# Supporting information file

# Preferential Separation of Radioactive $TcO_4^-$ Surrogate from a Mixture of Oxoanions by a Cationic MOF

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#### Section S1: Materials, General Characterizations and Physical Measurements

**S1.1. Materials:** All the reagents, starting materials and solvents were commercially purchased from Sigma-Aldrich, TCI Chemicals and Spectrochem depending on their availability and used without further purification. All oxoanions capture experiments were performed at ambient temperature and Milli-Q water was used. The organic linker used to synthesized iMOF-2C was synthesized utilizing previous reported protocol. <sup>[1]</sup>

**S1.2. Safety Note:** Rhenium, Arsenic and Selenium salts are toxic in nature and proper protective gear (masks, gloves) is always to be used. Therefore, all capture experiments must be carried out under strict safety precautions.

#### **S1.3.** General Characterizations and Physical Measurements:

S1.3.1. Powder X-ray diffraction (PXRD): Powder X-ray diffraction (PXRD) experiments were performed on a Bruker D8 Advanced X-ray diffractometer at room temperature using Cu K $\alpha$  radiation ( $\lambda$  = 1.5406 Å) at a scan speed of 0.5 ° min<sup>-1</sup> and a step size of 0.01° in 2 $\theta$ .

**S1.3.2. Fourier transform infrared spectroscopy (FT-IR):** The FT-IR spectra were acquired by using Bruker Optics ALPHA-II spectrophotometer using KBr pellet in 500-4000 cm<sup>-1</sup> range. The FT-IR data are reported with a wave number (cm<sup>-1</sup>) scale in 500-4000 cm<sup>-1</sup> range.

**S1.3.3. Thermogravimetric analysis (TGA):** Thermogravimetric analyses were recorded on Perkin-Elmer STA 6000 TGA analyzer by heating the samples from 40 to 800 °C under N<sub>2</sub> atmosphere with a heating rate of 10 °C min<sup>-1</sup>.

**S1.3.4. X-ray photoelectron spectroscopy (XPS):** As-obtained powder samples was stuck to conductive paste and then measured by X-ray photoelectron spectroscopy using K-Alpha+model (Thermo Fischer Scientific, UK) with Al Kα source.

**S1.3.5. Transmission electron microscopy (TEM):** TEM, High-resolution TEM imaging and STEM-EDS were performed on the HRTEM (JEM-2200FS, JEOL) operating at acceleration voltage of 200 kV. For TEM analysis, all the samples were dispersed in ethanol (0.25 mg/mL) and sonicated for 20 min. Then, the samples were left for 2 min, and the upper part of the solution was taken for preparing TEM samples on a lacey carbon-coated copper grid (Electron Microscopy Science, 200 mesh).

#### Section-S2: Detailed procedures for synthetic preparation

**S2.1. Synthesis of iMOF-2C:** Synthesis of iMOF-2C was done by following our previously reported procedure with slight modification.<sup>[1]</sup> In a typical solvothermal synthetic protocol, 1.015 g of ligand and 0.560 g of metal ion (NiSO<sub>4</sub>.xH<sub>2</sub>O) were mixed in 100 mL of water and 200 mL of DMF solvent mixture. This mixture was then transferred in a 500 mL Teflon-capped glass jar and was heated at 120 °C for 2 days. After the reaction was complete, the mixture was cooled down to room temperature. Thereafter, the compound was separated by filtration and washed with methanol and water several times. Thus, off white color powder of iMOF-2C was obtained. Further, in order to get the desolvated phase, the powder was dipped in MeOH for 2 days prior to heating under high vacuum at 90 °C to acquire guest-free phase iMOF-2C. For all oxoanions capture studies, the desolvated phase of iMOF-2C was utilized.



Scheme-S1: Schematic representation of synthesis of iMOF-2C.

**S2.2. Stability test of iMOF-2C:** The solid crystals of iMOF-2C were exposed to certain mL of 100 ppm of oxoanionic aqueous solution ( $\text{ReO}_4^-$ ,  $\text{SeO}_4^{2-}$  and  $\text{HAsO}_4^{2-}$ , each) for ~12 hours. The solid samples were filtered, dried and were used for PXRD measurement. Furthermore, the iMOF-2C treated solution was taken out and Ni<sup>2+</sup> content was analyzed by ICP spectroscopy which would correspond to any decomposition. Moreover, to check the radiation stability of the material, we exposed iMOF-2C toward various doses of gamma radiation (50, 100 and 200 kGy) using 60Co source.

#### Section-S3: Experimental section

**S3.1. General Consideration:** The aqueous solution of oxoanions ( $\text{ReO}_4^-$ ,  $\text{SeO}_4^{2-}$  and  $\text{HAsO}_4^{2-}$ ) were prepared by dissolving a certain amount of their corresponding solid salts of NaReO<sub>4</sub>, Na<sub>2</sub>SeO<sub>4</sub> and Na<sub>2</sub>HAsO<sub>4</sub><sup>-</sup> 7H<sub>2</sub>O, respectively in milli-Q water, and the different concentrations were obtained by diluting the stock solution with the proper amount of distilled water unless otherwise indicated. The concentrations of oxoanion during all the experiments were detected by ICP-MS spectroscopic analysis. All the adsorption experiments were performed at ambient conditions.

**S3.2.** Sorption kinetic study of iMOF-2C towards oxoanions of ReO<sub>4</sub><sup>-</sup>, SeO<sub>4</sub><sup>2-</sup> and HAsO<sub>4</sub><sup>2-</sup>: Typically, 3 mg of iMOF-2C was exposed to 3 ml of 30 ppm aqueous solution of oxoanions of ReO<sub>4</sub><sup>-</sup>, SeO<sub>4</sub><sup>2-</sup> and HAsO<sub>4</sub><sup>2-</sup>. The solutions were stirred to ensure sufficient contact time. At specific time intervals ranging from 1 min to 1440 min, suspensions were separated by 0.22  $\mu$ m syringe filter and were diluted with 2-3% HNO<sub>3</sub> acid solution for further analysis by ICP spectroscopy.

The % removal was calculated by the following equation:

$$(C_o - C_t)/C_o] \ge 100\%$$
.

The kinetics data was fitted with different kinetic model using the following equations:

Pseudo Second order kinetic model:

$$t/q_t = 1/K_2 q_e^2 + t/q_e$$

Where,  $q_e$  is the amount adsorbed by sorbent after equilibration,  $q_t$  is the amount adsorbed by sorbent at time t,  $K_2$  (g.mg<sup>-1</sup>.min<sup>-1</sup>) is the equilibrium rate constants of second order.

S3.3. Sorption selectivity (with nonmetal-based anions) study of iMOF-2C towards oxoanions of ReO4<sup>-</sup>, SeO4<sup>2-</sup> and HAsO4<sup>2-</sup>: Selectivity experiments was performed by exposing 2 mg of iMOF-2C to 2 ml solution containing 10 ppm aqueous solution of oxoanions of ReO4<sup>-</sup>, SeO4<sup>2-</sup> and HAsO4<sup>2-</sup>, (each in individual) and solution of competing ions, Br<sup>-</sup>, NO3<sup>-</sup>, SO4<sup>2-</sup>, ClO4<sup>-</sup>, Cl<sup>-</sup>, CO3<sup>2-</sup> with an effective concentration 10 ppm, each. The solutions were stirred to ensure sufficient contact time and after 12 h, suspensions were separated by 0.22  $\mu$ m syringe filter and were diluted with 2-3% HNO3 acid solution for further analysis by ICP spectroscopy.

**S3.4.** Sorption selectivity (with metal-based oxoanions) study of iMOF-2C towards oxoanions of ReO4<sup>-</sup>: For selectivity test in the presence of metal-based oxoanions, 2 mg of iMOF-2C was exposed to 2 mL of 10 ppm aqueous solution of  $\text{ReO4}^{-}$  along with equal and higher concentration ratios of 10 ppm, 100 ppm and 10000 ppm of aqueous solution of  $\text{SeO4}^{-2}$  and  $\text{HAsO4}^{-2}$  (in both individual (binary) and mix (ternary)). After 12 h, the solutions were separated by 0.22 µm syringe filter and were diluted with 2-3% HNO3 acid solution for further analysis by ICP spectroscopy.

S3.5. Sorption capacity study of iMOF-2C towards oxoanions of ReO<sub>4</sub>, SeO<sub>4</sub><sup>2-</sup> and HAsO<sub>4</sub><sup>2-</sup>: The uptake capacities were performed by batch experiments, wherein 5 mg of iMOF-2C was dispersed in 5 ml (m/V = 1 g/L) aqueous solution of oxoanions of ReO<sub>4</sub><sup>-</sup>, SeO<sub>4</sub><sup>2-</sup> and HAsO<sub>4</sub><sup>2-</sup> and the mixture was stirred to ensure maximum contact. After 24 h, the solutions were separated by 0.22  $\mu$ m syringe filter and solutions were diluted further with 2-3% HNO<sub>3</sub> acid solution for ICP spectroscopic analysis. The ICP measurements were performed three times.

The adsorption capacity was determined by the following formula:

 $Q = (Co - Ct) \times V/m$  where Co and Ct are the initial and final concentration of elements in solution, V = volume of the oxoanionic solution taken, m = mass of the adsorbent (MOF).

**S3.6.** Sorption study of iMOF-2C in different waste-water condition: Different real water systems such as lake, river, tap, sea and D.I. water was spiked with 20 ppm of  $\text{ReO}_4^-$  salt. Similar sorption kinetic study was performed in each case, as described in section S3.2.

# Section S4: Structural Characterizations of iMOF-2C



Fig. S1: SCXRD structure of iMOF-2C showing the octahedral geometry of  $Ni^{2+}$  metal center.



Fig. S2: SCXRD structure of iMOF-2C showing the 2D layers and hydrophobic pore environment.



Fig. S3: PXRD profile of iMOF-2C.



Fig. S4: TGA profile of iMOF-2C.



Fig. S5: FTIR spectra of iMOF-2C.



Fig. S6: TEM and high resolution (HRTEM) images of iMOF-2C.



Fig. S7: STEM-EDS data and corresponding elemental mapping images of iMOF-2C.



Fig. S8a: PXRD profile of iMOF-2C treated with water and aqueous oxoanionic solution.



Fig. S8b: PXRD profile of iMOF-2C after irradiation of various doses of gamma radiation.





**Fig. S9:** (a)  $\text{ReO}_4^-$  concentration decrease with respect to time, (b)  $\text{ReO}_4^-$  sorption capacity with respect to time.



**Fig. S10:** (a)  $SeO_4^{2-}$  concentration decrease with respect to time, (b)  $SeO_4^{2-}$  sorption capacity with respect to time.



**Fig. S11:** (a)  $HAsO_4^{2-}$  concentration decrease with respect to time, (b)  $HAsO_4^{2-}$  sorption capacity with respect to time.



**Fig. S12:** Selectivity of  $SeO_4^{2-}$  capture in the presence of non-metal-based oxoanions.



**Fig. S13:** Selectivity of  $HAsO_4^{2-}$  capture in the presence of non-metal-based oxoanions.



**Fig. S14:**  $\operatorname{ReO}_4^-$  and  $\operatorname{SeO}_4^{2-}$  concentration decrease with respect to time.



**Fig. S15:** ReO<sub>4</sub><sup>-</sup> and HAsO<sub>4</sub><sup>2-</sup> concentration decrease with respect to time.



**Fig. S16:**  $\text{ReO}_4^-$ ,  $\text{SeO}_4^{2-}$  and  $\text{HAsO}_4^{2-}$  concentration decrease with respect to tiICPme.



Fig. S17: Sequestration efficiency of iMOF-2C for ReO<sub>4</sub><sup>-</sup> in different waste water systems.

# Section S6: Post Oxoanions Capture Characterizations

**Table S1:** Concentration of Ni<sup>2+</sup> ion in the supernatant of iMOF-2C exposed to toxic oxoanions of  $\text{ReO}_4^-$ ,  $\text{SeO}_4^{2^-}$ , and  $\text{HAsO}_4^{2^-}$  as recorded by ICP-MS.

Oxoanion solution	Conc. of Ni (ppb)
ReO <sub>4</sub> <sup>-</sup>	0.29
SeO4 <sup>2-</sup>	0.17
HAsO4 <sup>2-</sup>	0.21



Fig. S18: FTIR spectra of iMOF-2C treated with the oxoanionic solutions.



Fig. S19: XPS survey spectra of iMOF-2C treated with the oxoanionic solutions.



Fig. S20: Deconvoluted XPS spectra of Re 4f energy level of ReO<sub>4</sub><sup>-</sup>@iMOF-2C.



**Fig. S21:** Deconvoluted XPS spectra of Se 3d energy level of SeO<sub>4</sub><sup>2-</sup>@iMOF-2C.



**Fig. S22:** Deconvoluted XPS spectra of As 3d energy level of HAsO<sub>4</sub><sup>2-</sup>@iMOF-2C.



**Fig. S23:** (a) TEM and HRTEM images of (a, b)  $\text{ReO}_4^-@i\text{MOF-2C}$ , (c, d)  $\text{SeO}_4^{2-}@i\text{MOF-2C}$  and (e, f)  $\text{HAsO}_4^{2-}@i\text{MOF-2C}$ .



C Kα1\_2

Ν Κα1\_2

Ο Κα1



Fig. S24: STEM-EDS data and corresponding elemental mapping images of ReO<sub>4</sub><sup>-</sup>@iMOF-2C.

	Element	Wt%	Wt% Sigma	Atomic %
	C	59.51	0.81	83.75
25 CM12	Ν	1.18	0.11	2.01
2 c c c c c c c c c c c c c c c c c c c	0	5.34	0.23	5.66
1.5-	S	1.08	0.12	0.57
	Ni	12.82	0.47	3.70
- 0 ra [] - [] [se tot.2 0.5 - [N Ket.2]	Se	20.07	0.83	4.31
	Total	100.00		100.00

C Kα1\_2

Ν Κα1\_2

Ο Κα1







C Kα1\_2

Ν Κα1\_2





Fig. S26: STEM-EDS data and corresponding elemental mapping images of HAsO<sub>4</sub><sup>2-</sup>@iMOF-2C.

Compounds	Type of	Capacity	Contact time	Selectivity	Ref.
•	Material	(mg/g)			
iMOF-2C	MOF	87	10 min	$Cl^{-}, NO_{3}^{-}, Br^{-}, SO_{4}^{2-}, ClO_{4}^{-},$	This
				CO <sub>3</sub> -	work
NU-1000	MOF	85	1 min	N.D.	2
MOF-808	MOF	118	5 min	N.D.	3
UiO-66-NH <sub>2</sub>	MOF	11.9	N.D.	Cl <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , PO <sub>4</sub> <sup>3-</sup>	4
UiO-66-HCl	MOF	86.8	10 h	N.D.	5
iMOF-3C	MOF	73	5 min	Cl <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , CO <sub>3</sub> <sup>2-</sup>	6
iMOF-1C	MOF	100	4320 min	Cl <sup>-</sup> , HCO <sub>3</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> ,	7
				CO <sub>3</sub> <sup>2-</sup>	
CAU-17	MOF	20.3	600 min	NO <sub>2</sub> <sup>-</sup> , Cl <sup>-</sup> , F <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , PO <sub>4</sub> <sup>3-,</sup>	8
				$SO_4^{2-}$ , $CO_3^{2-}$ Ac <sup>-</sup> , LAS <sup>-</sup> ,	
				$B_4O_7^{2-}$ , $HPO_4^{2-}$	
Cu <sup>2+</sup> anchored	Polymer	83	600 min	SO4 <sup>2-</sup>	9
diaminofunctionalized					
MCM-41					
MgAl-MoS <sub>4</sub> -LDH	LDH	85	30 min	N.D.	10

**Table S2:** Comparison for state-of-the-art materials available for capture of  $SeO_4^{2^-}$  oxoanion in water.

#### Section S7: References

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