Electronic Supporting Information

Highly efficient sorption and luminescence sensing of oxoanionic species by 8-connected alkyl-amino functionalized Zr⁴⁺ MOFs

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Table of Contents

Experimental Section	2
CHEMICALS	2
Synthesis and characterization of Alkyl-amino functionalized MOFs	2
PREPARATION OF BUT-MOF/ CALCIUM ALGINATE BEADS	2
Characterization Techniques	2
SORPTION STUDIES	3
FLUORESCENCE SENSING STUDIES	4
Results and Discussion	6
SORPTION STUDIES WITH ALKYL-AMINO FUNCTIONALIZED MOFS	6
COMPARISON OF ALKYL-AMINO FUNCTIONALIZED MOFS WITH OTHER MOF-BASED SORBENTS	19
CHARACTERIZATION OF LOADED-BUT-MOF	22
DETAILS OF THE STRUCTURAL REFINEMENT	28
FLUORESENCE SORPTION STUDIES OF BUT-MOF	32
References	36

Experimental Section

Chemicals

Zirconium chloride (ZrCl₄), 2-aminoterephthalic (NH₂-H₂BDC) and NaBH₄ were purchased from Aldrich. Acetylaldehyde (CH₃CHO), propionaldehyde (CH₃CH₂CHO), isobutyraldehyde ((CH₃)₂CHCHO) and butyraldehyde (CH₃CH₂CH₂CHO) were purchased from Alfa Aesar. Sodium alginate powder was purchased from Aldrich and used as received. The solvents were used as received.

Synthesis and characterization of alkyl-amino functionalized MOFs

The synthesis and characterization of alkyl-amino functionalized MOFs was reported previously by us.¹

Activation of alkyl-amino functionalized MOFs. Prior to sorption and fluorescence sensing experiments BUT-MOF was treated with HCl acid solution for 2h (0.1 g/10 mL HCl 4M). The activated solid was isolated by centrifugation, washed with water, acetone and dried in air. The activation of the material was essential for the purpose of improving the electrostatic interactions between the sorbent and the oxoanionic species. The same procedure was followed for the activation of ET-MOF, PROP-MOF and SBUT-MOF in advance of batch sorption studies.

Preparation of BUT-MOF/ calcium alginate beads

A suspension of MOF was prepared by dispersing 0.510 g **BUT-MOF** in 10 ml distilled water via ultrasonication. The mixture was kept under stirring for 30 min. To this suspension, 0.06 g of sodium alginate were added, and the mixture was kept under vigorous stirring for 1-2 h. The resulting suspension was dropped through a syringe needle into 2% (w/v) CaCl₂ solution where the spherization was performed. The solution containing suspend beads was stirred with a magnetic stir bar for 10 min to improve the mechanical strength of the beads. The fully formed yellow beads were left in the gelatinization bath for 30 min, isolated via filtration using a Buchner funnel, washed with excess of water to remove the spare amount of unbound calcium, and dried overnight at 60 °C (Yield: 0.514 g).

Characterization Techniques

Powder X-ray diffraction measurements were performed on a Bruker D2-Phaser X-ray diffractometer (CuKa radiation source, wavelength = 1.54184 Å). High quality diffraction data, suitable to be used for Rietveld refinement, were obtained using a step of 0.01° and

scan rate of 1.8 second/0.01° (overall measurement time was approximately 172 min). IR spectra were recorded in the range of 4000-400 cm⁻¹ range using an Agilent Cary 630 ATR. UV/Vis Cr(VI) and Re(VI) solution spectra were obtained on a Agilent Cary 4000 in the wavelength range of 200-800 nm. The method for analysis of ReO_4^- via UV-Vis spectroscopy is described in literature.² 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 120s 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. N_2 adsorption-desorption isotherms were measured at 77K on a Quantachrome Nova 3200e sorption analyzer. Before analysis, all samples were EtOH exchanged, activated via supercritical CO₂ drying and then, degassed at 150 °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 absorption branch of isotherms in the 0.04– 0.23 relative pressure (P/P_o) range. XPS measurements were performed on a SPECS spectrometer using a Phoibos 100 1D-DLD electron analyzer and an Al K α radiation as the energy source (1486.6 eV). Binding energy values were corrected for charging by assigning a binding energy of 284.8 eV to the C 1s signal of adventitious carbon.

Sorption studies

Preparation of the column. 850 mg of **BUT-MOF/calcium alginate** beads were used to fill a glass column (0.7 cm ID column). Prior the sorption study, the column was washed with ~ 50 mL HCl (1 M) solution and 200 mL deionized water to remove the excess of HCl.

Batch sorption studies. A typical sorption experiment of **BUT-MOF** with $Cr_2O_7^{2-}$ is the following: In a solution of $K_2Cr_2O_7$ (0.4 mmol) in water (10 mL, pH ~ 3), **BUT-MOF** (100 mg, ~ 0.042 mmol of **BUT-MOF**) was added as a solid. The mixture was kept under magnetic stirring for ~ 1 h. Then, the polycrystalline material was isolated by filtration, washed several times with water and acetone and dried in the air. 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. 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 $Cr_2O_7^{2-}$ solution (initial dichromate concentration = 21.6 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 UV-Vis spectroscopy. Batch chromate and perrhenate sorption studies was carried similarly as those for dichromate anions. The isolation of CrO_4^{2-} and ReO_4^{--} exchanged products was performed similarly as that of $Cr_2O_7^{2-}$ loaded material, with the exception that K_2CrO_4 or NaReO₄ was used instead of K_2CrO_7 .

The suspensions from the various reactions were filtrated and the resulting solutions were analyzed for their Cr/Re content with UV-Vis spectroscopy. Each sorption experiment has been done at least twice and the reported sorption data represent the average of sorption results from the different sorption experiments. The difference between the concentrations of toxic oxoanions determined for the different sorption experiments was <2%.

Regeneration/reusability study. 100 mg of Cr(VI) and Re(VII) loaded materials were immersed in 10 mL HCl 4 M and kept under stirring for 2h in order to release the oxoanions from the loaded sorbent. The regenerated materials were isolated by centrifugation, washed with water to remove the excess of HCl, acetone and dried in air. The regenerated **BUT-MOF** was reused for the treatment of Cr(VI) and Re(VII) solutions (CrO_4^{2-} 10 mM, $Cr_2O_7^{2-}$ 12 mM and ReO_4^{-} 20 mM) at V:m ~ 1000 mL/g, room temperature and 15 min contact time.

Column sorption study. The sample tested (total $Cr(VI) \sim 330$ ppb) was prepared by diluting a chrome plating waste solution (~ 2910 ppm of Cr(VI)) provided by the metal plating company, A. Nestorides & Sons, Sindos, Thessaloniki, Greece). The Cr(VI) waste solution was pumped through the column in up-flow mode (flow rate of 2.5 mL/min). In order to achieve the desirable efficiency, a secondary treatment of the sample was necessary. The concentration of the residual Cr(VI) was analyzed every 400 mL via UV-Vis spectroscopy (DPC method).³ The regeneration of the column was performed by its treatment with ~ 50 mL of HCl acid (1 M) solution. Then, the column was washed with 200 mL of water to remove excess acid and tested again for Cr(VI) sorption. Similar sorption experiments with calcium alginate showed no Cr(VI) sorption capacity.

Fluorescence sensing studies

The fluorescence spectra were recorded on a Hitachi F7000 spectrofluorometer. The spectrofluorometer was equipped with a Xenon arch lamp as light source and a red sensitive Hamamatsu R928 photomultiplyer tube detector. All spectra are corrected for instrument

response using the correction function generated after calibration of the instrument with a standard light source. Appropriate long pass filters were used to remove scattering from the sample and the monochromators. For the Cr(VII) sensing experiments, 1 mg of the MOF in the form of a fine powder were suspended in 10 mL of the respective medium (doubly distilled water or bottled water) the pH of which was previously adjusted to 3 by careful addition of 4 M HCl. The system was sonicated for 30 min and 1 mL of the resulting fine suspension was transferred to a luminescence quartz cuvette. Aliquots of $K_2Cr_2O_7$ 10⁻⁴ M (dissolved in the same medium as the MOF) were added using a HamiltonTM precision microsyringe (50 µL range) in order to achieve the desired Cr(VI) concentration. Emission spectra were recorded 2 min after each addition. The emission spectrum after each addition was recorded three times to ensure signal stability.

The detection and quantification limits in the fluorescence titrations were calculated by the following equations:⁴

$$LOD = \frac{3SD}{S}$$

$$LOQ = \frac{10SD}{S}$$

where *S* is the slope of the linear calibration curve and *SD* is the standard deviation of the initial emission intensity. The standard deviation for each titration was calculated using the following equation:⁵

$$SD = \sqrt{\frac{\Sigma(F - F_0)^2}{N - 1}}$$

where F_0 represents the emission intensity for the suspension of the MOF and F represents the average of F_0 . The standard deviations were calculated for N = 5.

The quenching data was also analyzed using the linear form of the Stern–Volmer equation:⁶

$$\frac{I_0}{I} = 1 + K_{sv}[M]$$

where I_0 and I are the fluorescence intensities of the **BUT-MOF** suspension before and after the addition of the analyte respectively, K_{sv} is the quenching constant (M⁻¹) of the titration and [*M*] is the corresponding molar concentration of the analyte.

In order to diminish the influence of the so-called inner filter effect of Cr(VI) to the luminescence intensity, the fluorescence titrations were performed using the excitation wavelength of 400 nm. At such wavelength and the low Cr(VI) concentrations (<2 ppm) used in titration studies, the absorption of Cr(VI) (and thus, the inner filter effect) is negligible.

Results and Discussion

Sorption studies with alkyl-amino functionalized MOFs

Lagergren's First-order equation and Ho-Mckay's pseudo-second-order equation were used to fit the kinetics data. The expressions of these equations are the following:

Lagergren's First-order equation:

$$q_t = q_e [1 - \exp(-K_L t)]$$

where $q_e =$ the amount (mg g⁻¹) of ion sorbed in equilibrium, $K_L =$ the Lagergren's or firstorder rate constant.⁷

Ho and Mckay's pseudo-second-order equation:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$$

where q_t = the amount (mg/g) of ion sorbed at different reaction times (t), q_e = the amount (mg/g) of ion sorbed in equilibrium, and where k_2 is the second-order rate constant [g/(mg·min)].⁷

	Lagergren's Firs	Ho-Mckay's Second - Order Equation										
	q _e mg g⁻¹	K⊥ g (mg min) ⁻¹	R ²	q _e <i>mg g</i> ⁻¹	K ₂ g (mg min) ⁻¹	R²						
BUT- MOF/Cr ₂ O ₇ ²⁻	21.59 ± 3.79 10 ⁻⁴	7.82 ± 0.14	0.85	21.59 ± 2.42 10 ⁻⁴	95.85 ± 5.67	0.97						
BUT-MOF/ CrO4 ²⁻	11.59 ± 1.57 10 ⁻⁴	7.82 ± 0.14	0.98	11.59 ± 6.03 10 ⁻⁴	88.27 ± 12.01	0.86						
BUT-MOF/ ReO4 ⁻	43.53 ± 0.19	1.45 ± 0.05	0.98	45.87 ± 0.56	0.07 ± 0.01	0.91						

Table S 1. The parameters of Lagergren's first-order equation and Ho-Mckay's second-order equation, found after the fitting of kinetics data for the sorption of $Cr_2O_7^{2-}$, CrO_4^{2-} and ReO_4^{-} by BUT-MOF.

Langmuir, Freundlich and Langmuir-Freundlich isotherms were used to fit the sorption equilibrium data. The expressions of the three model equations are the following:

a) Langmuir

$$q = q_m \frac{bC_e}{1 + bC_e}$$

b) Freundlich

$$q = K_F C_e^{\frac{1}{n}}$$

c) Langmuir-Freundlich

$$q = q_m \frac{(bC_e)^{\frac{1}{n}}}{1 + (bC_e)^{\frac{1}{n}}}$$

where q (mg/g) is the amount of the ion 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.^{8,9}

		00								
Cr₂O7 ²⁻ STEP 1		Langmuir		Freundlich				Langmuir -Freundlich		
MOF	q₌ (mg/g)	b (L/mg)	R²	K (L/g)	n	R²	q₌ (mg/g)	b (L/mg)	n	R²
ET-MOF	158±3	0.13±0.02	0.96	62±10	6.8±1.3	0.87	169±5	0.11±0.02	1.5±0.2	0.99
PROP-MOF	150±8	1.76±0.72	0.80	73±12	8.9±2.1	0.78	162±33	1.84±0.53	2.3±1.9	0.78
SBUT-MOF	162±11	0.03±0.02	0.86	49±8	5.6±0.8	0.93	NA	NA	NA	NA
BUT-MOF	188±8	0.05±0.02	0.99	55±8	5.4±0.7	0.93	235±34	0.03±0.02	2.1±0.5	0.96
STEP 2		Langmuir			Freundlich			Langmuir-Freundl	ich	
MOF	q₌ (mg/g)	b (L/mg)	R ²	K (L/g)	n	R ²	q₀ (mg/g)	b (L/mg)	n	R ²
ET-MOF	290±42	0.2 10 ⁻² ±0.9 10 ⁻⁵	0.57	25±21	3.4 ±1.3	0.51	217±1	1.0 10 ⁻³ ±1.3 10 ⁻⁵	0.08±0.01	0.99
PROP-MOF	NA	NA	NA	NA	NA	NA	447±26	6.3 10 ⁻⁴ ±2.7 10 ⁻⁵	0.17±0.05	0.88
SBUT-MOF	NA	NA	NA	NA	NA	NA	451±47	6.4 10 ⁻⁴ ±8.3 10 ⁻⁵	0.37±0.14	0.86
BUT-MOF	NA	NA	NA	NA	NA	NA	505±80	6.45±1.8 10⁻⁵	0.14±0.03	0.94

Table S 2. The parameters of Langmuir, Freundlich and Langmuir-Freundlich isotherms, found after the fitting of the isotherm sorption data of $Cr_2O_7^{2-}$ for the reported Zr⁴⁺ MOFs. The fitting data with the best R² values are highlighted with bold characters.

CrO ₄ ²⁻	Langmuir		Freundlic	Freundlich							
STEP 1											
MOF	q _e	b	R ²	K _F	n	R ²	q _e	b	n	R ²	
	(mg/g)	(L/mg)		(L/g)			(mg/g)	(L/mg)			
ET-MOF	89±10	0.03±0.02	0.78	25±4	4.8±0.6	0.95	NA	NA	NA	NA	
PROP-MOF	64±3	5.99±2.22	0.91	35±5	8.1±1.9	0.85	72±8	1.72±1.3	2.2±0.8	0.93	
SBUT-MOF	65±5	0.03±0.01	0.88	17±3	16.6±2.9	0.96	NA	NA	NA	NA	
BUT-MOF	65±4	5.56±3.12	0.70	39±3	9.6±1.3	0.94	103±38	0.09±0.35	4.5±1.9	0.95	
STEP 2	Langmuir			Freundlic	Freundlich			eundlich			
MOF	q _e	b	R ²	K _F	n	R ²	q _e	b	n	R ²	
	(mg/g)	(L/mg)		(L/g)			(mg/g)	(L/mg)		n	
ET-MOF	NA	NA	NA	NA	NA	0.51	187±2	0.2 10 ⁻² ±6.6 10 ⁻⁶	0.03±0.01	0.99	
PROP-MOF	NA	NA	NA	NA	NA	NA	139±16	0.02±1.9 10 ⁻⁴	0.27±0.12	0.85	
SBUT-MOF	NA	NA	NA	NA	NA	NA	156±4	0.2 10 ⁻² ±4.3 10 ⁻⁵	0.12±0.02	0.97	
BUT-MOF	NA	NA	NA	NA	NA	NA	153±1	0.2 10 ⁻² ±2.7 10 ⁻⁶	0.07±0.02	0.99	

Table S 3. The parameters of Langmuir, Freundlich and Langmuir-Freundlich isotherms, found after the fitting of the isotherm sorption data of CrO₄²⁻ for the reported Zr⁴⁺ MOFs. The fitting data with the best R² values are highlighted with bold characters.

ReO4 ⁻	Langmuir			Freundlie	ch		Langmuir -Freundlich				
STEP 1											
MOF	q _e	b	R ²	K _F	n	R ²	q _e	b	n	R ²	
	(mg/g)	(L/mg)		(L/g)			(mg/g)	(L/mg)			
ET-MOF	NA	NA	NA	9±42	1.8±0.1	0.99	NA	NA	NA	NA	
PROP-MOF	455±84	0.002±8.2 10 ⁻⁴	0.93	8±4	1.9±0.3	0.94	NA	NA	NA	NA	
SBUT-MOF	524±74	0.002±7.1 10 ⁻⁴	0.93	13±3	2.1±0.1	0.99	NA	NA	NA	NA	
BUT-MOF	354±40	0.05±0.02	0.89	23±3	2.7±0.1	0.99	NA	NA	NA	NA	
STEP 2	Langmuir			Freundlich			Langmuir-Fre	eundlich			
MOF	q _e	b	R ²	K _F	n	R ²	q _e	b	n	R ²	
	(mg/g)	(L/mg)		(L/g)			(mg/g)	(L/mg)			
ET-MOF	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
PROP-MOF	NA	NA	NA	NA	NA	NA	734±10	7.2 10 ⁻⁴ ±1.1 10 ⁻⁵	0.27±0.02	0.99	
SBUT-MOF	NA	NA	NA	NA	NA	NA	640±51	6.3 10 ⁻⁴ ±5.6 10 ⁻⁶	0.03±0.01	0.95	
BUT-MOF	NA	NA	NA	NA	NA	NA	868±23	6.1 10 ⁻⁴ ±1.7 10 ⁻⁵	0.24±0.04	0.96	

Table S 4. The parameters of Langmuir, Freundlich and Langmuir-Freundlich isotherms, found after the fitting of the isotherm sorption data of ReO₄⁻ for the reported Zr⁴⁺ MOFs. The fitting data with the best R² values are highlighted with bold characters.



Figure S 1. ReO_4^- isotherm sorption data for BUT-MOF in a 1 M HNO₃ solution. The blue lines represent the fitting with the Langmuir - Freundlich model.



Figure S 2. ReO_4^- isotherm sorption data for BUT-MOF in pH[~]9, fitting with the various models. Red: Langmuir model; Blue: Langmuir - Freundlich model.

ReO ₄ -	Langmuir			Freundlich La			Langmuir -Freundlich				
STEP 1											
BUT-MOF	q e	b	R ²	K _F n		R ²	q _e	b	n	R ²	
	(mg/g)	(L/mg)		(L/g)			(mg/g)	(L/mg)			
Isotherm in 1 M HNO ₃	239±40	6.4 10 ⁻³ ±3.4 10 ⁻³	0.81	18±15	2.8±1.1	0.68	186±10	0.01 ±7.7 10 ⁻⁴	0.20±0.08	0.94	
Isotherm in pH~9	142±21	0.02±0.01	0.84	NA	NA	NA	NA	NA	NA	NA	
STEP 2	Langmuir			Freundlich			Langmuir-Fre	eundlich			
BUT-MOF	q e	b	R ²	K _F	n	R ²	q e	b	n	R ²	
	(mg/g)	(L/mg)	N	(L/g)		n	(mg/g)	(L/mg)		n	
Isotherm in 1 M HNO ₃	NA	NA	NA	NA	NA	NA	776±59	8.8 10 ⁻⁴ ±5.3 10 ⁻⁵	0.21±0.07	0.88	
Isotherm in pH~9	NA	NA	NA	NA	NA	NA	504±7	0.002 ±7.5 10 ⁻⁵	0.40±0.04	0.99	

Table S 5. The parameters of Langmuir, Freundlich and Langmuir-Freundlich isotherms, found after the fitting of the isotherm sorption data of ReO₄- in cHNO₃ and pH~9 solutions for the BUT-MOF. The fitting data with the best R² values are highlighted with bold characters.



Figure S 3. $Cr_2O_7^{2-}$, CrO_4^{2-} and ReO_4^{-} isotherm sorption data for ET-MOF fitting with the various models. Red: Langmuir model; Blue: Langmuir - Freundlich model; Green: Freundlich model.



Figure S 4. $Cr_2O_7^{2^\circ}$, $CrO_4^{2^\circ}$ and ReO_4^{-} isotherm sorption data for PROP-MOF fitting with the various models. Red: Langmuir model; Blue: Langmuir - Freundlich model.



Figure S 5. $Cr_2O_7^{2-}$, CrO_4^{2-} and ReO_4^{-} isotherm sorption data for SBUT-MOF fitting with the various models. Red: Langmuir model; Blue: Langmuir - Freundlich model.



Figure S 6. Percentage (%) sorption of Cr(VI) by ET-MOF in the pH range of 1-10.



Figure S 7. Percentage (%) sorption of Cr(VI) by PROP-MOF in the pH range of 1-10.



Figure S 8. Percentage (%) sorption of Cr(VI) by SBUT-MOF in the pH range of 1-10.



Figure S 9. Percentage (%) sorption of ReO_4^- by BUT-MOF in the pH range of 1-10.



Figure S 10. ReO_4^- sorption data for alkyl-amino functionalized MOFs in the presence of various competitive anions.



Figure S 11. $Cr_2O_7^{2-}$ sorption data for alkyl-amino functionalized MOFs in the presence of various competitive anions.



Figure S 12. CrO_4^{2-} sorption data for alkyl-amino functionalized MOFs in the presence of various competitive anions.

Table S 6. Ph	ysicochemical	characteristics of	f bottled	water	sample.
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	Total Hardness (CaCO _{3,} mg/L)	рН	NO ₃ ⁻ (mg/L)	Cl [.] (mg/L)	SO4 ²⁻ (mg/L)	HCO ₃ - (mg/L)	Ca²+ (mg/L)	Mg ²⁺ (mg/L)	Na⁺ (mg/L)	K+ (mg/L)
Bottled water	223.5	7.8	0.83	5.02	7.71	241.5	80.7	5.34	2.24	0.6



Figure S 13. a) Photographic image of as synthesized BUT-MOF/alginate beads and b) SEM image of a single BUT-MOF/alginate bead.



Figure S 14. Experimental setup for the continuous flow sorption experiments.

10 min

2 h

NA

NA

NA

3 min

5-9

NA

5-10

5-10

5-10

5-10

TMU-30

13@Fe₃O₄

PROP-MOF

SBUT-MOF

BUT-MOF

ET-MOF

HPU-

323.4

471.69

187

139

156

153

	•						
Target	MOF-based sorbent	Capacity mg/g	Equilibrium time	Working pH range	Selectivity	Reusability	Sorption under Flow condition
CrO ₄ ²⁻	SLUG-21	60	48 h	NA	vs. NO ₃ ⁻ , CO ₃ ²⁻	NA	NA
	1-ClO ₄	62.88	6 h	NA	vs. halide ions	Limited	NA
	Zn-Co-SLUG- 35	68.5	2 h	NA	vs. NO ₃ ⁻ , SO ₄ ²⁻	NA	NA
	1-NO ₃	82.5	90 min	5-6	vs. NO ₃ ⁻ , SO ₄ ²⁻	Reusable	NA
	Zn-MOF	97.8	5 h	NA	vs. NO ₃ ⁻ , ClO ₄ ⁻ , Cl ⁻ , Br ⁻ , BF ₄ ⁻ , SO ₄ ²⁻	Reusable	NA
	SCNU-Z1-Cl	149.5	30 min	NA	vs. Cl ⁻ , N ₃ ⁻ , NO ₃ ⁻ , ClO ₄ ⁻ , SO ₄ ²⁻	Reusable	NA
	MOR-2	263.8	1 min	5-10	vs. Cl ⁻ , NO ₃ ⁻ , Br ⁻ and mixture of various ions in genuine water sample	Reusable	Performed
	AI-MOF-1	277.6	1 min	5-7	vs. Cl^2 , NO_3^2 HCO $_3^2$ and mixture of various ions in genuine water sample	Not reusable but recyclable	NA
	TJU-1	279	24 h	NA	vs. Cl ⁻ . HCO ₂ ⁻ . SO ₄ ²⁻ . NO ₂ ⁻	Reusable	NA

vs. various competitive ions

vs. F⁻, NO₃⁻, Cl⁻, H₂PO₄⁻, Br⁻, SO₄²⁻

vs. Cl⁻, HCO₃⁻, SO₄²⁻, NO₃⁻, HPO₄²⁻ and mixture NA

vs. Cl⁻, HCO₃⁻, SO₄²⁻, NO₃⁻, HPO₄²⁻ and mixture NA

vs. Cl⁻, HCO₃⁻, SO₄²⁻, NO₃⁻, HPO₄²⁻ and mixture NA

vs. Cl⁻, HCO₃⁻, SO₄²⁻, NO₃⁻, HPO₄²⁻ and mixture NA

of various ions in genuine water sample

Table S 7. Comparison of the CrO₄²⁻ sorption properties of Alkyl-amino functionalized MOFs with other state-of-the-art MOF-based sorbents.

Ref

10 11 12

17

18 19

20

This study

This study

This study

This study

NA

Reusable

NA

NA

NA

NA

NA

NA

Target	MOF-based sorbent	Capacity mg/g	Equilibri um time	Working pH range	Selectivity	Reusability	Sorption under flow conditions	Ref.
Cr ₂ O ₇ ²⁻	FIR-53	74.2	30 min	NA	vs. Cl ⁻ , Br ⁻ , NO ₃ ⁻	Reusable	NA	21
	γ-Fe ₂ O ₃ /C@HKUST-1	101.4	35 h	NA	NA	Reusable	NA	22
	FIR-54	103	30 min	NA	NA	Reusable	NA	21
	Al-MOF-1	130.8	1 min	2-4	vs. Cl ⁻ , NO ₃ -	Not reusable but recyclable	NA	17
	MP@ZIF-8	136.56	8 h	2-4	NA	Reusable	NA	23
	1- SO ₄	166	72 h	NA	vs. NO ₃ ⁻ , BF ₄ ⁻ , CF ₃ SO ₃ ⁻ , ClO ₄ ⁻	NA	NA	24
	MONT-1	211.8	24 h	NA	NA	Reusable	NA	25
	JLU-MOF60	222.5	91 min	NA	NA	NA	NA	26
	ZJU-101	245	10 min	NA	vs. halide ions, NO ₃ ⁻ , SO ₄ ²⁻	NA	NA	27
	ABT·2ClO ₄	214-272	48 h	NA	vs. NO ₃ ⁻ , BF ₄ ⁻ , CF ₃ SO ₃ ⁻	NA	NA	28
	MOR-1-HA	242 ²⁹ - 280 ³⁰	3 min	1-4	vs. Cl ⁻ , Br ⁻ , NO ₃ ⁻ , SO ₄ ²⁻	Reusable	Performed	29,30
	IL-MIL-100(Fe)	285.7	5h	2-4	NA	NA	NA	31
	Cd(II) MOF	228	30 min	NA	vs. halide ions, NO_3^- , SO_4^{2-}	NA	NA	32
	SCNU-Z1-Cl	305.8	30 min	NA	vs. Cl ⁻ , N ₃ ⁻ , NO ₃ ⁻ , ClO ₄ ⁻ , SO ₄ ²⁻	Reusable	NA	15
	HPU-13@Fe ₃ O ₄	398.41	10 h	NA	vs. F ⁻ , NO ₃ ⁻ , Cl ⁻ , H ₂ PO ₄ ⁻ , Br ⁻ , SO ₄ ²⁻	Reusable	NA	20
	MOR-2	402.3	1 min	1-4	vs. Cl ⁻ , NO ₃ ⁻ , Br ⁻ and mixture of various ions in genuine water sample	Reusable	Performed	16
	UTSA-74@FeSO ₄	1653.3	50 min	NA	NA	NA	NA	33
	Fe-GA (D)	1709.2	10 min	3-4	vs. various ions	Not reusable	NA	34
	ET-MOF	217	NA	1-4	Cl ⁻ , SO ₄ ²⁻ , NO ₃ ⁻ and mixture of various ions in genuine water sample	NA	NA	This study
	PROP-MOF	447	NA	1-4	Cl ⁻ , SO ₄ ²⁻ , NO ₃ ⁻ and mixture of various ions in genuine water sample	NA	NA	This study
	SBUT-MOF	451	NA	1-4	Cl ⁻ , SO ₄ ²⁻ , NO ₃ ⁻ and mixture of various ions in genuine water sample	NA	NA	This study
	BUT-MOF	505	3 min	1-4	Cl ⁻ , SO ₄ ²⁻ , NO ₃ ⁻ and mixture of various ions in genuine water sample	Reusable	Performed	This study

Table S 8. Comparison of the Cr₂O₇²⁻ sorption properties of alkyl-amino functionalized MOFs with other state-of-the-art MOF-based sorbents.

Target	MOF-based sorbent	Capacity	Equilibri	Working	Selectivity	Reusability	Sorption under	Ref.
		mg/g	um	pH range			flow conditions	
			time					25
ReO ₄ -	Zr-tcppMe	121	24 h	NA	vs. NO_3^- , CO_3^{2-} , NO_2^-	Reusable	NA	35
	Zr-tcbpMe	128	24 h	NA	vs. NO_3^-, CO_3^{2-}	Reusable	NA	35
	NU-1000	210	5 min	NA	vs. Cl ⁻ , Br ⁻ , l ⁻ , NO ₃ ⁻ , SO ₄ ²⁻	Reusable	NA	36
	SCU-101	217	10 min	3-12	vs. CO ₃ ²⁻ , PO ₄ ³⁻ , PO ₄ ²⁻ , NO ₃ ⁻ , ClO ₄ ⁻	Reusable	NA	37
	SCNU-Z1-Cl	303	30 sec	NA	vs. Cl ⁻ , ClO ₄ ⁻ , SO ₄ ²⁻	Reusable	NA	15
	SCU-100	541	30 min	1-13	vs. SO ₄ ²⁻ , NO ₃ ⁻ , PO ₄ ³⁻ , CO ₃ ²⁻	Reusable	NA	38
	SLUG-21	601.83	48 h	NA	vs. CO ₃ ²⁻ , NO ₃ ⁻ , ClO ₄ ⁻ , CrO ₄ ²⁻	NA	NA	10
	SBN	786	10 min	3-9	vs. CO ₃ ²⁻ , H ₂ PO ₄ ⁻ , SO ₄ ²⁻ , Cl ⁻ , NO ₃ ⁻ , ClO ₄ ⁻	NA	NA	39
	SCU-CPN-1	999	30 sec	2-12	vs. SO ₄ ²⁻ , NO ₃ ⁻	Reusable	NA	40
	SCU-CPN-2	1467	30 sec	2-12	vs. SO ₄ ²⁻ , NO ₃ ⁻	Reusable	NA	41
	MOR-1	367.8	5 min	NA	vs. Cl ⁻ , Br ⁻ , NO ₃	Reusable	NA	42
	MOR-2	1025.8ª	8 min	NA	vs. Cl ⁻ , Br ⁻ , NO ₃ ⁻	Reusable	Performed	42
		800.6						
		000 7¢						
		500.7		ΝΔ	Cl^2 SO l^2 NO l^2 and mixture of various ions in		NA	
	ET-MOF	960	NA	NA .	genuine water sample	NA		This study
		734	NΔ	NA	Cl^2 , $SO_4^{2^2}$, NO_3^2 and mixture of various ions in	NΔ	NA	This study
		/34			genuine water sample			inio study
	SBUT-MOF	640	NA	NA	Cl , SO_4^2 , NO_3 and mixture of various ions in	NA	NA	This study
				• •	genuine water sample			-
		868		2-9			NA	
		776			Cl ⁻ , SO_4^{2-} , NO_3^{-} and mixture of various ions in			
	BUT-MOF	//6	4 min		genuine water sample	Reusable		This study
		FOAd						
		504"						

Table S 9. Comparison	of the ReO ₄ -sorption prope	rties of alkyl-amino functio	onalized MOFs with other sta	te-of-the-art MOF-based sorbents.
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^apH=7, ^bpH=2, ^cHNO₃ 1M, ^dpH=9

Characterization of loaded-BUT-MOF



Figure S 15. EDS spectrum of BUT-MOF/ $Cr_2O_7^{2-}$.



Figure S 16. EDS spectrum of BUT-MOF/ CrO₄²⁻.



Figure S 17. EDS spectrum of BUT-MOF/ ReO₄.



Figure S 18. XPS spectra of BUT-MOF/ $Cr_2O_7^{2-}$ and magnification of the binding energy region where the characteristic Cr $2p_{3/2}$ - $2p_{1/2}$ peaks are assigned. The Mo 3d peaks are observed as a result of the holder used for the measurement.



Figure S 19. XPS spectra of BUT-MOF/CrO₄² and magnification of the binding energy region where the characteristic Cr $2p_{3/2}$ - $2p_{1/2}$ peaks are assigned. The Mo 3d peaks are observed as a result of the holder used for the measurement.



Figure S 20. XPS spectra of BUT-MOF/ReO₄⁻ and magnification of the binding energy region where the characteristic Re $4f_{7/2}$ - $4f_{5/2}$ peaks are assigned. The Mo 3d peaks are observed as a result of the holder used for the measurement.



Figure S 21. EDS spectrum of BUT-MOF.



Figure S 22. XPS spectra of BUT-MOF/ $Cr_2O_7^{2-}$ after regeneration and magnification of the binding energy region where the characteristic Re $4f_{7/2}$ - $4f_{5/2}$ peaks are assigned. The Mo 3d peaks are observed as a result of the holder used for the measurement.



Figure S 23. XPS spectra of BUT-MOF/ReO₄⁻ after regeneration and magnification of the binding energy region where the characteristic Re $4f_{7/2}$ - $4f_{5/2}$ peaks are assigned. The Mo 3d peaks are observed as a result of the holder used for the measurement.



Figure S 24. EDS spectra of BUT-MOF/ $Cr_2O_7^{2-}$ after regeneration.



Figure S 25. EDS spectra of BUT-MOF/ReO₄ after regeneration.



Figure S 26. High resolution Cr 2p core-level photoelectron spectra of BUT-MOF/CrO₄²⁻ and BUT-MOF/Cr₂O₇²⁻ and Re 4f core-level photoelectron spectra of BUT-MOF/ReO₄⁻. The peaks appear at 578 (Cr 2p_{3/2}), 587.7 (Cr 2p_{1/2}) eV and 577.7 (Cr 2p_{3/2}), 587.2 (Cr 2p_{1/2}) for BUT-MOF/CrO₄²⁻ and BUT-MOF/Cr₂O₇²⁻ respectively. For BUT-MOF/ReO₄⁻ the peaks appear at 46.2 and 48.6 eV for $4f_{7/2}$ and $4f_{5/2}$ respectively. The corresponding values are consistent with Cr(VI) and Re(VII).



Figure S 27. N₂ sorption isotherms (77 K) for a) BUT-MOF/ $Cr_2O_7^{2-}$, b) BUT-MOF/Cr O_4^{2-} and c) BUT-MOF/ Re O_4^{-} .

Details of the structural refinement

Cell indexing, Le Bail and Rietveld refinements were performed using TOPAS.⁴³



Figure S 28. Le Bail plot of BUT-MOF/Cr₂O₇²⁻. Blue crosses: experimental points; Red line: calculated pattern; Violet line: difference pattern (exp. – calc.); Green bars: Bragg positions.



Figure S 29. Le Bail plot of BUT-MOF/CrO₄²⁻. Blue crosses: experimental points; Red line: calculated pattern; Violet line: difference pattern (exp. – calc.); Green bars: Bragg positions.



Figure S 30 Le Bail plot of BUT-MOF/ReO₄. Blue crosses: experimental points; Red line: calculated pattern; Violet line: difference pattern (exp. – calc.); Green bars: Bragg positions.

For all materials, the **BUT-MOF** framework was kept fixed during refinement and thus, refinement of coordinates or/and occupancies was performed only for oxoanions and lattice solvent molecules. We should mention that CrO_4^{2-} , $Cr_2O_7^{2-}$ or ReO_4^{-} anions were initially placed in random positions in the pores. However, after simulating annealing these anions were found near Zr^{4+} centers: Two of the O atoms of Cr(VI) anions were found in close distance to Zr^{4+} (2.2-2.3 Å), whereas only one of the O atoms of ReO_4^{-} was located close to Zr^{4+} centers. Thus, we built models with bridging CrO_4^{2-} or $Cr_2O_7^{2-}$ ligands for the Cr(VI)-loaded MOFs, whereas the model we built for the perrhenate-loaded material involved monodentate binding of the ReO_4^{-} anions. Concerning **BUT-MOF/Cr_2O_7^{2-}**, each of the four dichromate anions was described with a model based on a) two Cr atoms with half occupancies, b) one Cr atom with full occupancy and c) some of the oxygen atoms with half occupancies:



Figure S 31. Representation of the model used for the dichromate anions in BUT-MOF/ $Cr_2O_7^{2-}$.

About **BUT-MOF/CrO₄²⁻**, due to the restrictions of the space group (*I4/m*), CrO_4^{2-} anions are placed in four positions in each Zr_6 cluster and each of the Cr(VI) anion is positionally disordered over two positions:



Figure S 32. Representation of the positionally disordered chromate anions in BUT-MOF/CrO₄²⁻.

Based on the analytical data (indicating 2 CrO_4^{2-} per cluster), the occupancy of the Cr atoms and the O atoms that are not connected to Zr^{4+} metal ions were fixed to 0.25. However, the occupancies of the O atoms of chromate anions connected to the Zr^{4+} centers were fixed to 0.5, as these O atoms represent not only Cr(VI) oxygen groups but also O atoms of terminal H₂O/OH⁻ ligands that have not been replaced by the Cr(VI) species.

In the case of the ReO_4^- -loaded MOF, the structural refinement was performed in the lower symmetry I-4 space group, as refinements in I4/m space group resulted in significantly higher R_p , R_{wp} values (3-4% higher) and higher residual peaks. Initially, we tested a structural model, in I-4 space group, with 4 ReO_4^- anions (with full occupancy for the ReO_4^- anions) placed in four positions in each Zr_6 cluster. However, the results of the Rietveld refinement

were not much improved compared to those for the refinement with a model in I4/m space group. Then, we decided to build a model in which 4 ReO_4^- are distributed in eight positions in each Zr_6 cluster (see Fig. 10 in main text). Thus, the occupancies of Re and O atoms that are not bonded to Zr^{4+} were fixed to 0.5 (to consider the analytical data indicating 4 $\text{ReO}_4^$ per cluster), whereas the occupancies of O atoms ligated to Zr^{4+} were kept full as these atoms also represent terminal H₂O/OH⁻ ligands that have not been replaced by the Re(VII) species. Using the above structural model, Rietveld refinement data were much improved.

The results of the Rietveld analyses for all anion-loaded materials confirmed the accuracy of the proposed structural models. Finally, we should mention that water solvent molecules were also placed in the pores of the structures of the anion-loaded materials. The positions of water O atoms were initially found via simulating annealing methods. During Rietveld analysis, refinement of coordinates and occupancies of the O atoms of water molecules was performed. The inclusion of solvent molecules significantly improved the statistics (R_p, R_{wp} were 2-3% smaller for the solvent-containing materials than those for solvent-free MOFs) of the refinements and reduced residual peaks. Representations of the arrangement of the water solvent molecules in the pores of anion-loaded **BUT-MOF** materials are provided below:



Figure S 33. Representation of the structures of oxoanion-loaded MOFs showing the positions of water O atoms (shown as large red balls) in the pores of the materials.

CCDC 2204055-2204057 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <u>www.ccdc.cam.ac.uk/data_request/cif</u>.

Fluoresence sorption studies of BUT-MOF



Figure S 34. BUT-MOF as synthesized before (left) and after (right) excitation with a laboratory UV lamp at 360 nm.



Figure S 35. Stern-Volmer plots for the Cr(VI) quenching data in distilled water. The slope of the linear fitting represents the K_{sv} constant.

Table S 10. Comparison of the Cr(VI) sensing properties of BUT-MOF with other state-of-the-art Cr(VI) sensing probes based on MOFs.

MOF-based Sensor	LOD (ppb Cr(VI))	Quenching mechanism	K _{sv} (M ⁻¹)	Ref.
NH ₂ -Zn-MOF	405.5ª	NA	3.79 x 10 ³	44
NU-1000	187.16ª	PET	6.68 x 10 ³	6
Eu-MOF	52ª	Static and dynamic	6.65 x 10 ³	45
JLU-MOF60	39.5ª	excitation absorption and resonance energy transfer	2.96 x 10 ⁴	46
MONT-1	19.76ª	NA	9.85 x 10 ³	25
MOR-2	4ª, 35 ^b	PET	NA	16
NH ₂ -Cu-MOF Nanosheets	0.94ª	chemical reduction-oxidation and IFE	9.6 x 10⁵	47
Al-MOF-1	12.2ª, 9.2 ^b	PET/Dynamic	5.6 x 10 ^{5 a} ,	17
			3.1 x 10 ^{5 d}	
BUT-MOF	9ª, 12 ^b	collisional (dynamic) quenching /static quenching	3.2 × 10 ⁵ a	This Study

^a distilled water, ^b bottled water



Figure S 36. Control experiments of an aqueous suspension of acid-activated BUT-MOF with KNO_3 solution (10⁻² M). The numbers correspond to the total added NO_3^- in ppm.



Figure S 37. Control experiments of an aqueous suspension of acid-activated BUT-MOF with NaCl solution (10^{-2} M). The numbers correspond to the total added C¹ in ppm.



Figure S 38. Control experiments of an aqueous suspension of BUT-MOF with Na_2SO_4 solution (10⁻² M). The numbers correspond to the total added SO_4^{2-} in ppm.



Figure S 39. Fluorescence titration ($\lambda_{exc} = 400 \text{ nm}$) of acid activated BUT-MOF in aqueous suspension (0.1 mg mL⁻¹) upon the addition of aliquots of a 10⁻⁴M solution of K₂Cr₂O₇ in the presence of 100-fold excess (10⁻² M) of Cl⁻ anions. b) The linear part of the calibration curve with black circles corresponding to experimental results and the red line corresponding to a linear fit. c) Digital photograph of two samples of activated BUT-MOF suspended in water at pH 3 and illuminated with a laboratory UV lamp (360 nm). The sample in the left is free of Cr(VI) while the one in the right contains 1500 ppb Cr(VI) in the presence of 100-fold excess of Cl⁻ anions.



Figure S 40. Fluorescence titration ($\lambda_{exc} = 400 \text{ nm}$) of acid activated BUT-MOF in aqueous suspension (0.1 mg mL⁻¹) upon the addition of aliquots of a 10⁻⁴M solution of K₂Cr₂O₇ in the presence of 100-fold excess (10⁻² M) of NO₃⁻ anions. b) The linear part of the calibration curve with black circles corresponding to experimental results and the red line corresponding to a linear fit. c) Digital photograph of two samples of activated BUT-MOF suspended in water at pH 3 and illuminated with a laboratory UV lamp (360 nm). The sample in the left is free of Cr(VI) while the one in the right contains 1500 ppb Cr(VI) in the presence of 100-fold excess of NO₃⁻ anions.



Figure S 41. Fluorescence titration ($\lambda_{exc} = 400 \text{ nm}$) of acid activated BUT-MOF in aqueous suspension (0.1 mg mL⁻¹) upon the addition of aliquots of a 10⁻⁴M solution of K₂Cr₂O₇ in the presence of 10-fold excess (10⁻³ M) of SO₄²⁻ anions. b) The linear part of the calibration curve with black circles corresponding to experimental results and the red line corresponding to a linear fit. c) Digital photograph of two samples of activated BUT-MOF suspended in water at pH 3 and illuminated with a laboratory UV lamp (360 nm). The sample in the left is free of Cr(VI) while the one in the right contains 1500 ppb Cr(VI) in the presence of 100-fold excess of SO₄²⁻ anions.

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