Supporting Information

Metal-Organic framework@silica as stationary phase sorbent for rapid and cost-effective removal of hexavalent chromium

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Experimental details

All reagents were used as received without further purification. Solvents and common chemicals were purchased from Sigma-Aldrich or Fisher Scientific-UK. Nitrogen gas for sorption were purchased from Airliquide (N_2 AlphaGaz2 99.9999%), $ZrCl_4$ anhydrous (Acros, 98%), $K_2Cr_2O_7$ (Sigma Aldrich, 99.5%), 2-aminoterephthalic acid (ACROS Organics, 99%) HCl (Honeywell, 37%), DMF (Fischer, analytical reagent grade 99.99%), Silica gel (high-purity grade, pore size 60 Å, 70-230 mesh, particle size 63-200μm, sigma-aldrich).

Gas sorption analysis was performed on Micromeretics ASAP2020. The apparent surface areas were determined from the nitrogen adsorption isotherms collected at 77 K by applying the Brunauer-Emmett-Teller (BET) and Langmuir models. Pore size analyses were performed using the NLDFT of carbon slit pores for the MOF and MOF@silica while using the DFT model of cylindrical pores on oxide surface for the Silica. Infra-red absorption spectra were recorded on ThermoScientific Nicolet is-10. Thermogravimetric analyses were conducted on Thermal Analysis-Q50 under nitrogen atmosphere. TEM images were acquired on JEOL JEM-2100 and SEM images were taken with NOVA NANOSEM 450, equipped with EDAX Octane Silicon Drift Detector (SDD) EDX detector and operated at 30 KV. X-ray powder diffractions were taken on D8 Bruker x-ray powder diffractometer. ICP-OES was conducted on Agilent Technologies 5100 ICP-OES.

XPS measurements: X-ray photoelectron spectroscopy measurements were performed using a Kratos AXIS Ultra DLD XPS system with a monochromatic Al Ka source operated at 15 keV and 150W and a hemispherical energy analyzer. The X-rays were incident at an angle of 45° with respect to the surface normal. Samples were placed in small powder pockets on the holder and analysis was performed at a pressure below 1x10-9 mbar. High resolution core level spectra were measured with a pass energy of 40eV. The XPS experiments were performed by using an electron beam, directed on the sample, for charge neutralization.

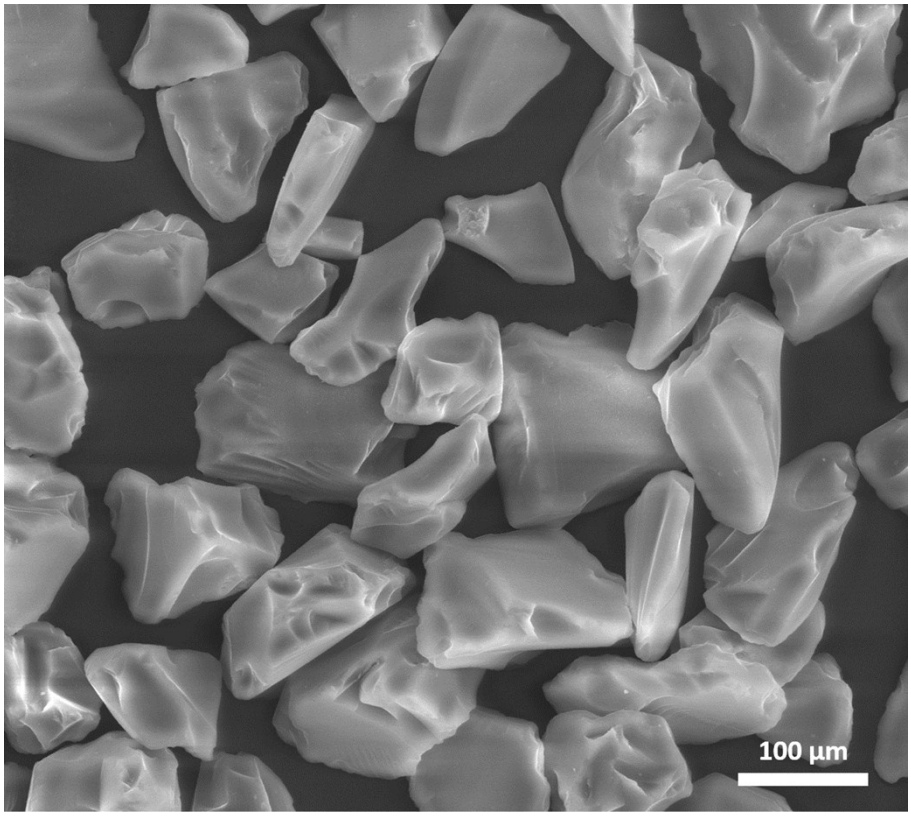

Figure S1. The SEM image for the bare Silica particles used in this study.

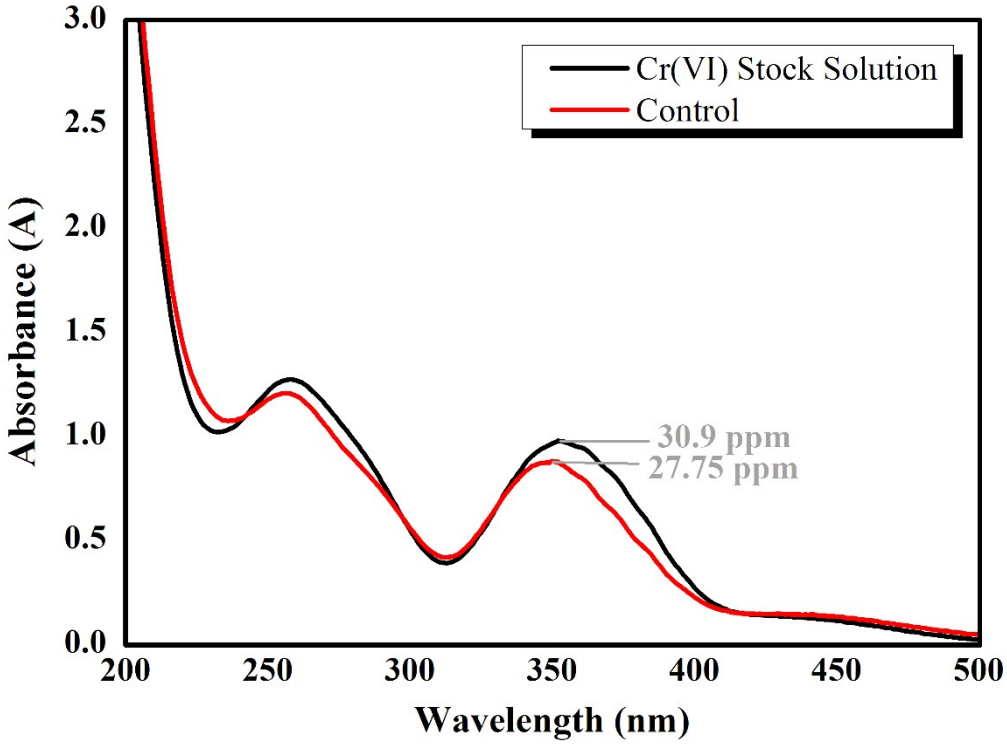

Figure S2. Cr(VI) absorption Capacity of the control (Silica + Sand + Cotton).

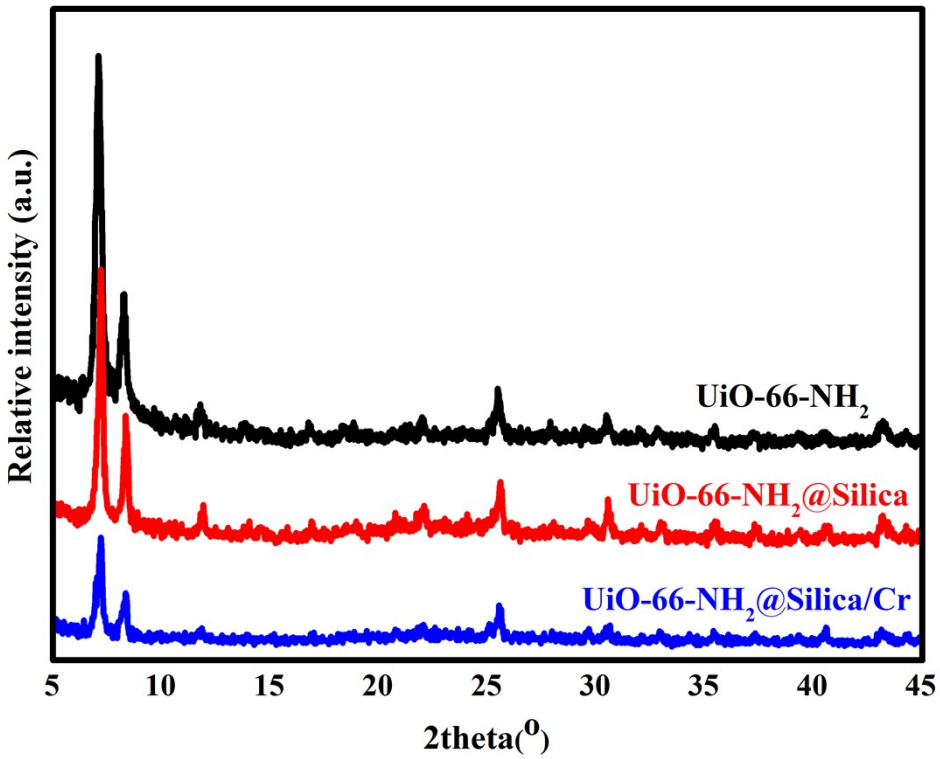

Figure S3. PXRD patterns for the UiO-66-NH_2, UiO-66-NH_2@Silica, and after loading with Cr(VI) UiO-66-NH_2@Silica/Cr.

Column Capacity Calculations

1. A ~1000 ppm Cr^{+6} solution was prepared by dissolving 2.829 g of $K_2Cr_2O_7$ in 1L deionized water. The absorbance of 3.11 was recorded on a 10x diluted sample, allowing calculating the actual concentration of the stock to be 982 ppm.

2. To investigate the column capacity, 10 ml of the 982 ppm Cr^{+6} was passed through the column (containing 72 mg of the UiO-66-NH_2@Silica and 5 g of sand), the recorded absorbance of the eluent was 1.52 (after 10x dilution), equivalent to 47.99 ppm Cr(VI) using a separately established calibration curve. This value corresponds to a Cr(VI) concentration of 479.9 ppm in the eluent after single column passage. Accordingly, the column uptake of 502.1 ppm was calculated, corresponding to uptake of a 5.02 mg Cr(VI) from the 10 ml portion by the 72 mg of the composite.

3. To calculate the column capacity, the mass of UiO-66-NH_2@silica used for this study was 72 mg, which corresponds to 37.44 mg of the MOF (the UiO-66-NH_2@silica contains 48% silica), and an uptake of 5.02 mg of Cr(VI), ~0.1 mmol of Cr(VI), equivalent to 10.43 mg, 0.048 mmol of the dichromate ion. The column capacity accordingly was ((5.02/37.44)*100 = 13.4 wt% of Cr (VI) or 27.8 wt% for dichromate ions. The column capacity can alternatively be expressed in terms of mol% considering the unit formula of the UiO-66-NH_2 ($(Zr_6(O)_4(OH)_4(BDC\text{-}NH_2)_6$, f_{wt} = 1754.15 g/mol) where the 37.44 mg of the MOF corresponds to $2.13x10^{-5}$ mol, and the corresponding column capacity for Cr(VI) and dichromate to be 4.6 mol Cr^{6+}/mol MOF and 2.25 mol $Cr_2O_7^{2-}$/mol MOF respectively. Additionally, the active MOF phase within the column material can effectively uptake Cr(VI) up to 133 mg/g, or dichromate up to 277 mg/g, surpassing any of previously reported active phase solids for Cr(VI) uptake.

Column Capacity Calculations (continued)

	Ref.50	Ref.50	Ref.51	Ref.58	Ref.59	This work
Sorbent	**FIR-53**	**FIR-54**	**1-ClO_4**	**SLUG-21**	**MOR-1**	**UiO-66-NH_2**
Sorbent Weight	60mg		78mg	25mg		37.44mg
Sorbent Mol. Wt.	1200 g/mol	**N/A**	1560 g/mol	788.64 g/mol.		1754.15 g/mol
Sorbent No. of Moles	**$5x10^{-5}$ mol.**		**$5x10^{-5}$ mol.**	**$3.17x10^{-5}$ mol.**		**$2.13x10^{-5}$ mol.**
Adsorbate	**$K_2Cr_2O_7$**		**K_2CrO_4**			**$K_2Cr_2O_7$**
Adsorbate Volume	4ml	5ml	10ml	50ml		10ml
Adsorbate No. of Moles	$6x10^{-3}$ mol./L		$5x10^{-5}$mol	$3.17x10^{-5}$mol		$9.6x10^{-5}$mol
Adsorbate Weight	7.06mg	8.83mg	9.71mg	6.16mg		28.29mg
Amount Sorbed	90%	**N/A**	85%	41%		50.19%
Amount sorbed Weight	6.35mg **$K_2Cr_2O_7$**		8.25mg **K_2CrO_4**	2.52mg **K_2CrO_4**		14.20mg **$K_2Cr_2O_7$**
	4.67mg **Cr_2O_7**		4.93mg **CrO_4**	1.51mg **CrO_4**	**N/A**	10.43mg **Cr_2O_7**
Amount sorbed No. of Moles	**$2.16x10^{-5}$ mol.** **Cr_2O_7**		**$4.25x10^{-5}$ mol.** **CrO_4**	**$1.30x10^{-5}$ mol.** **CrO_4**		**$4.8x10^{-5}$ mol.** **Cr_2O_7**
	$4.32x10^{-5}$ mol. **Cr(VI)**		**$4.25x10^{-5}$ mol.** **Cr(VI)**	**$1.30x10^{-5}$ mol.** **Cr(VI)**		**$9.8x10^{-5}$ mol.** **Cr(VI)**
Capacity (mol. /mol.) ***Calculated***	**0.43** **Cr_2O_7**		**0.85** **CrO_4**	**0.41** **CrO_4**		**2.25** **Cr_2O_7**
	0.86 **Cr(VI)**		0.85 **Cr(VI)**	0.41 **Cr(VI)**		4.5 **Cr(VI)**
Capacity (mol. /mol.) ***Published***	**N/A**		**0.85** **(CrO_4)**	**0.41** **(CrO_4)**		**1.84** **(Cr_2O_7)**
Capacity (mg/g) ***Calculated***	**77.40** **Cr_2O_7**		**63.20** **CrO_4**	**60.30** **CrO_4**		**277.4** **Cr_2O_7**
	37.26 **Cr(VI)**		28.33 **Cr(VI)**	27.03 **Cr(VI)**		133.4 **Cr(VI)**
Capacity (mg/g) ***Published***	**74.2** **(Cr_2O_7)**	**103** **(Cr_2O_7)**	**62.88** **(CrO_4)**	**60** **(CrO_4)**	**286** **(Cr_2O_7)**	**277.4** **(Cr_2O_7)**

Column Capacity Calculations (continued)

	Ref.37	Ref.49	Ref.52	Ref.60	Ref.61
Sorbent	**Zn-SLUG-35**	**ABT.2CLO$_4$**	**ZJU-101**	**MONT-1**	**2-D-Ag-3**
Sorbent Weight	20mg	37mg	10mg	69.2mg	36.4 mg
Sorbent Mol. Wt.	710.04 g/mol.	740g/mol.	**N/A**	692.18g/mol	727.74g/mol
Sorbent No. of Moles	**2.8x10^{-5} mol.**	**5x10^{-5} mol.**		**10x10^{-5} mol.**	**5x10^{-5} mol.**
Adsorbate	**K_2CrO_4**	**$K_2Cr_2O_7$**			
Adsorbate Volume	10ml	20ml	20ml	10ml	10ml
Adsorbate No. of Moles	1.4x10^{-5} mol.	5x10^{-5} mol.	0.46x10^{-5} mol.	8x10^{-5} mol.	5x10^{-5} mol.
Adsorbate Weight	2.72mg	14.7mg	1.36mg	23.5mg	14.71mg
Amount sorbed	84%	73%	96%	86.5%	56%
Amount Sorbed Weight	1.36 mg **CrO_4**	7.88mg **Cr_2O_7**	0.95mg **Cr_2O_7**	14.90mg **Cr_2O_7**	6.05mg **Cr_2O_7**
Amount Sorbed No. of Moles	**1.17x10^{-5} mol. CrO_4**	**3.65x10^{-5} mol. Cr_2O_7**	**0.44 x10^{-5}mol. Cr_2O_7**	**6.9x10^{-5} mol. Cr_2O_7**	**2.8 x10^{-5}mol. Cr_2O_7**
	1.17x10^{-5} mol. Cr(VI)	**7.3x10^{-5} mol. Cr(VI)**	**0.88 x10^{-5}mol. Cr(VI)**	**13.8x10^{-5} mol. Cr(VI)**	**5.6x10^{-5}mol. Cr(VI)**
Capacity (mol. /mol.) *Calculated*	**0.42 CrO_4**	**0.73 Cr_2O_7**	**N/A**	**0.69 Cr_2O_7**	**0.56 Cr_2O_7**
	0.42 Cr(VI)	1.46 Cr(VI)		1.38 Cr(VI)	1.12 Cr(VI)
Capacity (mol. /mol.) *Published*	**0.43 (CrO_4)**	**0.73 (Cr_2O_7)**		**N/A**	**0.56 $K_2Cr_2O_7$**
Capacity (mg/g) *Calculated*	**68.8 CrO_4**	**213.07 Cr_2O_7**		**215.3 Cr_2O_7**	**166.20 Cr_2O_7**
	30.76 Cr(VI)	102.59 Cr(VI)		103.66 Cr(VI)	80 Cr(VI)
Capacity (mg/g) *Published*	**68.5 (CrO_4)**	**213 (Cr_2O_7)**	**245 (Cr_2O_7)**	**211.8 (Cr_2O_7)**	**167 (Cr_2O_7)**

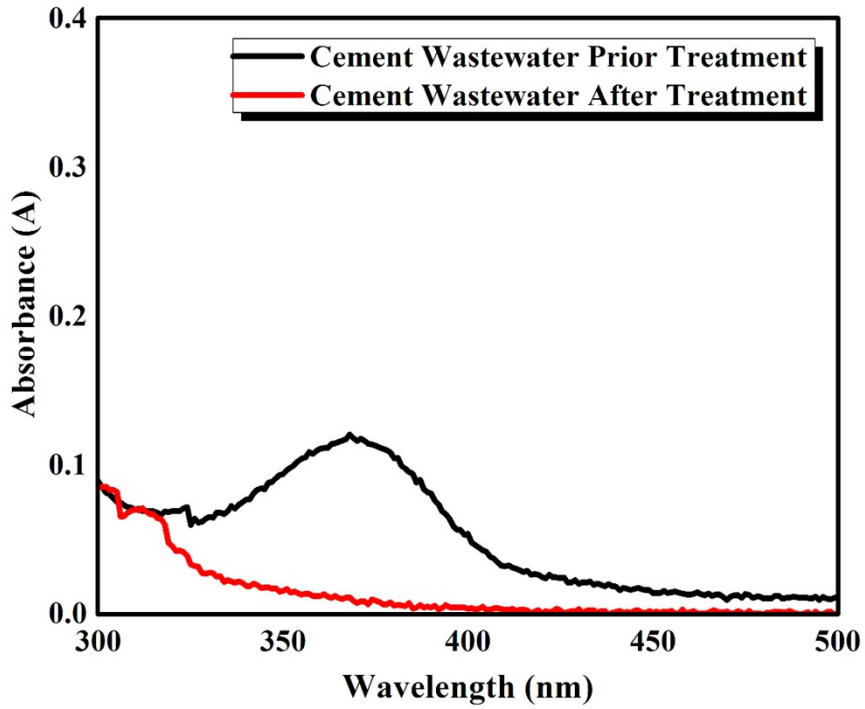

Figure S4. UiO-66-NH_2@Silica sorption capability of Cr(VI) containing cement wastewater

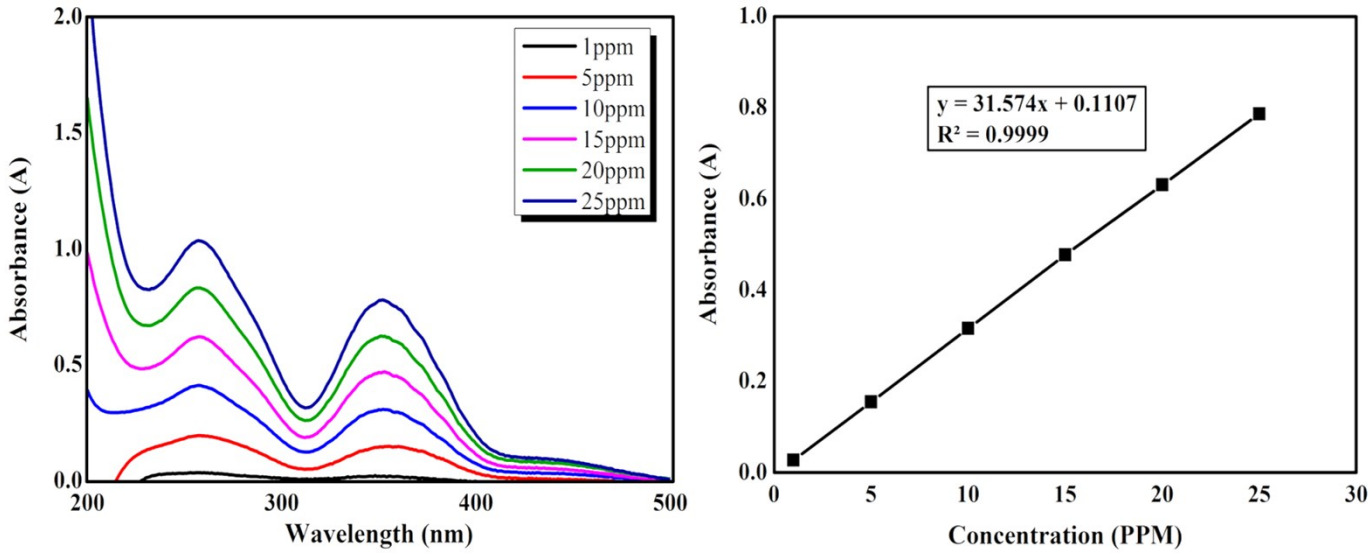

Figure S5. Cr(VI) stock solutions calibration curve.