

ELECTRONIC SUPPORTING INFORMATION

Rapid, green and inexpensive synthesis of high quality UiO-66 amino-functionalized materials with exceptional capability for removal of hexavalent chromium from industrial waste

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EXPERIMENTAL SECTION

Materials. All reagents and solvents were commercially available and used as received.

Synthesis of MOR-1. A mixture of ZrCl_4 (0.625 gr, 2.7 mmol) and $\text{NH}_2\text{-H}_2\text{BDC}$ (0.679 gr, 3.75 mmol) in 40 mL H_2O and 10 mL CH_3COOH (pH~2) is heated at 110 °C under reflux conditions. Within 5-10 min, the initial intense yellow color of the $\text{NH}_2\text{-H}_2\text{BDC}$ suspension changed to light yellow. The reflux reaction is stopped after 1 h. A fine suspension of the **MOR-1** is formed and it was allowed to cool. **MOR-1** can be isolated via centrifugation of the suspension and is purified by treating the product with HCl 4 M. Yield: 0.80 g (~ 68 %). Based on elemental (C,H,N) analysis and TGA data (see below) **MOR-1** was analyzed as $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{NH}_3\text{C}_8\text{O}_4\text{H}_3)_6]\text{Cl}_6\cdot 35\text{H}_2\text{O}$. Anal. Calc. for $\text{C}_{48}\text{H}_{110}\text{C}_{16}\text{N}_6\text{O}_{67}\text{Zr}_6$: C, 22.14; H, 4.26; N, 3.23. Found: C, 21.92; H, 4.02; N, 3.86. EDS analysis for **MOR-1** indicated Zr:Cl molar ratio ~1.

Synthesis of MOR-1-HA

MOR-1-HA was isolated with the same procedure as that followed for the isolation of **MOR-1** with the exception that SA solution (40 mL of 0.05% wt. SA water solution=20 mg of SA) is added to the suspension of **MOR-1**. Precipitation of the **MOR-1-HA** is immediately observed. To complete the precipitation, fully protonate the NH_2 -groups and remove any unreacted amount of $\text{NH}_2\text{-H}_2\text{BDC}$ ligand, HCl is also added (final concentration ~ 4 M). **MOR-1-HA** is isolated by filtration, washed with water and acetone and vacuum dried. Yield:0.85 g. Considering that the sodium alginate (20 mg, 0.1 mmol) is completely transformed to the insoluble (under acidic conditions) alginic acid (17.6 mg, 0.1 mmol), the weight percentage of alginic acid in the composite will be equal to $\text{alginic acid mass (g)} \times 100 / \text{composite mass (g)} = 0.0176 \times 100 / 0.85 \sim 2.1$

% wt and thus, the composite contains ~97.9% wt. **MOR-1**. The number of water molecules of **MOR-1-HA** were calculated based on TGA (see below). EDS analysis for **MOR-1-HA** indicated Zr:Cl molar ratio ~1.

Physical measurements. Elemental analyses (C, H, N) were performed by the in-house facilities of the University of Science and Technology, Center for Materials Science, Zewail City of Science and Technology, Giza, Egypt. PXRD diffraction patterns were recorded on a Bruker D8 Advance X-ray diffractometer (CuK α radiation, $\lambda = 1.5418 \text{ \AA}$). IR spectra were recorded on KBr pellets in the 4000-400 cm^{-1} range using a Perkin-Elmer Spectrum GX spectrometer. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer Diamond system. Thermal analysis was conducted from 25 to 600 $^{\circ}\text{C}$ in air atmosphere (100 mL min^{-1} flow rate) with a heating rate of 10 $^{\circ}\text{C min}^{-1}$. Energy dispersive spectroscopy (EDS) analyses were performed on a JEOL JSM-6390LV scanning electron microscope (SEM) equipped with an Oxford INCA PentaFET-x3 energy dispersive X-ray spectroscopy (EDS) detector. Data acquisition was performed with an accelerating voltage of 20 kV and 120 s accumulation time. Scanning electron microscopy (SEM) images were taken with a field emission JEOL JSM 7000F electron microscope operating at 15 kV accelerated voltage. The samples were sputter-coated with a 5-10 nm Au film to reduce charging. X-ray photoelectron spectroscopy (XPS) was performed on a Perkin Elmer Phi 5400 ESCA system equipped with a Mg K α x-ray source. Samples were analyzed at pressures between 10^{-9} and 10^{-8} Torr with a pass energy of 29.35 eV and a take-off angle of 45° . All peaks were referred to the signature C $_{1s}$ peak for adventitious carbon at 284.6 eV. Fitting of the peaks has been made by using the software XPSPEAK41. UV/vis Cr(VI) solution spectra were obtained on a Shimadzu 1200 PC in the wavelength range of 200-800 nm. N $_2$ adsorption-desorption isotherms were measured at 77 K on a Quantachrome

Nova 3200e sorption analyzer. Before analysis, all samples were EtOH-exchanged, activated via supercritical CO₂ drying and then, degassed at 120 °C under vacuum (<10⁻⁵ Torr) for 12 h. The specific surface areas were calculated by applying the Brumauer-Emmett-Teller (BET) method to the branch of isotherms in the 0.05–0.25 relative pressure (P/P₀) range. CO₂ adsorption isotherms were measured at 273 K using an IGA-003 gravimetric sorption analyzer (Hiden Isochema, UK). The activation of the materials was done as with the N₂ sorption measurements. The pore size distribution plot was obtained from the CO₂ adsorption data using the density functional theory (DFT) method. Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) analyses were performed using a computer-controlled Thermo Scientific iCAP Q ICP-MS with a quadruple setup equipped with Collision Cell Technology.

Preparation of the column. 50 mg of **MOR-1-HA** composite (treated before with 4 M HCl acid) and 5 g of sand (50-70 mesh SiO₂) was mixed in a mortar and pestle and filled in a glass column (0.7 cm ID column). Prior the ion exchange studies, the column was washed with ~ 10 mL HCl (4 M) solution and deionized water.

Batch ion-exchange studies. A typical ion-exchange experiment of **MOR-1-HA** with Cr₂O₇²⁻ is the following: In a solution of K₂Cr₂O₇ (118 mg, 0.4 mmol) in water (10 mL, pH ~ 3), compound **MOR-1-HA** (100 mg, ~ 0.038 mmol of **MOR-1**) was added as a solid. The mixture was kept under magnetic stirring for ≈ 1 h. Then, the polycrystalline material, which had orange(red)-brown color, was isolated by filtration, washed several times with water and acetone and dried in the air.

Prior the Cr(VI) sorption studies, the **MOR-1-HA** composite was treated with 4 M HCl acid for ~ 1h. The Cr(VI) uptake from solutions of various concentrations was studied by the batch method at *V:m* ~ 1000 mL/g, room temperature and 1 h contact. These data were used for the

determination of Cr(VI) sorption isotherms. UV-Vis was used for analysis of dichromate solutions with concentration ≥ 1 ppm. The solutions with Cr(VI) content less than 1 ppm were analyzed with ICP-MS.

The competitive and variable pH ion exchange experiments were also carried out with the batch method at $V: m$ ratio (1000) mL/g, room temperature and 1 h contact.

For the determination of the sorption kinetics, Cr(VI) ion-exchange experiments of various reaction times (1-60 min) have been performed. For each experiment, a 10 mL sample of $\text{Cr}_2\text{O}_7^{2-}$ solution (initial dichromate concentration = 21.2 ppm, pH~3) was added to each vial and the mixtures were kept under magnetic stirring for the designated reaction times. The suspensions from the various reactions were filtrated and the resulting solutions were analyzed for their chromium content with ICP-MS.

Alginic acid was tested for Cr(VI) sorption, showing no Cr(VI) sorption capacity.

Column Ion-Exchange studies

Several bed volumes of the solution are passed through the column and collected at the bottom in glass vials. The solutions with $\text{Cr}_2\text{O}_7^{2-}$ concentration ≥ 1 ppm were analyzed with UV-Vis, whereas the Cr content of those with smaller concentration was determined with ICP-MS. The regeneration of the column is performed by its treatment with ~ 10 mL of HCl acid (4 M) solution. Then, the column is washed with enough water to remove excess acid. Column containing only sand as stationary phase showed no Cr(VI) sorption capacity.

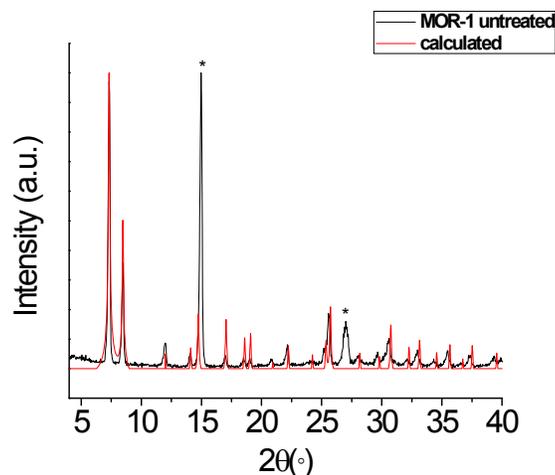


Fig. S1. The PXRD pattern of **MOR-1** that was isolated by reflux reaction without any treatment contained unidentified peaks (marked with *), possibly due to unreacted amount of the NH_2 -BDC ligand. These impurities were removed by treating the product with HCl acid (see PXRD patterns in Fig. 5A, main article).

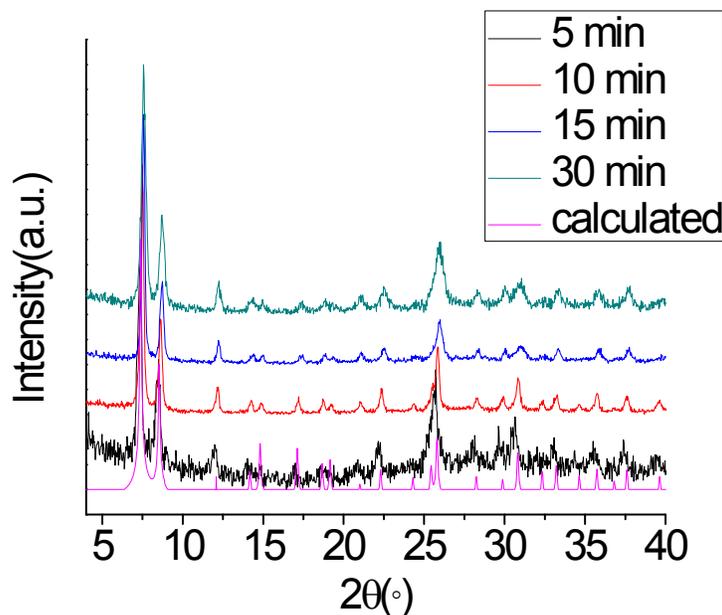


Fig. S2. PXRD patterns of **MOR-1-HA** samples isolated at various reaction times vs. the calculated PXRD pattern for UiO-66. It is apparent that the material is formed even within 5 min and product with high purity and crystallinity can be isolated with a 10 min reaction.

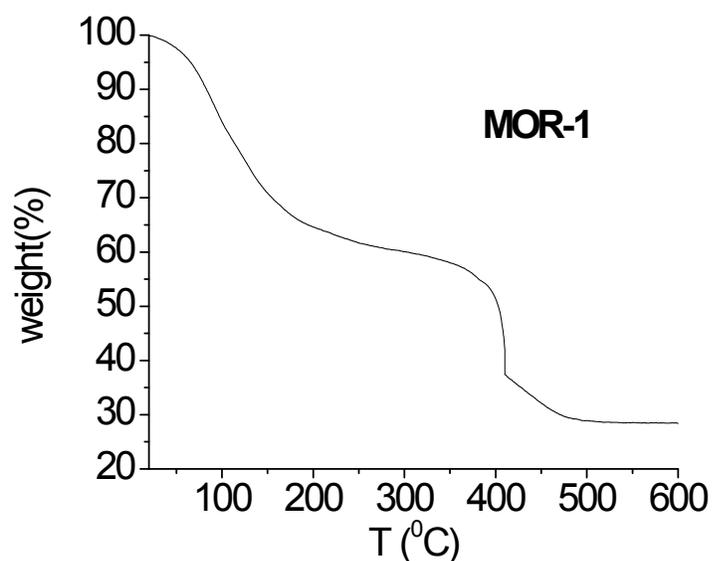
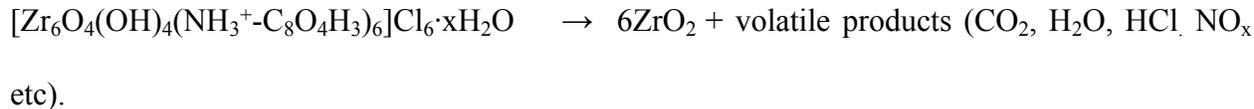


Fig. S3. The TGA data for **MOR-1** measured in air. There is a continuous weight loss starting at 20 °C and ending at ~ 500 °C. The **MOR-1** is finally transformed to ZrO₂ according to the equation



Thus, one mole of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{NH}_3^+-\text{C}_8\text{O}_4\text{H}_3)_6]\text{Cl}_6 \cdot x\text{H}_2\text{O}$ yields 6 moles of ZrO₂ or molecular weight (g) of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{NH}_3^+-\text{C}_8\text{O}_4\text{H}_3)_6]\text{Cl}_6 \cdot x\text{H}_2\text{O}$ (= 1972.9+18x) yields 6 × molecular weight (g) of ZrO₂ (6 × 123.2 = 739.2) .

From the TGA data, we know that 100 g of of **MOR-1** are converted to 28.4 g of ZrO₂. Thus, **MOR-1**/ZrO₂ mass ratio = 100/28.4= 3.52 or 1972.9+18x/739.2 = 3.52 and x ~ 35. This result is in agreement with the elemental analysis (C,H, N) data.

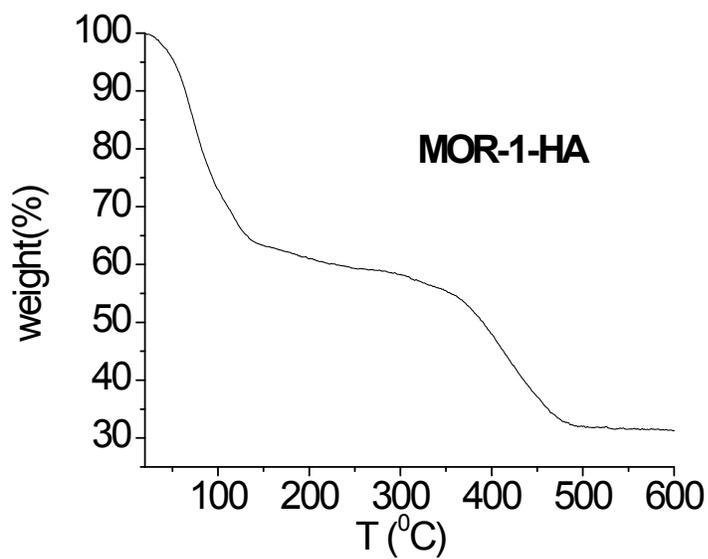


Fig. S4. The TGA data for **MOR-1-HA** measured in air. There is a continuous weight loss starting at 20 °C and ending at ~ 500 °C. From the TGA data, we know that 100 g of **MOR-1-HA** composite or 97.9 g of **MOR-1** (the **MOR** initial weight is the 97.9% of the initial **MOR-1-HA** weight) are converted to 31.2 g of ZrO_2 (organic molecules including HA are decomposed to CO_2 , NO_x , H_2O and Cl^- are released as HCl). Thus, **MOR-1**/ ZrO_2 mass ratio = $97.9/31.2 = 3.14$ or $(\text{Molecular weight of MOR-1})/6 \times (\text{Molecular weight of } ZrO_2) = 1972.9 + 18x/739.2 = 3.14$ and x (number of water molecules) ~ 19.

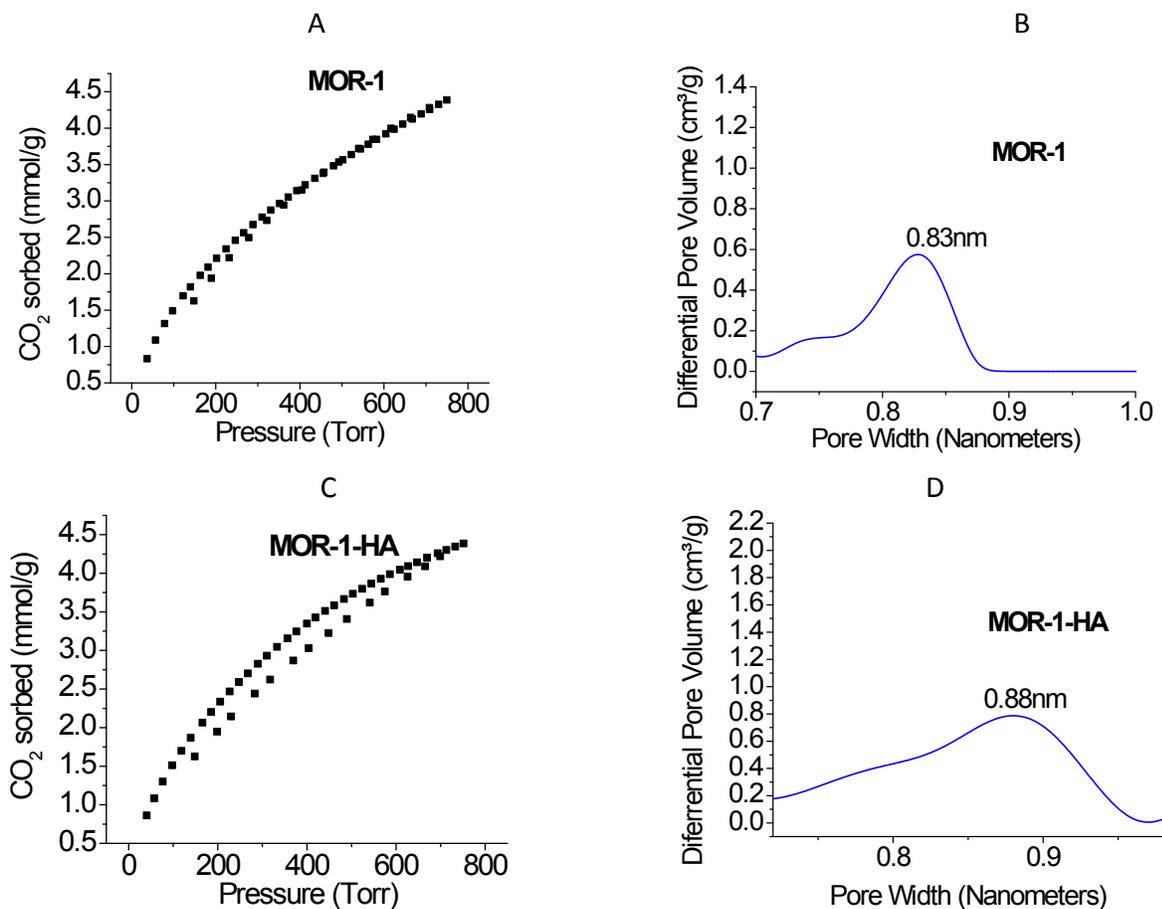


Fig. S5. CO₂ adsorption isotherms at 273 K for **MOR-1** and **MOR-1-HA** and the resultant DFT micropore size distribution (assuming slit-type pores). The DFT analysis of the adsorption data indicates a pore size of ~ 0.8-0.9 nm for these materials.

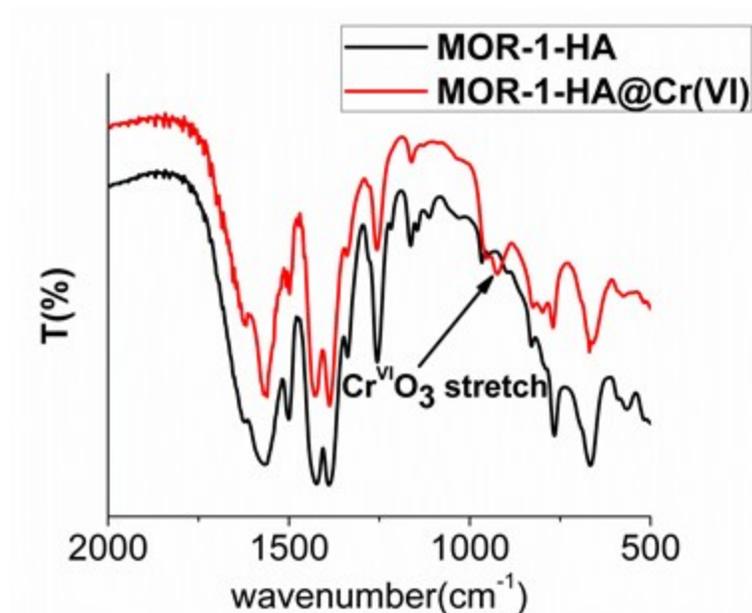


Fig. S6. IR spectra of **MOR-1-HA** and **MOR-1-HA@Cr(VI)**.

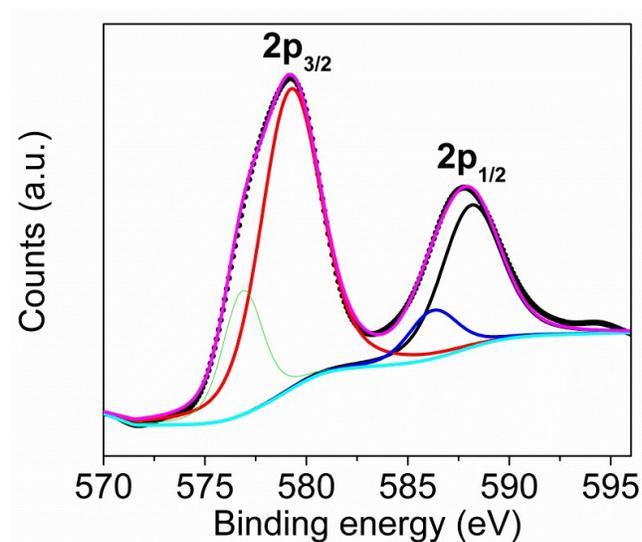


Fig. S7. High resolution Cr $2p_{1/2}$ and Cr $2p_{3/2}$ core-level photoelectron spectra of **MOR-1-HA** and their de-convolution into two components. The minor signals with binding energy at 586.2 and 576.9 eV are due to Cr(III) traces produced from the reduction effects under X-ray irradiation (see a) M. C. Biesinger, C. Brown, J. R. Mycroft, R. D. Davidson and N. S. McIntyre, *Surf. Interface Anal.*, 2004, **36**, 1550 and b) E. Desimoni, C. Malitesta, P. G. Zambonin and J. C. Riviere, *Surf. Interface Anal.*, 1988, **13**, 173).

Fitting of isotherm Cr(VI) batch sorption data

The fitting of the data with two different isotherm models is given in Table S1 and the graphs are shown in Fig. S6. The models used were the

a) Langmuir
$$q = q_m \frac{bC_e}{1 + bC_e} \quad (1)$$

b) Freundlich
$$q = K_F C_e^{\frac{1}{n}} \quad (2)$$

where q (mg/g) is the amount of the cation sorbed at the equilibrium concentration C_e (ppm), q_m is the maximum sorption capacity of the sorbent, b (L/mg) is the Langmuir constant related to the free energy of the sorption, K_F and $1/n$ are the Freundlich constants (see references a) Do, D. D. in *Adsorption Analysis: Equilibria and Kinetics*. pp. 13-17,49-57 (Imperial College Press, 1998); b) Calvet, R. *Environ. Health Persp.* **1989**, 83, 145-77; c) Arias, M.; Perez-Novo, C.; Lopez, E.; Soto, B. *Geoderma* **2006**, 133, 151-159; d) Han, R.; Zou, W.; Wang, Y.; Zhu, L. J. *Environ. Radioact.* **2007**, 93, 127-143).

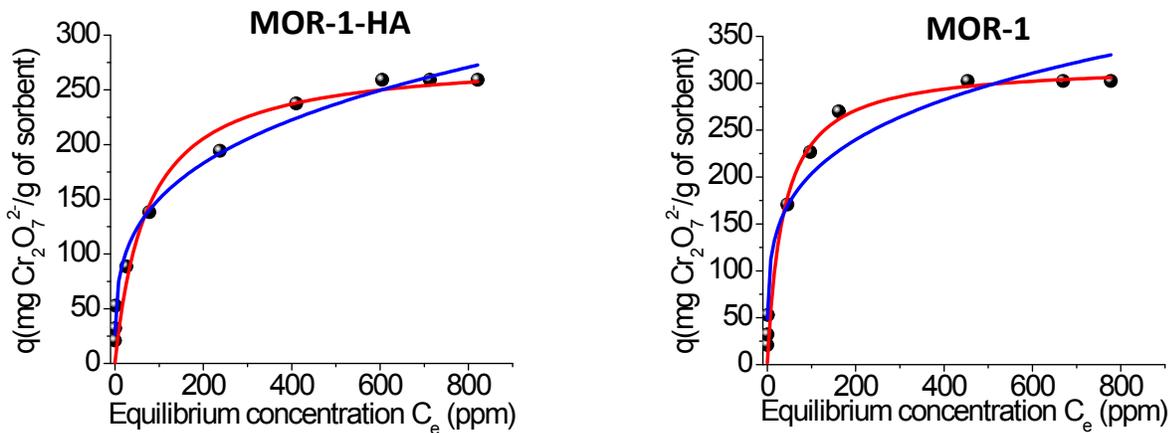


Fig. S8. Fitting of the isotherm Cr(VI) sorption data for **MOR-1-HA** and **MOR-1** with the Langmuir (red line) and Freundlich (blue line) models.

Table S1. Fitting of the isotherm data for **MOR-1-HA** and **MOR-1**

Compound	Langmuir			Freundlich		
	q_e (mg/g)	b (L/mg)	R^2	K_F	n	R^2
MOR-1-HA	280±19	0.014±0.005	0.94	40.6±4.2	3.5±0.2	0.99
MOR-1	321±16	0.027±0.008	0.97	68.7±12.5	4.2±0.6	0.95

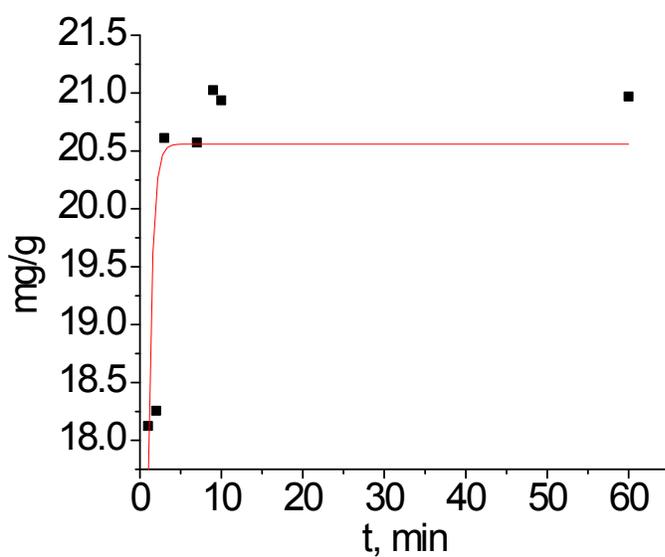


Fig. S9. : Fitting of the kinetics data with the Lagergren's first order equation (fitting parameters $q_e = 20.6 \pm 0.4$ mg/g, $K_L = 1.9 \pm 0.3$ min⁻¹, $R^2 = 0.48$).

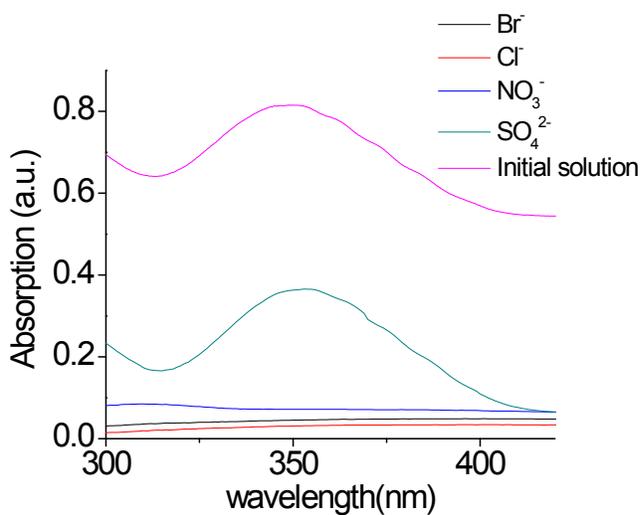


Fig. S10. UV-Vis data from the selectivity ion-exchange experiments (initial concentration of $\text{Cr}_2\text{O}_7^{2-}$ 0.25 mM, $\text{pH}\sim 3$, concentration of Cl^- , Br^- , NO_3^- and SO_4^{2-} was 2.5 mM). The dichromate anions could not be detected with UV-Vis in the experiments in the presence of Cl^- , Br^- or NO_3^- and thus, the total Cr concentration was determined by ICP-MS.

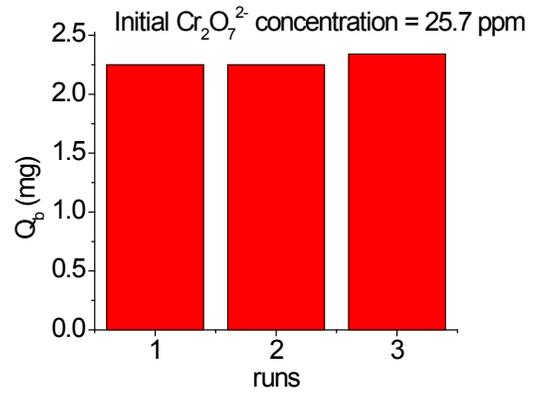
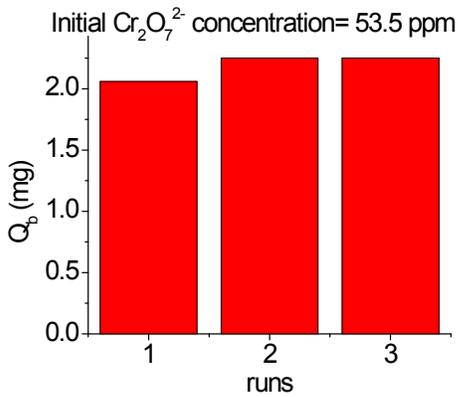
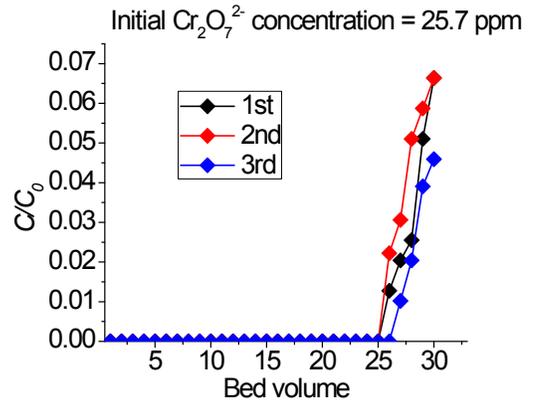
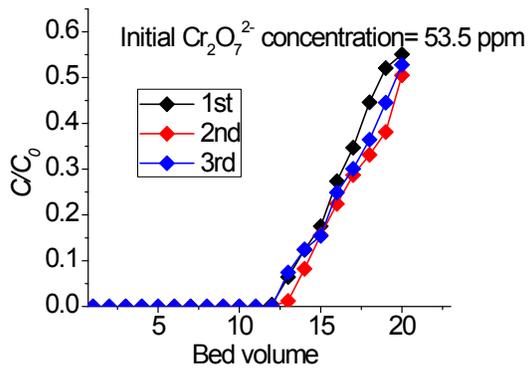


Fig. S11. Breakthrough curves and breakthrough capacities of **MOR-1-HA/sand** (0.05 g:5 g) column determined for dichromate initial concentrations of 25.7 and 53.5 ppm (pH~3). The number of bed volumes passed through the column till the breakpoint concentration (i.e. total Cr concentration ≤ 50 ppb) was 11, 12 and 12 for the 1st-3th column runs respectively for initial dichromate concentration of 53.5 ppm, whereas the corresponding numbers were 25, 25 and 26 for the column sorption experiments with initial dichromate concentration of 25.7 ppm.

Fitting of the column sorption data for chrome plating wastewater sample B with the Thomas equation

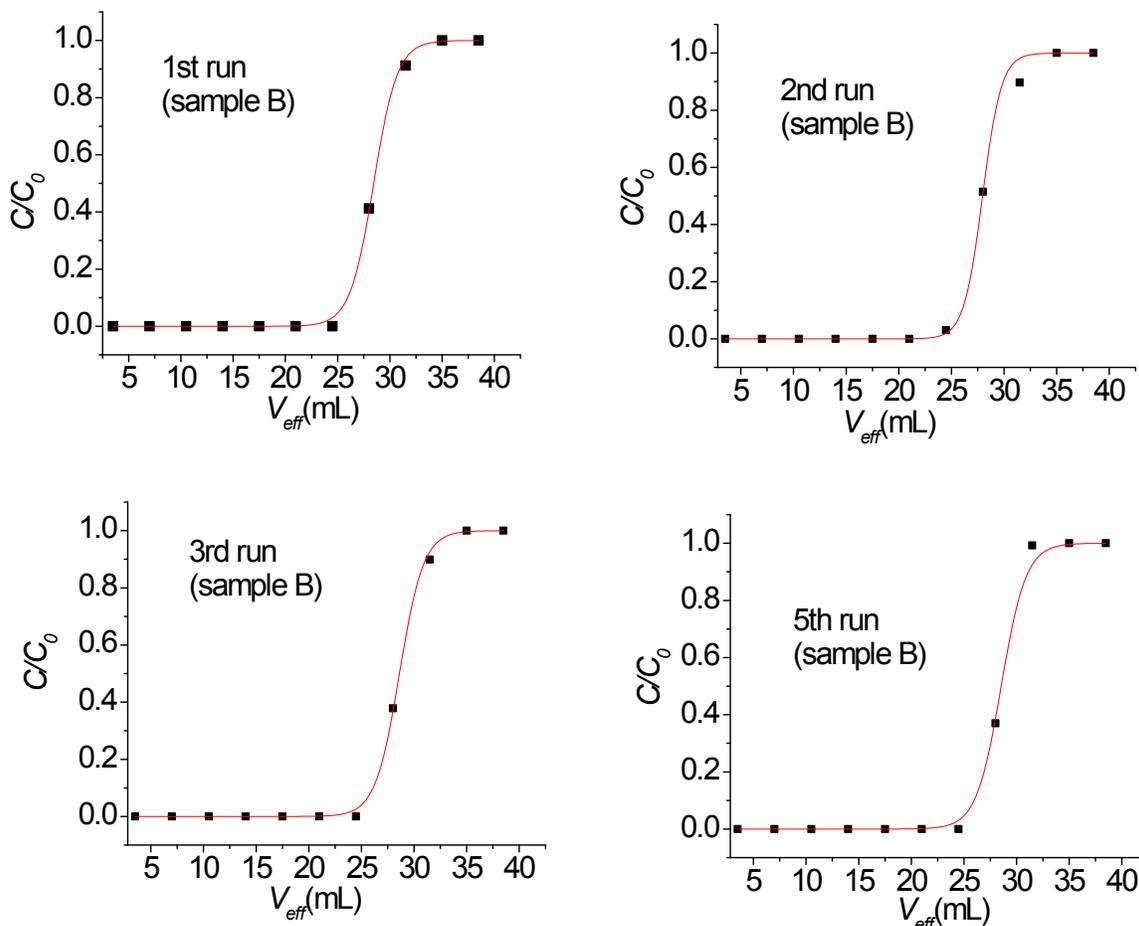


Fig. S12. Fitting of the breakthrough curves for the column sorption experiments with the chrome plating wastewater sample B (the fitting for the breakthrough curve obtained in the 4th column run is shown in the main article, Fig. 14C).

The data are fitted with an equation of the type $y = \frac{1}{1 + \exp(A - Bx)}$

where $A = \frac{k_{Th} q_{max} m}{Q}$, $B = \frac{k_{Th} C_0}{Q}$

Table S2. Fitting of the column sorption data for sample B

Run	Fitting results			Thomas model parameters	
	A	B	R ²	k_{Th} (L mg ⁻¹ min ⁻¹)	q_{max} (mg/g)
1	25.1	0.88	0.999	0.0098	61.6
2	36.0	1.28	0.995	0.0142	60.8
3	25.2	0.88	0.999	0.0098	61.8
4	22.6	0.78	0.999	0.0087	62.6
5	24.3	0.85	0.997	0.0094	61.8