Supplementary Information

Can metal organic frameworks outperform adsorptive removal of harmful phenolic compound 2-chlorophenol by activated carbon?

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1. Standard calibration plot

At least five 2-CP solutions (5 – 50 ppm) were analysed to plot the calibration curve. The linear equation derived from Fig. S1 can be used to calculate initial and final concentrations of 2-CP in the solution. The relationship Beer-Lambert's Law is only valid at dilute concentration (A < 1) which states that:

$$A = \epsilon l c$$

Where A is absorbance, ϵ is the molar absorptivity ($L.(mol.cm)^{-1}$), l is the path length of the cuvette (cm) and c is the concentration of the compound in the solution ($mol.L^{-1}$).

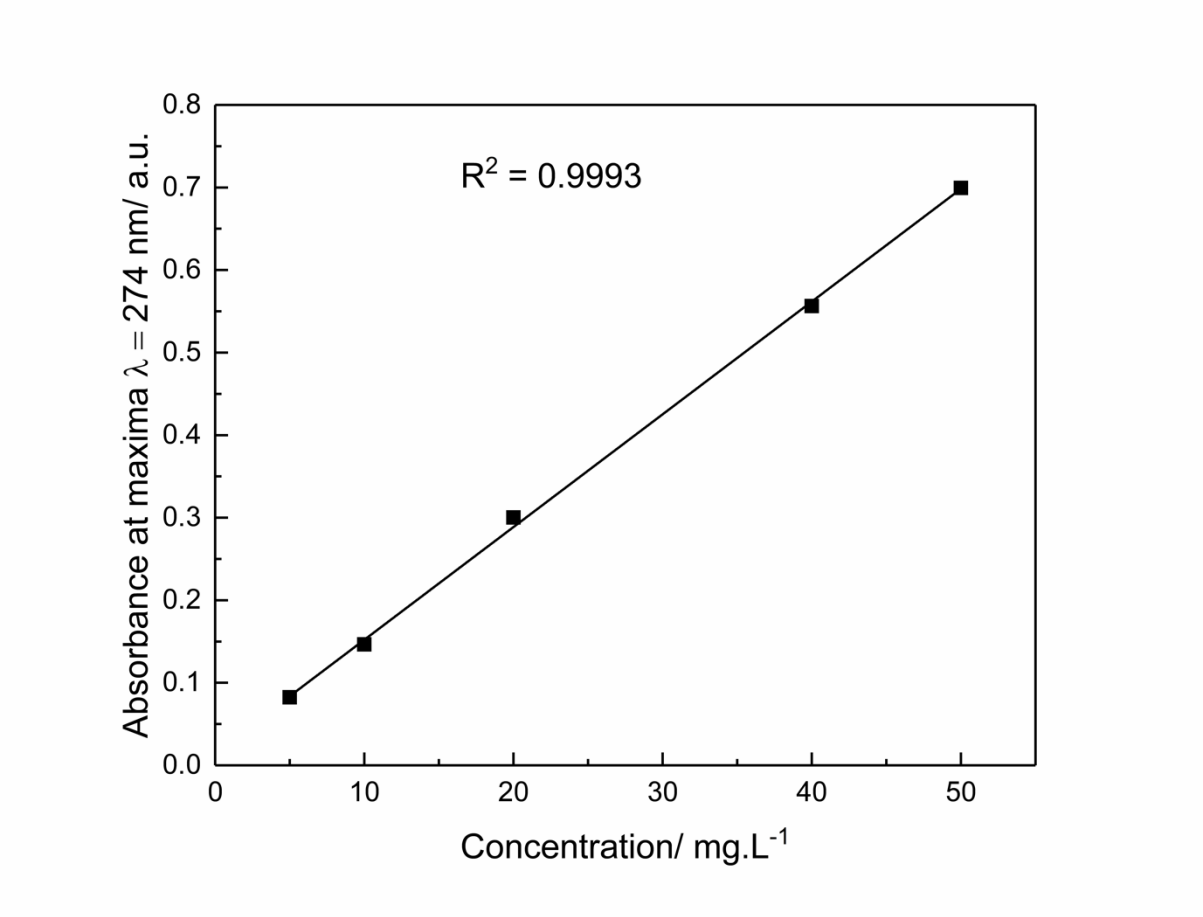

Fig. S1: Standard calibration plot for 2-CP where molar absorptivity (ε) equals to 0.0137 L.(mol.cm)$^{-1}$

1. XRD

Fig. S2 proves that acetic acid can is a good modulating agent to make MIL-101 with similar crystallinity. Fig. S3 shows additional XRD analysis for MIL-101 after immersion in pH = 1 and pH = 11 solutions. All peaks remain intact at the same position with the simulated MIL-101.

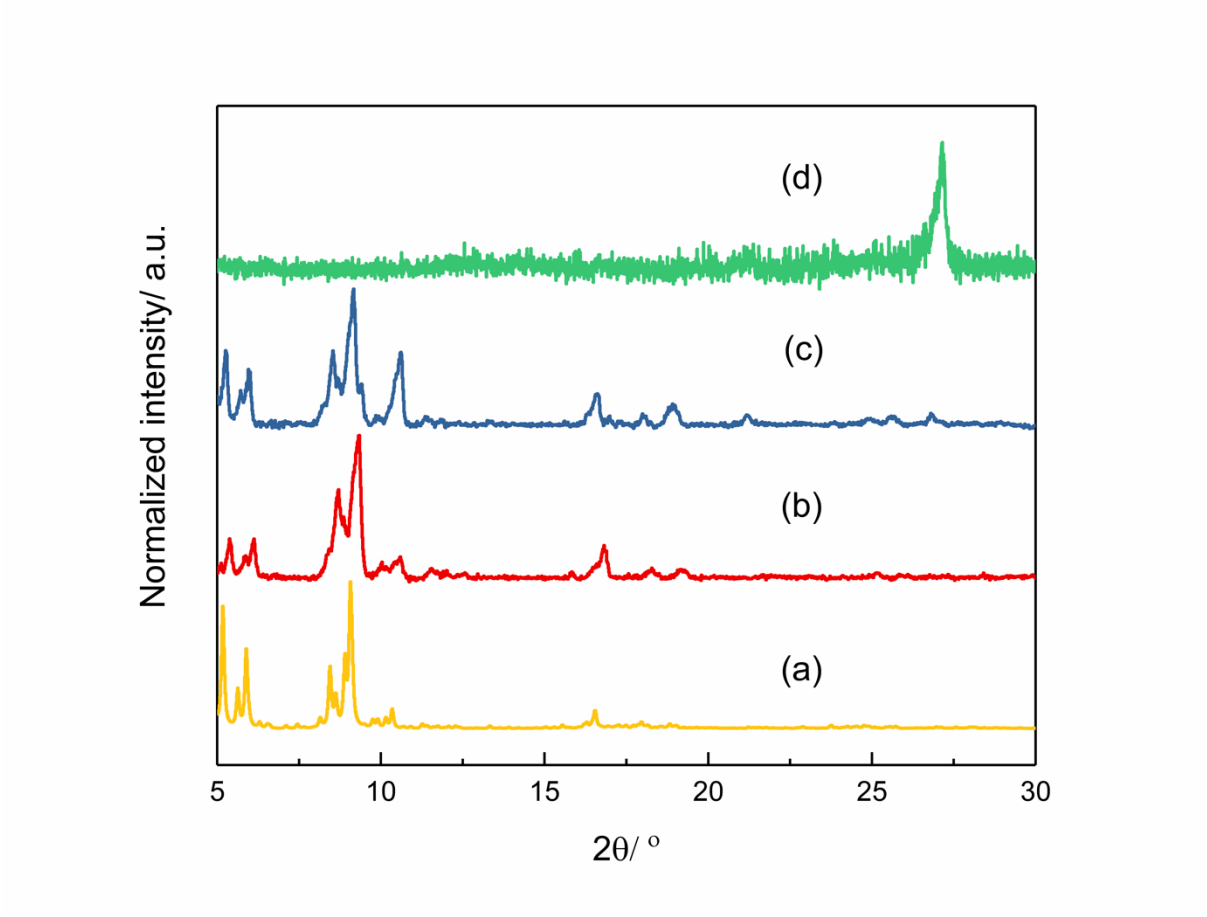

Fig. S2: PXRD spectra analysis of (a) simulated MIL-101, (b) prepared MIL-101, (c) prepared MIL-101-NH2 and (d) AC

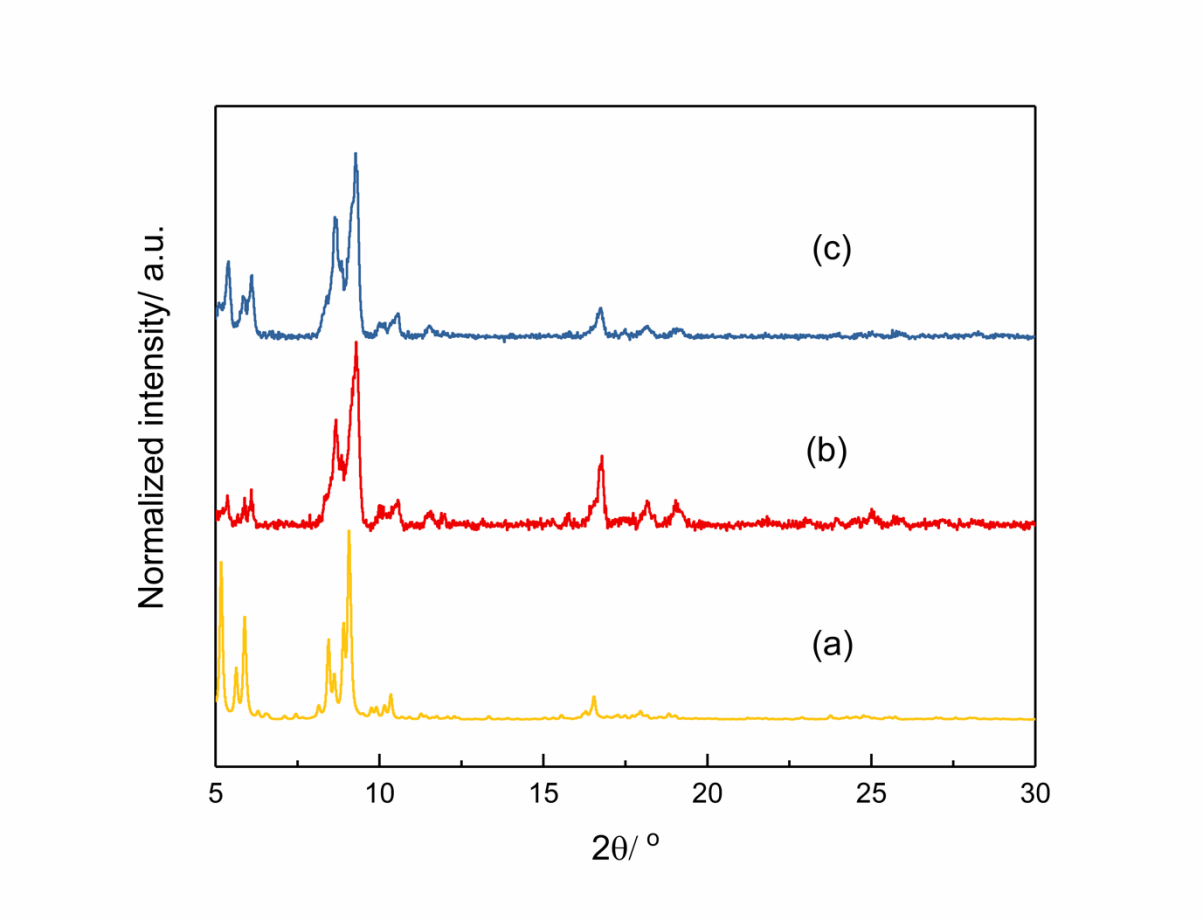

Fig. S3: PXRD spectra between (a) simulated MIL-101 and after immersion in (b) pH = 1 and (c) pH = 11 solutions

2. BET

Fig. S4 shows a summary of the BET surface areas of all adsorbents and Fig. S5 is the plot of N_2 adsorption and desorption isotherms for all studied adsorbents.

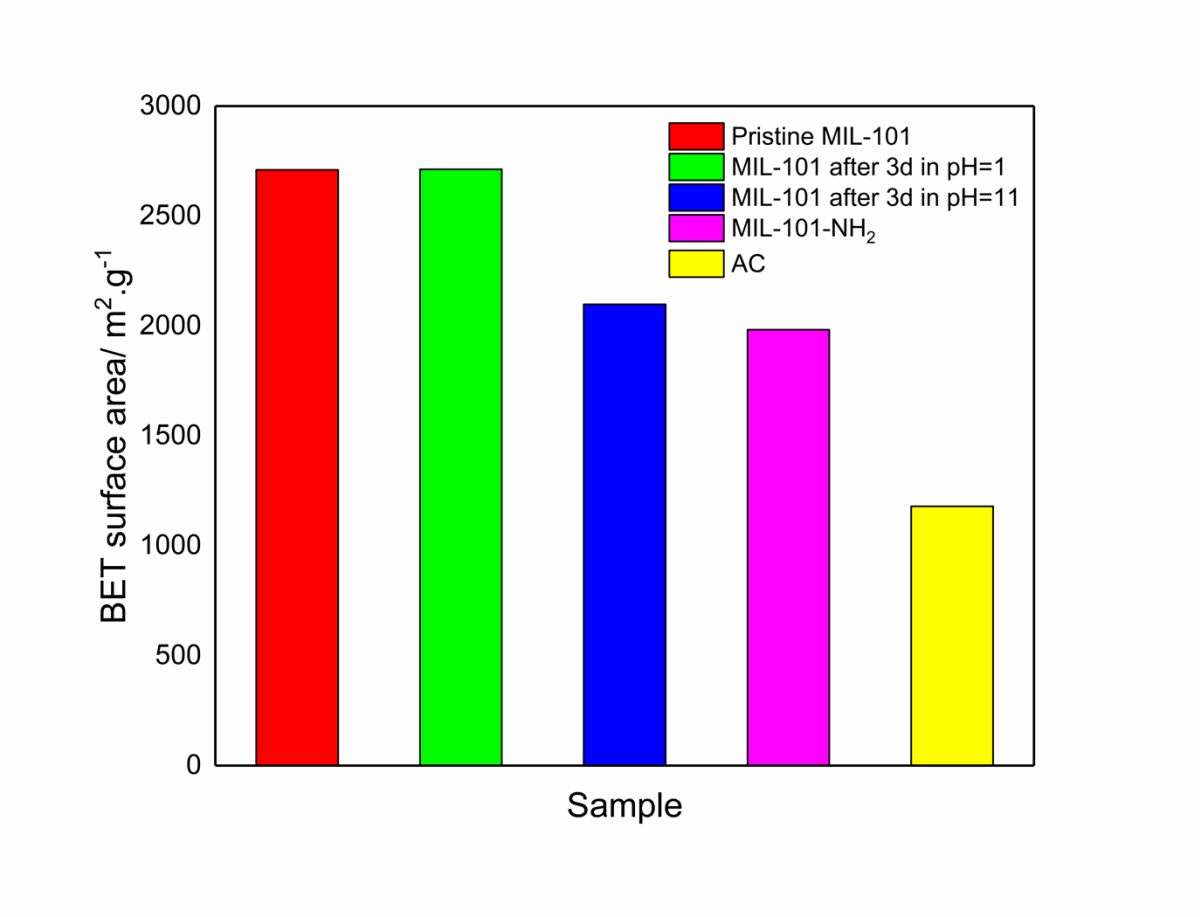

Fig. S4: Calculated BET surface area of studied adsorbents

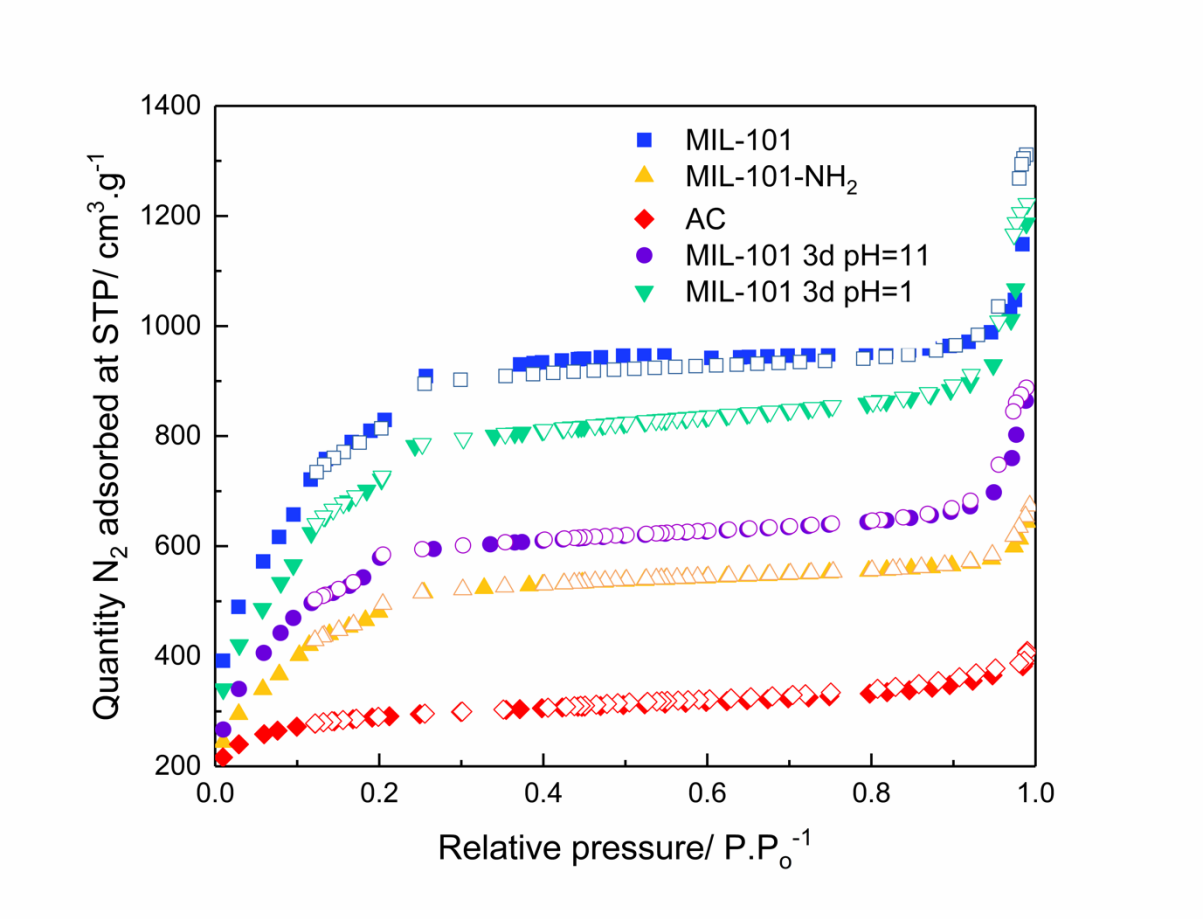

Fig. S5: N_2 adsorption and desorption isotherms of all tested adsorbents where full shape denotes adsorption and empty shape for desorption

3. FTIR

Fig. S6 compares the spectra of the MIL-101 before and after using it to remove 2-CP.

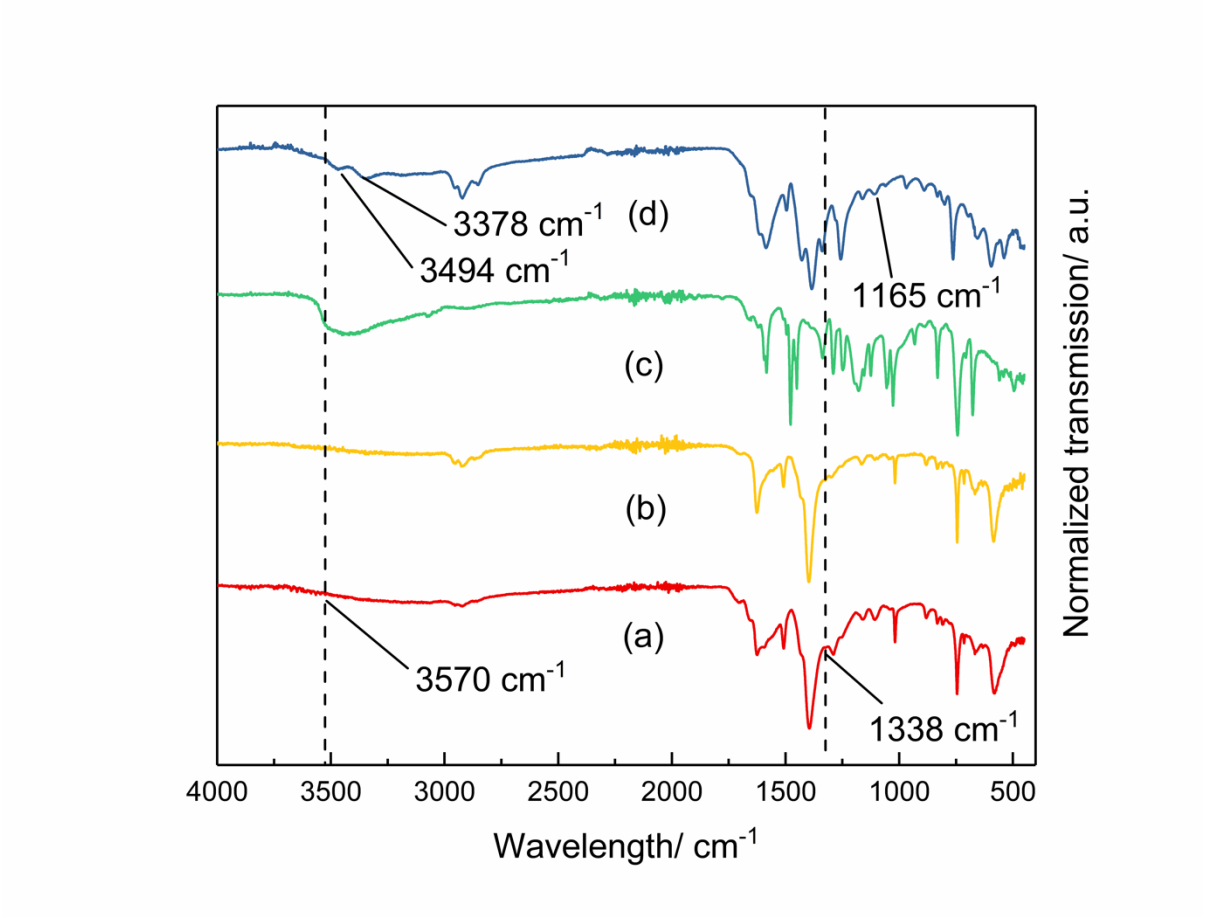

Fig. S6: Comparison between (a) fresh MIL-101, (b) 2-CP loaded MIL-101, (c) 2-CP and (d) MIL-101-NH_2

4. TGA

From Table S1, AC experienced the least weight loss across the tested temperature range (20 °C to 1000 °C) indicating its high hydrophobicity.

Table S1: Detailed description of the TGA profile

Temperature gradient, ΔT	**Range (°C)**	**Sample weight loss (%)**		
		MIL-101	**MIL-101-NH_2**	**AC**
ΔT1	20-150	13	33	2
ΔT2	150-370	10	6	0.4
ΔT3	370-1000	53	42	9

5. Langmuir isotherm

Maximum Langmuir adsorption capacity (q_m) can only be calculated for MIL-101 and AC because linear fitting for MIL-101-NH_2 gave a negative slope as seen in Fig. S7.

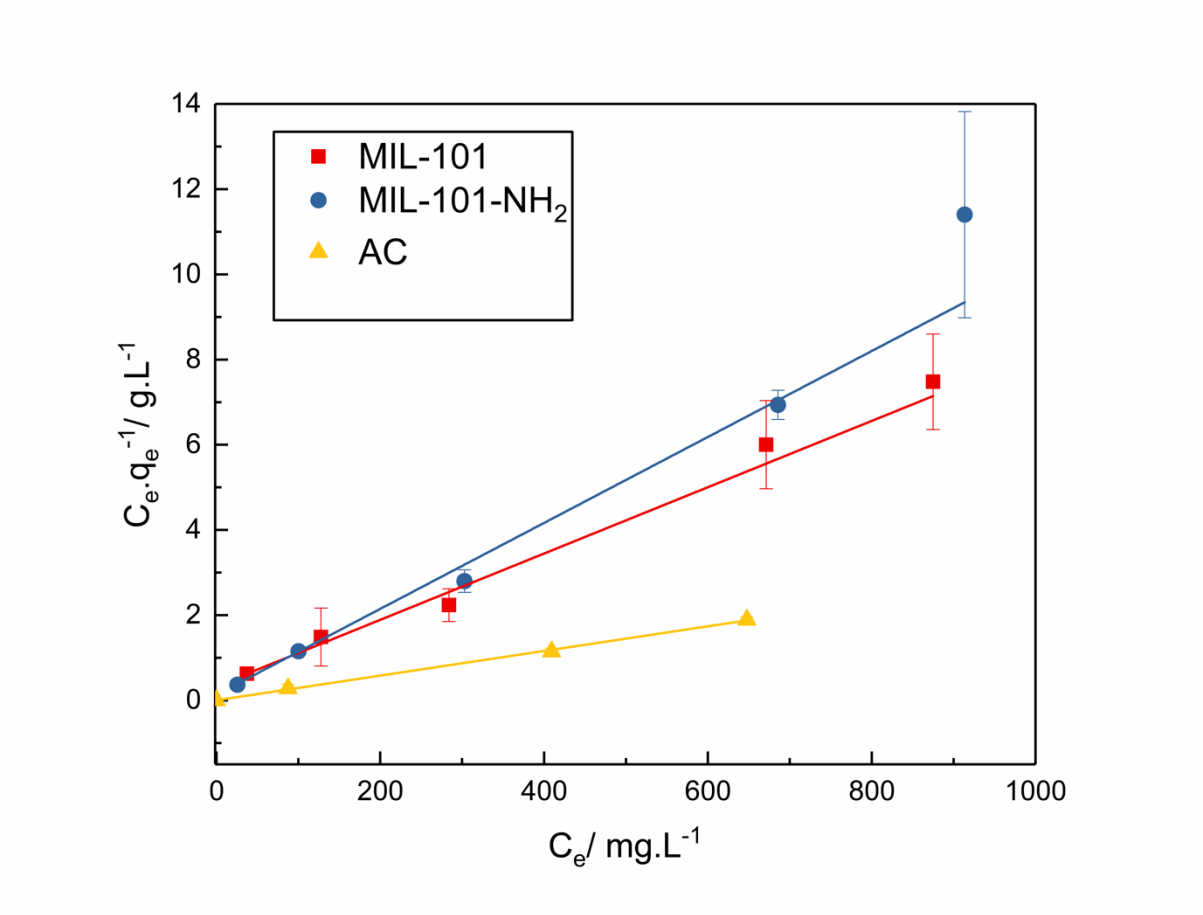

Fig. S7: Plot of Langmuir isotherm for all adsorbents

Respective linear equations for each adsorbent can be referred to Table S2.

Table S2: Details about the Langmuir isotherm plots

Sample	**Linear fit relation**	**R^2**
MIL-101	y = 0.0083x + 0.253	0.994
MIL-101-NH_2	y = 0.0119x – 0.293	0.976
AC	y = 0.0029x + 0.0039	0.999

Calculated R_L values for all adsorbents are shown in Table S3. Concentration of 2-CP, C_e ($mg.L^{-1}$) is derived from equilibrium data for batch adsorption study.

Table S3: Dimensionless separation factor values (R_L) calculated for each adsorbent

MIL-101		**MIL-101-NH_2**		**AC**	
Ce ($mg.L^{-1}$)	**R_L**	**Ce ($mg.L^{-1}$)**	**R_L**	**Ce ($mg.L^{-1}$)**	**R_L**
37	0.24	26	-0.34	0	0.014

128	0.14	100	-0.15	0	0.0070
284	0.068	303	-0.06	88	0.0032
671	0.037	686	-0.032	409	0.0017
875	0.030	914	-0.025	648	0.0014

6. Particle size analysis

Particle size analysis for all adsorbents are shown below in Table S4.

Table S4: Particle size distribution analysis obtained by dispersing the adsorbents in ultrapure water

Sample	**Effective diameter (nm)**	**Polydispersity**
AC	680 ± 62	0.348
MIL-101	184 ± 29	0.272
MIL-101-NH_2	435 ± 32	0.272

7. Pseudo second order kinetic model

Fig. S8 and Fig. S9 are resultant plots of AC and MIL-101 respectively using pseudo second order kinetic model.

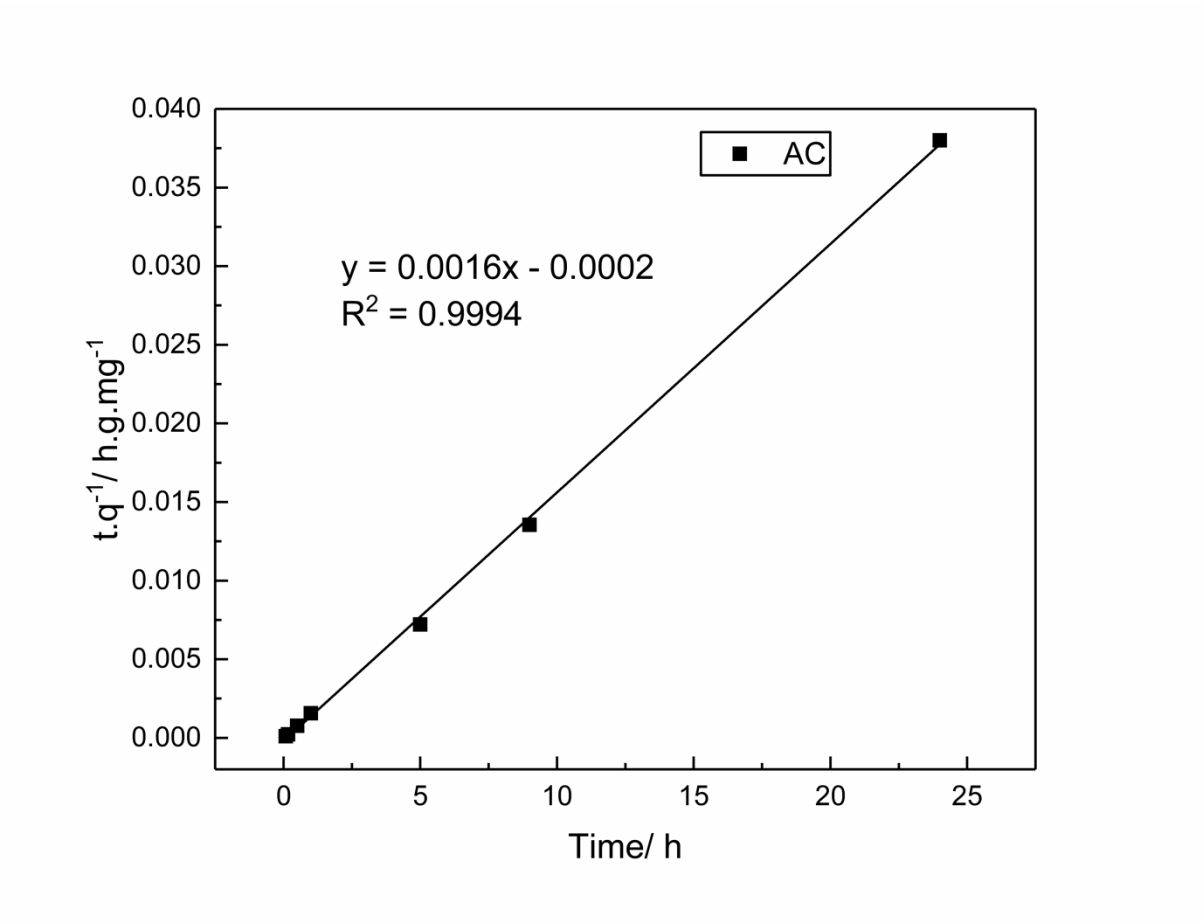

Fig. S8: Pseudo second order kinetic model fitting for AC

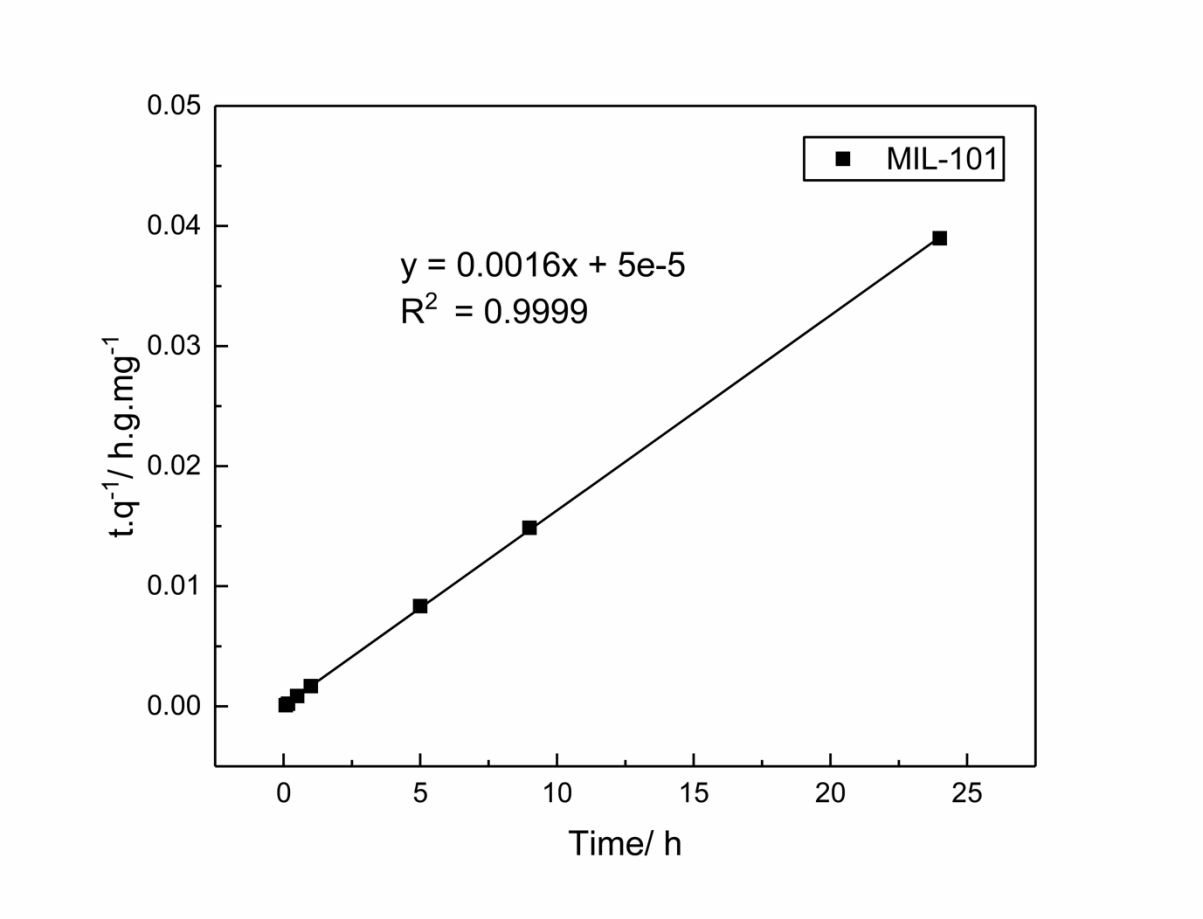

Fig. S9: Pseudo second order kinetic model fitting for MIL-101

8. Regeneration

Fig. S10 shows the change in adsorption capacity of MIL-101 and AC after washing with ethanol repeatedly for a maximum of 3 times.

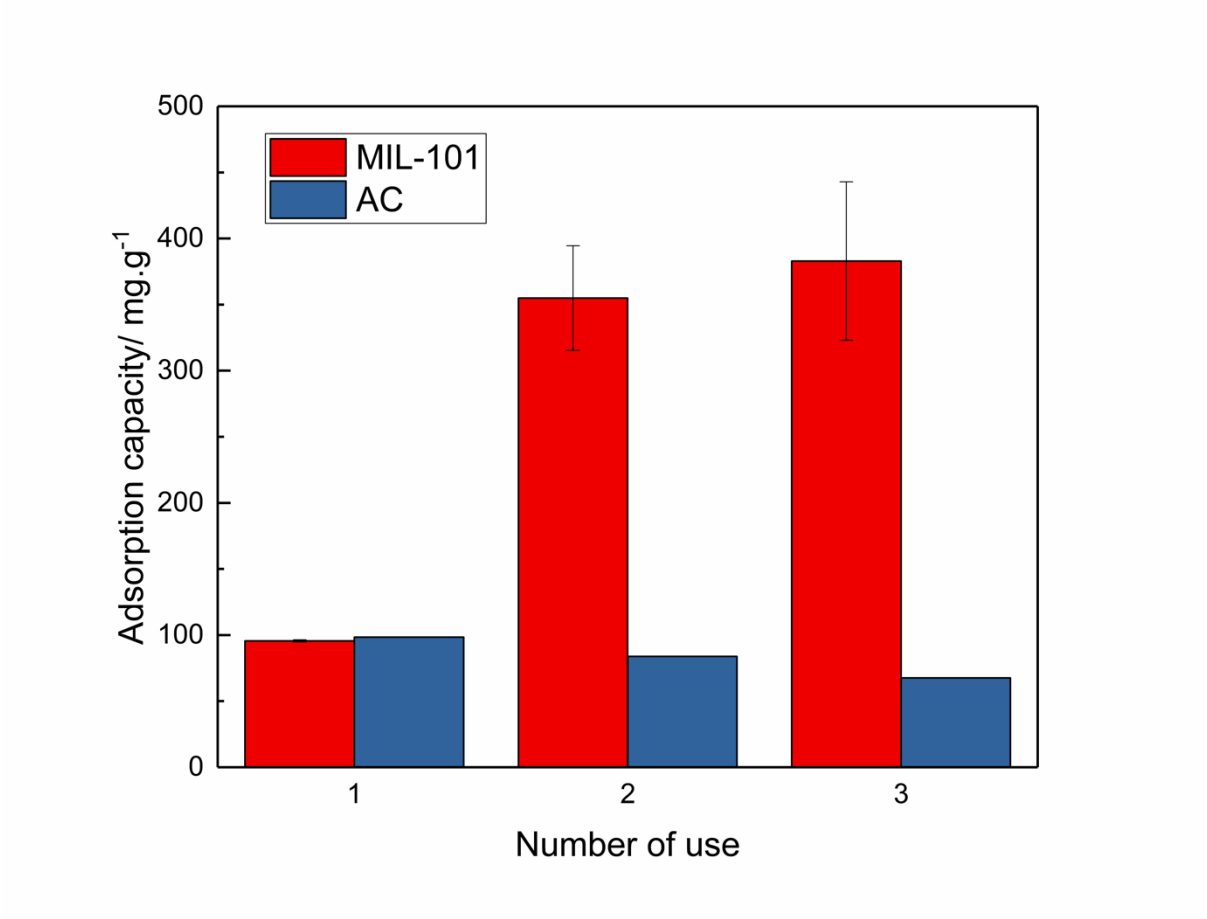

Fig. S10: Amount of 2-CP adsorbed by MIL-101 and AC after repeated washing up to 3 cycles

9. SEM

The SEM images of MIL-101 and MIL-101-NH_2 in Fig. S11 show good distribution of octahedral-shaped crystals, which is the typical morphology of MIL-101 (Zhao et al., 2017).

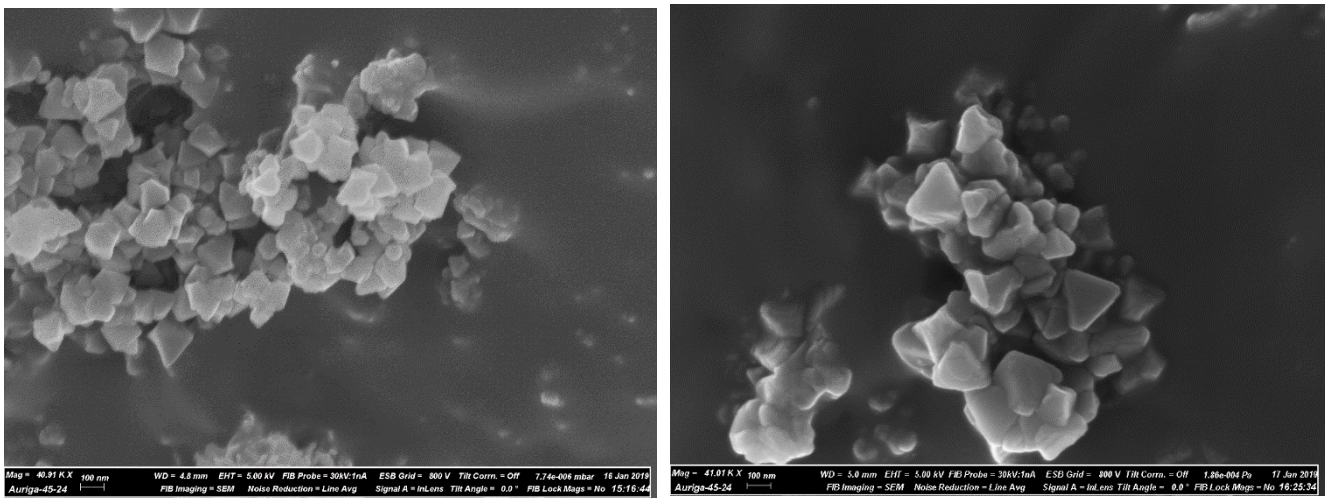

Fig. S11: SEM images for MIL-101 (left) and MIL-101-NH_2 nanocrystals (right)

10. Elemental analysis (CHNS)

Elemental analysis results for MIL-101, MIL-101-NH_2 and AC can be seen in Table S5:

Table S5: Elemental analysis of sorbents used in this study

Sample	N wt%	C wt%	H wt%	S wt%
AC	1.2 ± 0.03	88.3 ± 0.5	0.6 ± 0.04	1.0 ± 0.07
MIL-101	2.8 ± 0.2	42.6 ±1.8	4.4 ± 0.3	0
MIL-101-NH_2	5.1 ± 0.07	38.6 ± 0.8	4.6 ± 0.05	0

11. Contact angle measurements

MIL-101 proves to be very hydrophilic as seen from Figure S12. It took about 16 seconds for the water droplet to finally seep into the pores of the MOF and became flat.

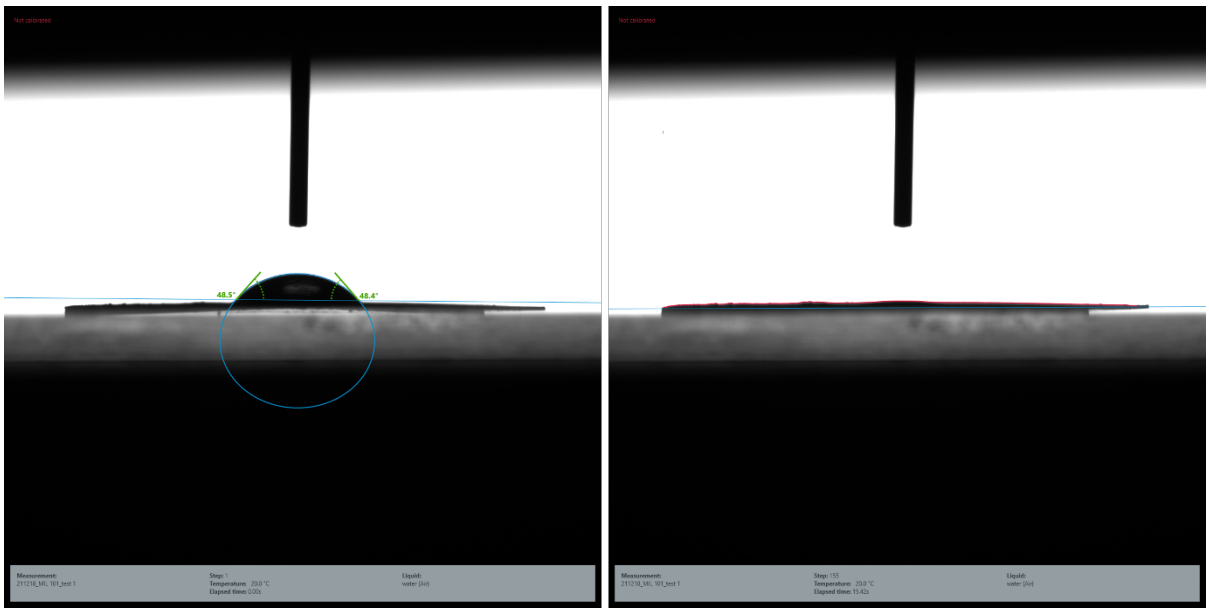

Figure S12: Water contact angle measurement on MIL-101 pellet at the start (left) and when fully wetted (right) after approximately 15 seconds

Reference

Zhao, T., Yang, L., Feng, P., Gruber, I., Janiak, C., Liu, Y., 2017. Facile synthesis of nano-sized MIL-101 (Cr) with the addition of acetic acid. Inorganica Chimica Acta 471, 440–445.