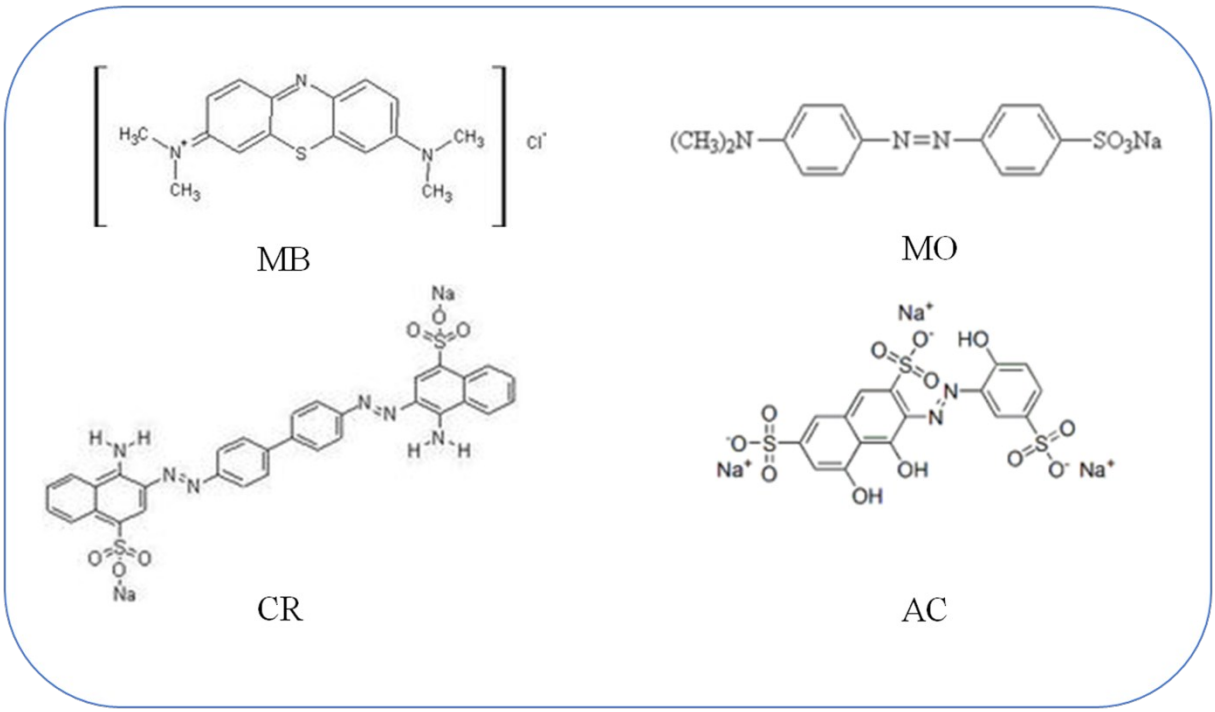

Fig. S4 Molecular structures of the investigated dyes.

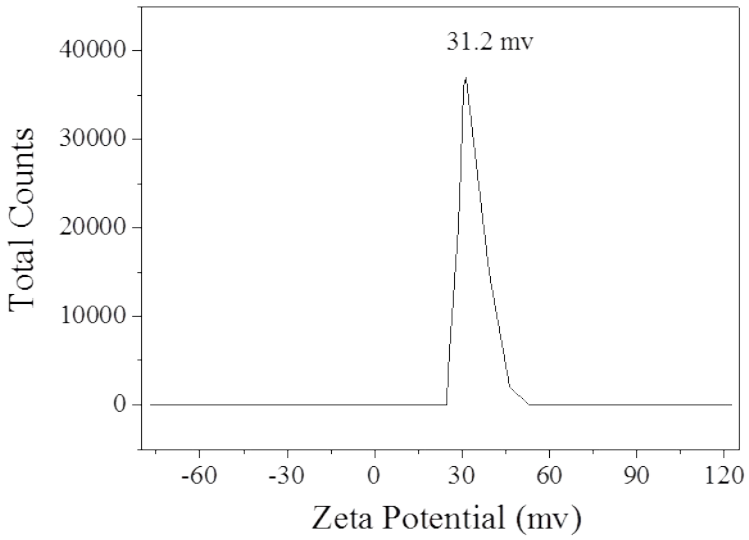

Fig. S5 Zeta potential of MIL-101-COOH-1microparticles directly dispersed in water.

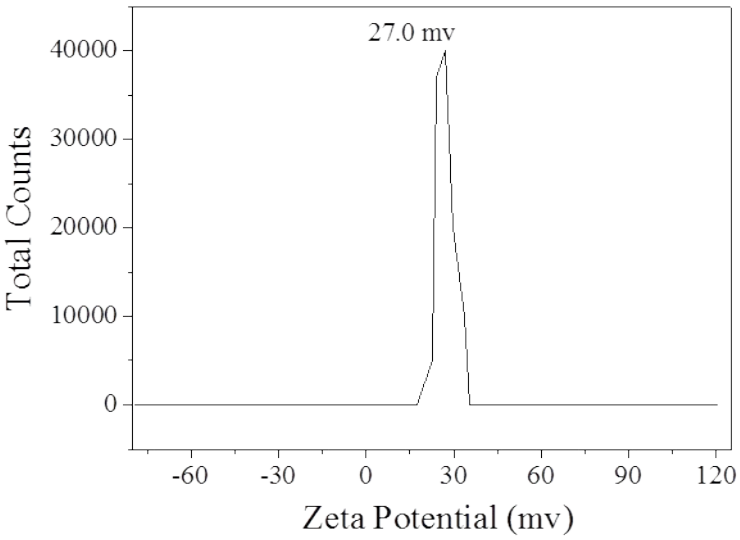

Fig. S6 Zeta potential of MIL-101-COOH-2 microparticles directly dispersed in water.

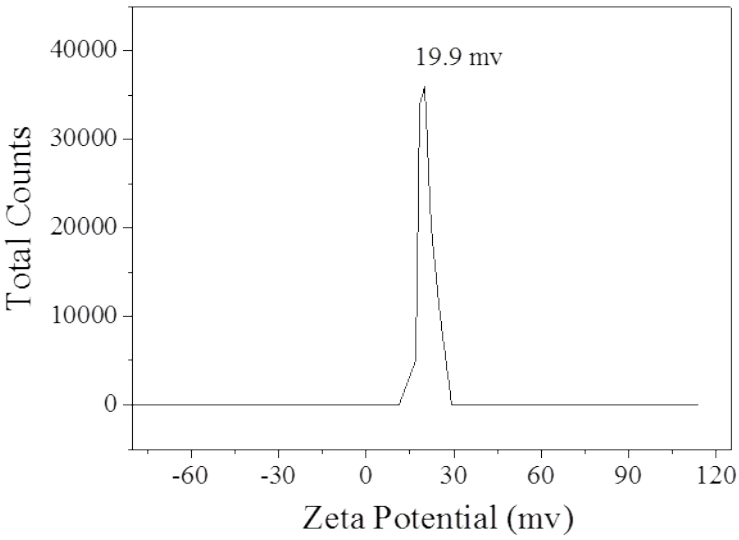

Fig. S7 Zeta potential of MIL-101-COOH-3 microparticles directly dispersed in water.

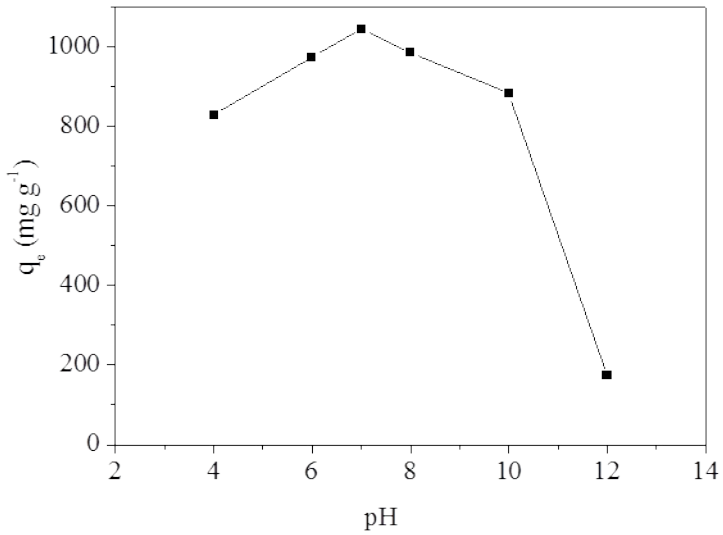

Fig. S8 Effect of pH on CR adsorption on theMIL-101-COOH-1 microcrystals.

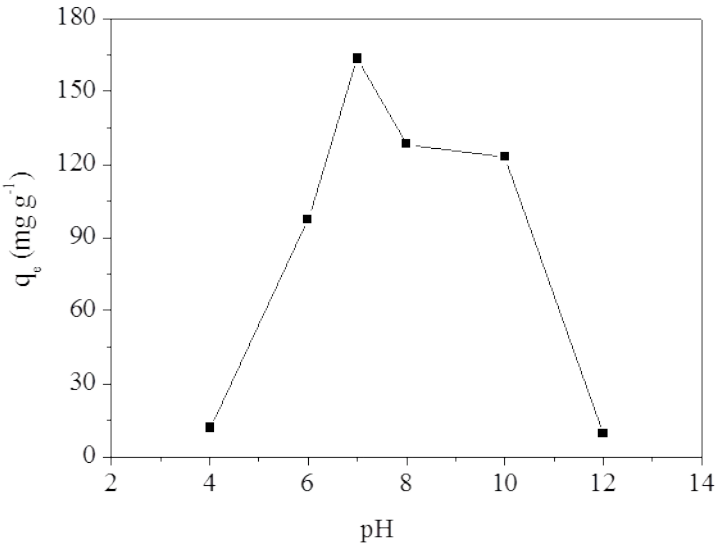

Fig. S9 Effect of pH on MO adsorption on theMIL-101-COOH-1 microcrystals.

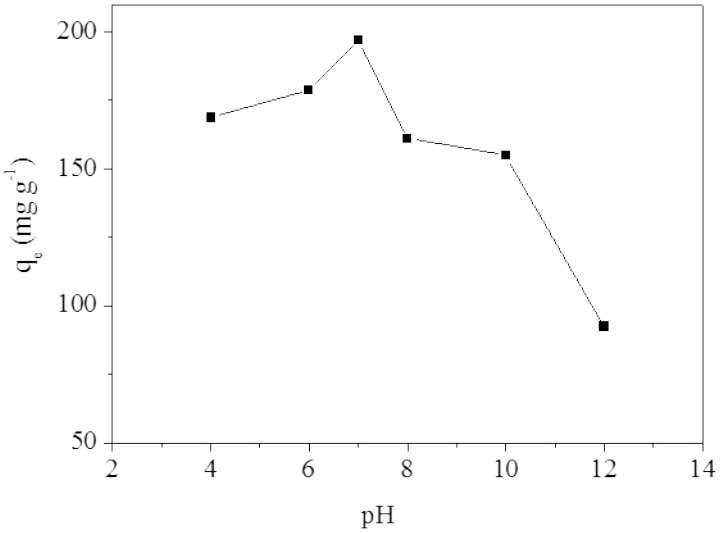

Fig. S10 Effect of pH on AC adsorption on theMIL-101-COOH-1 microcrystals.

Table S2 Characteristic parameters of the adsorption of CR on the MIL-101-COOH.

		parameters	MIL-101-COOH-1	MIL-101-COOH-2	MIL-101-COOH-3
Adsorption kinetics	Pseudo-first-order	$q_{e,Exp}$ (mg g^{-1})	1043.5	1071.9	964.7
		$q_{e,Cal}$ (mg g^{-1})	392.2	469.4	480.6
		k_1 (min^{-1})	0.0069	0.0095	0.0092
		R^2	0.8289	0.9263	0.9531
	Pseudo-second-order	$q_{e,Exp}$ (mg g^{-1})	1043.5	1071.9	964.7
		$q_{e,Cal}$ (mg g^{-1})	826.4	819.7	729.9
		k_2 (g mg^{-1} min^{-1})	2.3×10^{-5}	3.5×10^{-5}	7.7×10^{5}
		R^2	0.9999	0.9995	0.9993
Adsorption isotherm	Tempkin	A (L g^{-1})	16.8	7.0	27.1
		B	634.9	431.4	326.7
		R^2	0.9298	0.8652	0.9402
	Freundlich	n	1.8	2.5	2.7
		k_F (mg g^{-1} (L mg^{-1})$^{1/n}$)	44.8	118.8	64.5
		R^2	0.9072	0.7194	0.8519
	Langmuir	$q_{m,Exp}$ (mg g^{-1})	2835.7	2185.7	1887.5
		$q_{m,Cal}$ (mg g^{-1})	3146.2	2259.7	1989.0
		b (L mg^{-1})	0.0513	0.1309	0.0613
		R^2	0.9941	0.9994	0.9998
Thermodynamic constant		ΔG (kJ mol^{-1})	-7.4	-5.0	-6.9

Table S3 Characteristic parameters of the adsorption of MO on the MIL-101-COOH.

		parameters	MIL-101-COOH-1	MIL-101-COOH-2	MIL-101-COOH-3
Adsorption kinetics	Pseudo-first-order	$q_{e,Exp}$ (mg g^{-1})	304.6	263.1	232.0
		$q_{e,Cal}$ (mg g^{-1})	61.9	64.4	68.9
		k_1 (min^{-1})	0.0124	0.0338	0.0571
		R^2	0.8171	0.9306	0.9715
	Pseudo-second-order	$q_{e,Exp}$ (mg g^{-1})	304.6	263.1	232.0
		$q_{e,Cal}$ (mg g^{-1})	278.6	268.1	237.5
		k_2 (g mg^{-1} min^{-1})	4.6×10^{-3}	2.5×10^{-3}	2.3×10^{-3}
		R^2	0.9999	0.9999	0.9998
Adsorption isotherm	Tempkin	A (L g^{-1})	6.0	8.7	57.8
		B	62.8	48.6	31.4
		R^2	0.9963	0.9933	0.9888
	Freundlich	n	4.8	5.8	7.6
		k_F (mg g^{-1} (L mg^{-1})$^{1/n}$)	148.7	143.5	145.8
		R^2	0.9759	0.9843	0.9888
	Langmuir	$q_{m,Exp}$ (mg g^{-1})	473.9	405.6	319.3
		$q_{m,Cal}$ (mg g^{-1})	487.8	409.8	319.5
		b (L mg^{-1})	0.0836	0.0568	0.0928
		R^2	0.9996	0.9981	0.9989
Thermodynamic constant		ΔG (kJ mol^{-1})	-6.1	-7.1	-5.9

Table S4 Characteristic parameters of the adsorption of AC on the MIL-101-COOH.

		parameters	MIL-101-COOH-1	MIL-101-COOH-2	MIL-101-COOH-3
Adsorption kinetics	Pseudo-first-order	$q_{e,Exp}$ (mg g^{-1})	196.6	183.9	176.0
		$q_{e,Cal}$ (mg g^{-1})	121.1	120.2	114.9
		k_1 (min^{-1})	0.0026	0.0039	0.0040
		R^2	0.8281	0.8528	0.9224
	Pseudo-second-order	$q_{e,Exp}$ (mg g^{-1})	196.6	183.9	176.0
		$q_{e,Cal}$ (mg g^{-1})	142.6	138.5	136.1
		k_2 (g mg^{-1} min^{-1})	7.9×10^{-3}	4.5×10^{-3}	3.7×10^{-3}
		R^2	0.9999	0.9979	0.9988
Adsorption isotherm	Tempkin	A (L g^{-1})	1.25×10^{7}	3.95×10^{13}	2.3×10^{14}
		B	8.7	5.7	5.1
		R^2	0.9144	0.8908	0.9451
	Freundlich	n	24.9	35.3	36.8
		k_F (mg g^{-1} (L mg^{-1})$^{1/n}$)	185.2	178.2	171.9
		R^2	0.9227	0.9022	0.9510
	Langmuir	$q_{m,Exp}$ (mg g^{-1})	240.8	220.2	208.2
		$q_{m,Cal}$ (mg g^{-1})	243.9	219.7	207.0
		b (L mg^{-1})	0.1387	0.1246	0.1792
		R^2	0.9996	0.9991	0.9994
Thermodynamic constant		ΔG (kJ mol^{-1})	-4.9	-5.1	-4.2

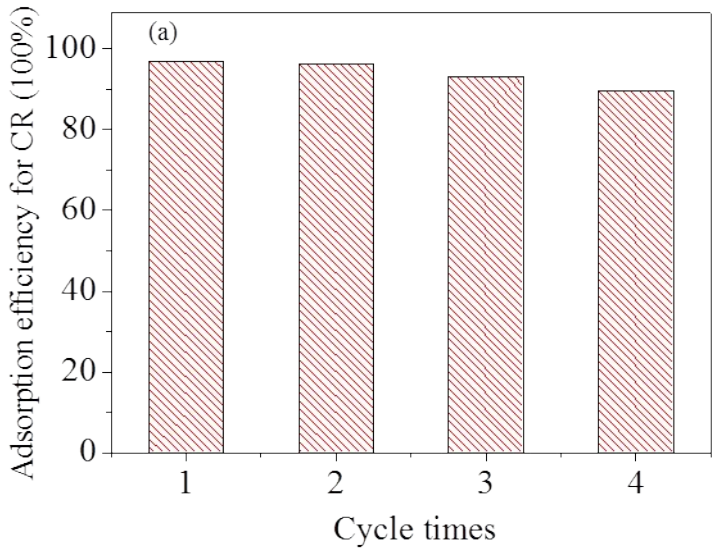

Fig. S8 Recycle of the removal efficiency of MIL-101-COOH-1 for CR.