Supplementary Information

A novel cationic organic network for ultra-fast and high-capacity removal of toxic oxo-anions from water

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1. General description of synthetic procedures

Liquid-state ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded using a Bruker AVANCE III 400 spectrometer. The chemical shifts (δ) are expressed in parts per million (ppm) downfield from tetramethylsilane, with the residual protonated solvent serving as an internal standard. Solid-state ¹³C cross-polarization/magic angle spinning (CP/MAS) NMR spectra were obtained on a Bruker AVANCE III 600 spectrometer. The chemical compositions and states of the samples were determined by X-ray photoelectron spectroscopy (XPS) with a Shimadzu/Kratos AXIS SUPRA+ spectrometer. Fourier transform infrared spectroscopy (FTIR) was performed on a Bruker Vertex 80V FT-IR instrument, utilising KBr discs, within the 4000-400 cm⁻¹ spectral range. Thermogravimetric analysis (TGA) was conducted using a Mettler TGA/DSC1 instrument under a nitrogen atmosphere at a heating rate of 10 °C min⁻¹. X-ray diffraction (XRD) patterns were collected on the Bruker D8Advance powder diffractometer. A Ni-filtered Cu Ka radiation source was employed at 40 kV and 20 mA, with the diffraction angles ranging from 5° to 80° and a scan rate of 0.2° s⁻¹. N₂ adsorption isotherms were measured at 77 K with an auto sorbanalyserr (Micromeritics ASAP 2460). The surface area of the samples was calculated using the Brunauer-Emmett-Teller (BET) method, and the pore size distribution was determined by the nonlocalised density functional theory (NLDFT) model.

2. Synthesis and characterisation of ImCON1

2.1 Synthesis of ImCON1



Scheme S1. Synthesis of ImCON1

Synthesis of TIMB. A 100 mL flask was charged with 1,3,5-tribromobenzene (1.260 g, 4.0 mmol), potassium carbonate (K₂CO₃, 10.000 g, 72.0 mmol), imidazole (8.170 g, 120 mmol), and copper(II) sulfate pentahydrate (CuSO₄.5H₂O, 0.100 g, 0.4 mmol). The mixture was heated under an argon atmosphere at 150 °C for 24 hours. Subsequently, the mixture was allowed to cool to ambient temperature. It was washed with water (3 × 100 mL). The solid residue was extracted using methanol (3 × 100 mL), and the obtained methanol solution was dried over sodium sulfate (Na₂SO₄). Removal of the solvent yielded a brown solid. Yield: 0.948 g (3.431 mmol, 86%). ¹H NMR (400 MHz, [*d*₆]DMSO): δ 8.55 (s, 3H, N-CH-N), 8.03 (s, 3H, imidazole-H), 7.96 (s, 3H, Ar-H), 7.18 ppm (s, 3H, imidazole-H). ¹³C NMR (100 MHz, [*d*₆]DMSO): δ 139.54 (Ar-C-N), 136.57 (N-C-N), 130.56 (imizazole-C), 118.76 (Ar-C-H), 109.76 ppm (imidazole-C). MS (EI): *m/z* (%) 276 (100) [M]⁺.

Synthesis of ImCON1. A sample of TIMB (0.221 g, 0.8000 mmol) and TBMB (0.286 g, 0.800 mmol) were dissolved in 20 mL of DMF. The solution was heated at 120 °C for 48 h under an argon atmosphere. After the reaction mixture was cooled to room temperature, the precipitate was filtered, washed with DMF and ethanol, and dried at 50 °C in vacuo overnight to afford ImCON1 (445 mg, 88% yield). FT-IR (KBr, cm⁻¹): 3406 (b), 3060 (b), 1621 (s), 1549 (s), 1502 (m), 1444 (m), 1419 (w), 1365 (w), 1268 (w), 1203 (s), 1096 (s), 1073 (w), 1010 (m), 857 (s), 774 (s), 749 (s), 675 (m), 635 (m).

2.2 Characterization of ImCON1



Fig. S1 X-ray diffraction patterns (XRD) patterns of ImCON



Fig. S2 N_2 adsorption-desorption isotherms (a) and pore size distributions (b) of ImCON1



Fig. S3 EDX mapping image of ImCON1

3. Dichromate removal studies

3.1 General procedure for dichromate exchange

Typically, ImCON1 (3 mg) was dispersed in an oxo-anions aqueous solution (0.17 mM, 10 mL) and then subjected to ultrasonic treatment for 30 seconds. After standing for the desired period, the sorbent was filtered using a syringe filter (PTFE, 0.22 µm), and a UV-vis spectrophotometer detected the resulting solution. The adsorption percentage (*Dt*) was determined based on the intensity reduction of the characteristic peak of oxo-anions, where $\lambda = 372$ nm for CrO₄²⁻, $\lambda = 350$ nm for Cr₂O₇²⁻, $\lambda = 525$ nm for MnO₄⁻. Subsequently, the exchange capacity of the material was computed using the following equation:

$$D_t = \frac{C_0 - C_t}{C_0} \times 100\% = \frac{A_0 - A_t}{A_0} \times 100\%$$

 D_t represents the exchange capacity, and C_0 and A_0 are the initial concentration and the corresponding absorbance of the oxo-anions aqueous solution, respectively. C_t and A_t are the concentration and the corresponding absorbance of the oxo-anions aqueous solution at time *t*.



Fig. S4. FTIR spectra of (a) ImCON1 and (b) CrO_4^{2-} @ImCON1 (inset, photographs of colour changes of ImCON1 before and after adsorption).



Fig. S5 FTIR spectra of (a) ImCON1 and (b) $Cr_2O_7^{2-}@ImCON1$ (inset, photographs of colour changes of ImCON1 before and after adsorption).



Fig. S6 FTIR spectra of (a) ImCON1 and (b) $MnO_4^-@ImCON1$ (inset, photographs of colour changes of ImCON1 before and after adsorption).

3.2 Kinetic Studies

An aqueous solution containing oxo-anion at a 0.5 mM concentration was prepared in 75 mL of water. This solution was blended with 3 mg of ImCON1 and subjected to ultrasonic treatment for 30 seconds. After standing for the desired period, the resultant mixture was passed through a syringe filter with a pore size of 0.22 μ m to isolate the solid component. Subsequently, the UV-Vis spectra of the filtered solution were acquired. The dichromate concentration in the treated solution was determined by comparing the UV-Vis spectra against a calibration curve. The exchange capacity of the material was computed using the methodology described previously.

Furthermore, the adsorption capacity (Q_t) at contact time t is acquired with the following equation:

$$Q_t = (\frac{C_0 - C_t}{m}) \times V$$

Herein, C_0 represents the initial concentration (mg/L) of the dichromate solution, C_t denotes the equilibrium concentration (mg/L) of the dichromate solution post-exchange at contact time *t*, *V* is the volume of the solution (L), and *m* is the weight (g) of the material employed in the experiment.

The kinetic data was fitted with the pseudo-second-order equation:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$$

Where k_2 is the kinetic constant of pseudo-second order.

Upon extending the treatment period to 1 minute, ImCON1 decreased the $\text{CrO}_4^{2^-}$ levels to below 82.5%. Further prolonging the treatment beyond 4 minutes showed no significant decline, suggesting equilibrium was reached. ImCON1 exhibited a high adsorption capacity of $\text{CrO}_4^{2^-}$ from aqueous solutions. The uptake capacity reached 259 mg g⁻¹. The kinetics data can be well-fitted with a pseudo-second-order model. The calculated rate constant was $k_2 = 0.0343$ g mg⁻¹ min⁻¹ ($R^2 > 0.999$), revealing the high adsorption rate of ImCON1. Furthermore, ImCON1 exhibited a high adsorption capacity (259 mg g⁻¹).



Fig. S7 (a) UV spectra of $\text{CrO}_4^{2^-}$ solutions before and after adding ImCON1 at different time intervals. (b) Linear fitting of the pseudo-second-order model using an initial 0.5 mM solution of $\text{CrO}_4^{2^-}$ ions.

Adsorbent name	Functional Group	CrO_4^{2-} (mg g- ¹)	References
CON-LDU5	pyridinium group	369	1
TJU-1	Positively charged unilamellar	279	2
iCON-5	Triamminoguanidium chloride	266	3
MOR-2	NH-CH ₂ -py	263	4
ImCON1	Imidazolium	259	This work
CON-LDU3	pyridinium group	232	5
Compound-1	Viologen-based cationic	133	6
1-NO3	Sliver-triazolate MOF	82.5	7
Zn-Co-SLUG-35	α, ω -alkanedisulfonate	68.5	8
1-ClO ₄	3D cationic MOF	62.9	9
PANI/CFs	Polyaniline	18.1	10

Table S1. Comparison of CrO_4^{2-} removal by materials reported in the literature.

Upon extending the treatment period to 1 minute, ImCON1 decreased the $Cr_2O_7^{2-}$ levels to below 59.6%. Further prolonging the treatment beyond 4 minutes showed no significant decline, suggesting equilibrium was reached. ImCON1 exhibited a high adsorption capacity of $Cr_2O_7^{2-}$ from aqueous solutions. The uptake capacity reached 1118 mg g⁻¹. The kinetics data can be well-fitted with a pseudo-second-order model. The calculated rate constant was $k_2 = 0.009$ mg g⁻¹ min⁻¹ ($R^2 = 0.999$), revealing the high adsorption rate of ImCON1.



Fig. S8 (a) UV spectra of $Cr_2O_7^{2-}$ solutions before and after adding ImCON1 at different time intervals. (b) Linear fitting of the pseudo-second-order model using an initial 0.5 mM solution of CrO_4^{2-} ions.

Adsorbent name	Functional Group	$Cr_2O_7^{2-}$ (mg g- ¹)	References
ImCON1	ImCON1 Imidazolium		This work
C-NSANaph-	N-spiro ammonium salt	745	11
CMPA-1	polyaniline	520	12
ImIP1	Imidazolium	423	13
QUST-iPOP-1	Imidazolium	396	14
CON-1	N-substituted pyridine	293	15
DA-POP-1	N/A(pseudo chemical	283	16
UiO-66-	amino-functionalized MOF	277	17
PTPA-PIP	Secondary and tertiary amines	230	18
TPP-ThZ CMP	Pyridine	209	19
POP-Im1	Imidazolium	172	20
1-SO4	3D cationic MOF	166	21
PANI/H-TNBs	Polyaniline-coated protonic	157	22
compound-1	N-substituted pyridine	133	23
IISERP-POF11	Phenolic OH, N-substituted	131	24
H-CMP-A2	secondary and tertiary amine	73	25

Table S2. Comparison of $Cr_2O_7^{2-}$ removal by materials reported in the literature.

Upon extending the treatment period to 3 minutes, ImCON1 decreased the MnO₄⁻ levels to below 54.5%. Further prolonging the treatment beyond 2 minutes showed no significant decline, suggesting equilibrium was reached. ImCON1 exhibited a high adsorption capacity of MnO₄⁻ from aqueous solutions. The uptake capacity reached 694.5 mg g⁻¹. The kinetics data can be well-fitted with a pseudo-second-order model. The calculated rate constant was $k_2 = 0.0037$ mg g⁻¹ min⁻¹ ($R^2 = 0.9979$), revealing the high adsorption rate of ImCON1.



Fig. S9 (a) UV spectra of MnO_4^- solutions before and after adding ImCON1 at different time intervals. (b) Linear fitting of the pseudo-second-order model using an initial 0.5 mM solution of MnO_4^- ions.

Adsorbent name	Functional Group	MnO_{4}^{-} (mg g- ¹)	References
ImCON1	Imidazolium	694.5	This work
QUST-iPOP-1	Imidazolium	514.7	14
compound-1	N-substituted pyridine	297.3	23
SLUG-21	a, ω -Alkanedisulfonate	283	26
iCON-5	Triamminoguanidium chloride	201	3
IISERP-POF11	Phenolic OH, N-substituted	40	24

Table S3. Comparison of MnO₄⁻ removal by materials reported in the literature.

3.3 Adsorption isotherm experiments

3 mg of ImCON1 was introduced into 10 mL of specific anion solutions with varying concentrations and then subjected to ultrasonic treatment for 30 seconds. The mixture was allowed to stand for 2 hours. Subsequently, the resulting mixture was filtered through a syringe filter with a pore size of $0.22 \,\mu$ m to separate the solid component. The filtrate was analysed using UV-vis spectroscopy. The data obtained were utilised to fit with the Langmuir isotherm model, which follows the equation:

$$\frac{C_{\rm e}}{Q_{\rm e}} = \frac{1}{Q_{\rm m}K_{\rm L}} + \frac{1}{Q_{\rm m}}C_{\rm e}$$

 C_e (mM) is the anionic pollutant concentration at equilibrium, and Q_m (mg g⁻¹) is the maximum capture capacity.



Fig. S10 Linear fitting of the pseudo-second-order model using an initial 0.5 mM solution of CrO_4^{2-1} ions.



Fig. S11 Linear fitting of the pseudo-second-order model using an initial 0.5 mM solution of $Cr_2O_7^{2-1}$ ions.



Fig. S12 Linear fitting of the pseudo-second-order model using an initial 0.5 mM solution of MnO_4^- ions.

3.4 pH-Dependency experiments

Solutions containing 0.17 mM oxo-anions at varied pH levels were prepared in 10 mL of water. These solutions were then combined with 3 mg of ImCON1, and then subjected to ultrasonic treatment for 30 seconds. After standing for 5 min, the sorbent was filtered using a syringe filter (PTFE, 0.22 μ m), and a UV-vis spectrophotometer detected the resulting solution. Finally, the exchange capacities of the materials were calculated using the equation mentioned above.



Fig. S13 FT-IR spectra of ImCON1, ImCON1 treated with HCl and ImCON1 treated with NaOH

3.5 Selectivity experiments in the presence of competing anions

The effect of competing anions was scrutinised to investigate the selectivity of ImCON1 in the presence of interfering anions. Aqueous solutions of oxo-anions (0.17 mM, 10 mL) and 10 molar equivalents of F^- , Cl^- , Br^- , I^- , SO_4^{2-} and NO_3^{-} concerning oxo-anions were prepared. In the presence

of a single competing anion, the experiments were performed by immersing ImCON1 (3 mg) into the mixture and then subjected to ultrasonic treatment for 30 seconds. After standing for 5 min, the sorbent was filtered using a syringe filter (PTFE, 0.22 μ m), and a UV-vis spectrophotometer detected the resulting solution. Finally, the exchange capacities of the materials were calculated using the equation mentioned above.

3.6 Temperature-dependency experiments

Solutions containing 0.51 mM $\text{CrO}_4^{2^-}$ at varied temperatures were prepared in 75 mL of water. These solutions were then combined with 3 mg of ImCON1, and then subjected to ultrasonic treatment for 30 seconds. After standing for 30 min, the sorbent was filtered using a syringe filter (PTFE, 0.22 μ m), and a UV-vis spectrophotometer detected the resulting solution. Finally, the exchange capacities of the materials were calculated using the equation mentioned above.



Fig. S14. The capacities of ImCON1 for CrO_4^{2-} ion at varied temperatures.

3.7 Column experiments

At the base of a glass column, 100 mg of ImCON1 was carefully packed. An oxo-anion solution with a concentration of 0.5 mM was then introduced into the column and allowed to flow through. The filtrate was collected in a conical flask. The UV–vis spectra of the filtrate were recorded after the treatment to evaluate the efficiency of the material in binding the oxo-anions. Subsequently, for the regeneration of the column, a 0.5 M aqueous NaBr solution was passed through the column that had previously captured oxo-anions. This process restored the column's functionality for further use in oxo-anions removal.

3.8 Adsorption experiments of industrial wastewater

ImCON1 (3 mg) was dispersed in an industrial wastewater sample containing $Cr_2O_7^{2-}$ anions (obtained from Dongzheng Chemical Co., Ltd. in Shangnan County, Shaanxi Province, China), and then subjected to ultrasonic treatment for 30 seconds. After standing for the desired period, the sorbent was filtered using a syringe filter (PTFE, 0.22 µm), and a UV-vis spectrophotometer detected the resulting solution. The dichromate concentration in the treated solution was determined by comparing the UV-Vis spectra against a calibration curve. The exchange capacity of the material was computed using the methodology described previously.



Fig. S15. UV spectra of industrial wastewater sample containing $Cr_2O_7^{2-}$ anions before and after adding ImCON1 at different time intervals.

3.9 Zeta potential measurements



Fig. S16. Zeta potential measurements on ImCON1 before (a) and after the adsorption of $Cr_2O_7^{2-}$ (b).

3.10 DFT simulation

Based on DFT, the saturated adsorption configuration is optimized by using the sorption package in Materials Studio. Electron exchanges and interactions are modelled using the Perdue-Berke-Enzerhoff (PBE) functional under the generalized gradient approximation (GGA). The all-electron dual-valued atomic orbitals augmented by the p-polarization function (DNP+) are selected as the basis set, and the orbital cutoff quality was set to fine. Since the numerical basis set minimization implemented by sorption even eliminates the basis set superposition error, the basis set superposition error (BSSE) is not considered in the calculation.



Fig. S17. Optimized structures of ImCON1 (a), $CrO_4^{2-}@ImCON1$ (b), $Cr_2O_7^{2-}@ImCON1$ (c), $MnO_4^{-}@ImCON1$ and after the adsorption of $Cr_2O_7^{2-}$ (d).

	Table S4. Averag	ge isosteric	heats and	adsorption	distance of	of sorbates.
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Sorbate	Average isosteric heats	Adsorption distance
	kcal/mol	Å
Br	66.938	2.738
$\mathrm{CrO_4}^{2-}$	611.961	2.116
$Cr_{2}O_{7}^{2-}$	609.029	2.447
MnO_4^-	612.196	3.133

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