

Imidazolium-Functionalized Chemically Robust Ionic Porous Organic Polymers (*i*POPs) toward Toxic Oxo-Pollutants Capture from Water

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Abstract: Fabricating new and efficient materials aimed at containment of water contamination, in particular removing toxic heavy metal based oxo-anions (e.g. CrO_4^{2-} , TcO_4^{-}) holds paramount importance. In this work, we report two new highly stable imidazolium based ionic porous organic polymers (*i*POPs) decorated with multiple interaction sites along with electrostatics driven adsorptive removal of such oxoanions from water. Both the *i*POPs (namely, *i*POP-3 and *i*POP-4) exhibited rapid sieving kinetics and very high saturation uptake capacity for CrO_4^{2-} anions (170 and 141 mgg⁻¹ for *i*POP-3 and *i*POP-4 respectively) and ReO_4^{-} (515.5 and

Introduction

Accessibility to fresh drinking water has become an imminent threat in the 21st century that have direct impact on human lives. The far-flung growth in industrialization and widespread urbanization across the globe are the two prime reasons behind such crisis and depletion of fresh water.^[1] This situation might become so dreadful that as many as one billion of global population will experience utmost water crisis by 2025, as predicted by United Nations.^[2] Among various contamination sources, water pollution by heavy metals (density $> 5 \text{ g cm}^{-3}$) and their oxo-anionic complexes (CrO₄²⁻, MnO₄⁻, SeO₃²⁻, AsO₄³⁻ etc.) have come forth as pressing concern, owing to their severe toxic effect on living organisms upon bioaccumulation.^[3] In addition, such toxic oxo-anions are considered as the "priority pollutants", listed by Environment Protection Agency (EPA, United States).^[4] In this context, special attention has been directed toward Cr(VI) based oxo-anions because of their

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350.3 mg g⁻¹ for *i*POP-3 and *i*POP-4 respectively), where ReO₄⁻ anions being the non-radioactive surrogative counterpart of radioactive TcO₄⁻ ions. Noticeably, both *i*POPs showed exceptional selectivity towards CrO_4^{2-} and ReO_4^{-} even in presence of several other concurrent anions such as Br⁻, Cl⁻, SO₄²⁻, NO₃⁻ etc. The theoretical binding energy calculations via DFT method further confirmed the preferential interaction sites as well as binding energies of both *i*POPs towards CrO_4^{2-} and ReO_4^{-} over all other competing anions which corroborates with the experimental high capacity and selectivity of *i*POPs toward such oxo-anions.

carcinogenic and mutagenic impact on living beings.^[5] Several industrial sectors including leather tanning, steel manufacturing, textile pigments & dyes, wood preservation etc. are involve in chromium usage in huge amounts for diverse applications. As is known, tanning industries generate ~35 L of chromium contaminated wastewater solely for one kilogram of leather production which subsequently pollute natural water bodies.^[6] Additionally, Cr (VI) based oxo-anions are found to weaken the integrity of nuclear waste glass during its vitrification process resulting in poor efficiency of the process.^[6] Moreover, the world has witnessed several incidents of ground water pollution because of improper disposal of Cr (VI) containing wastewater.^[7] Hinkley groundwater contamination in California is one of the famous example where ~1,400 million liters of chromium containing wastewater was disposed into the natural waterbodies.^[8] In addition, other than Cr(VI)-based water pollution issues, ground water contamination by nuclear power plant generated radioactive wastes have become another major concern.^[9] In this regard, nuclear safety has become a genuine concern as the last few decades have witnessed several nuclear accidents, which lead to contamination of radioisotopes in large scale along with their chemotoxicity and radiotoxicity to natural water bodies. Among them, pertechnetate (TcO₄⁻) anion has attracted much research attention mainly as one of its β emitting radioactive isotope technetium (99Tc), which possess a very prolonged half-life period of 2.1×10⁵ years. Moreover, nuclear fission of ²³⁹Pu and ²³⁵U result into a very large fission yield of radioactive ⁹⁹Tc and approximately 305 metric tons nuclear waste containing 99Tc have been discharged from several nuclear power plants and weapons testing activities.^[10] The non-complexing characteristic of TcO₄⁻ along with its high

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mobility and solubility in water allows it to remain as low-level nuclear-waste material.^[11] Several techniques, for example, adsorption, photocatalytic reduction, chemical precipitation, ion exchange etc. have been utilized to combat this concern, but among them, ion exchange based methods are preferred over other methods owing to its comparatively simple and safe processing, high affinity and selectivity, good performance in low-concentration waste solution etc.^[12] In addition, the state of the art ion-exchangers present pitfalls such as lower uptake efficiency, poor selectivity and slow kinetics which endows possibilities to develop new alternative and more efficient ion exchange materials.^[13]

To address this demand, tremendous efforts have been employed toward the development of new sorbent materials featuring higher binding affinity and uptake efficiency.^[14] To this end, metal-organic frameworks (MOFs) and porous-organic Polymers (POPs) have strongly established themselves as the new generation ion exchangers owing to features such as tailor made tunable pore surface, charge controllability, amenability of design etc.^[15] Although MOFs are known to offer good kinetics and selectivity towards such oxo-anion extraction, but poor physiochemical stability especially under highly acidic as well as basic conditions limits the utility of these materials as sorbents towards real-time environmental remediation and nuclear fuel processing.^[16] On the contrary, porous organic polymers fabricated from stable covalent bonds not only exhibit superior physiochemical stabilities even under extreme chemical conditions but their additional beneficial features for example high surface area, radiation resistibility etc. make them front runner in comparison with other contemporary porous materials.^[17] Moreover, strategic utilization of neutral N-donor based moieties such as imidazole and benzimidazole as different crosslinking terminals with multiple halogen sites (-CH₂X; X-halogen) yield cationic porous organic polymers with positive quaternized nitrogen site and exchangeable counter halide anions. The electrostatic interaction between the counter halide anions and the host framework are known to be very weak due to which the halide counter anions assist in dispersion of cationic iPOP particles in water, resulting in rapid and efficient trapping of the aimed anionic pollutants in water via ionexchange. Additionally, incorporation of different binding sites inside the network such as triazine core, imidazole based



Toxic Oxo-pollutants trapping by ionic POPs

Scheme 1. Schematic representation of toxic oxo-anion capture in *i*POPs.

moieties, π electron rich surface etc. contribute to superior selectivity of these materials toward such oxo-anions^[5c-d,11] On account of such structural diversity and physiochemical stability, cationic porous organic frameworks certainly can be an appropriate candidate for sequestration of such hazardous oxo-anionic pollutants from water.

Considering all these aspects, here we present two novel chemically stable ionic porous organic polymers (*i*POPs), *i*POP-3 and *i*POP-4 fabricated from nitrogen rich triazine core and imidazole derivatives, bearing exchangeable bromide (Br⁻) anions inside the porous networks (Figure 1). Both the compounds are found to show highly selective and efficient capture of toxic and hazardous CrO_4^{2-} and ReO_4^- anions from water, while ReO_4^- anions were being utilized as a corresponding surrogate for radioactive TcO_4^- ions (Scheme 1).

Results and Discussion

The compounds *i*POP-3 and *i*POP-4 were synthesized via onecondensation reaction between imidazole for *i*POP-3 and benzimidazole for *i*POP-4 with Tris-(4-bromomethyl-phenyl)-[1,3,5]triazine for 24 h under inert atmosphere (Schemes S1–S3). The as-made compounds were thoroughly washed with different solvents (DMF, DMSO, THF, Toluene, MeOH, acetone and



Figure 1. Schematic representation of synthesis of iPOP-3 and iPOP-4.

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water) post synthesis to remove the trapped small chain oligomers as well as unreacted starting materials. Further, both compounds were dipped in DCM, THF and acetonitrile (1:1:1) mixture for 72 h for solvent exchange with changing of solvents frequently in repeated interval of 12 h and were kept under vacuum around 90°C for 24 h to obtain the guest free desolvated phase of iPOP-3 and iPOP-4. The guest free phases of both polymers were thoroughly characterized with ¹³C-CP-MAS NMR (cross polarization magic angle spinning nuclear magnetic resonance), Fourier transform infra-red (FTIR) spectroscopy, field emission scanning electron microscopy (FESEM), energy dispersive X-ray analysis (EDX) and thermogravimetric analysis (TGA). The ¹³C-CP-MAS NMR studies exhibited peaks around ~114 ppm to ~142 ppm (d, e, f), which corresponds to presence of aromatic carbons of imidazole and benzene rings respectively. The peak around ~51 ppm (a,b) corresponds to the formation of the methylene linkages attached with both the nitrogens of imidazole for iPOP-3 and benzimidazole for iPOP-4 for the expansion of the cationic polymeric networks. The peaks around ~169 ppm (c) corresponds to the carbon atoms of the triazine rings present at the core of iPOP-3 and iPOP-4 (Figure 2a, S1).^[18,20] TGA analysis of *i*POP-3 showed an initial weight loss (~8%) around 75°C in the pristine phase which might be attributed to the trapped solvent molecules which were removed via desolvation. The TGA curve for the desolvated phase of iPOP-3 showed negligible weight loss until 300 °C while the profile for iPOP-4 shows negligible weight loss until 350 °C confirming guest free nature (Figures 2b, S3). FESEM images revealed the presence of agglomerated particles while EDX spectroscopy and elemental mapping showed the homogeneous presence of free Br- as the counter anions in the



Figure 2. (a) Solid state NMR for *i*POP-3, the *'*'* marked peaks correspond to side bands; (b) TGA profiles for compound *i*POP-3; (c) FTIR profiles for compound *i*POP-3.

desolvated iPOP-3 and iPOP-4 networks (Figure S13-S18). FTIR spectroscopy revealed peaks ~1520 cm⁻¹ corresponding to C=N stretching frequency of constituent triazine and imidazole linkages. The peaks around $\sim 1150 \text{ cm}^{-1}$ and 750 cm⁻¹ are indicative of the presence of imidazolium based functional groups. Moreover, the peaks around ~1420 cm⁻¹ represents the stretching frequency of the methylene (-CH₂-) functional groups present while the peak at ~1370 cm⁻¹ represents the presence of triazine rings present in iPOP-3 and iPOP-4 (Figures 2c, S9).^[18,20-21] To access the stability aspect of these *i*POPs, they were subjected to harsh condition treatment of acidic (1 N HCl) as well basic (1 N NaOH) solutions for 24 h. The post treated samples were thoroughly characterized with solid state NMR (SS NMR), TGA and FTIR techniques. ¹³C SS NMR did not show any deviation from original spectra with no emergence of any new peaks accounting for unaltered structural features (Figure S10-S11). The TGA data revealed analogous profile to that of the pristine phase of iPOP-3 and iPOP-4 (Figure S4-S5) confirming the retention of thermal as well as chemical stability. Moreover, FTIR measurements substantiated the presence of all the characteristic peaks when compared with the pristine compounds (Figure 2c, S9). Further, we have performed lowtemperature gas adsorption N₂ (77 K) as well as CO₂ (195 K) data to substantiate the porosity of both iPOPs (Figure S8). We observed very lower uptakes for N₂ (77 K) for both *i*POPs whereas the CO₂ (195 K) adsorption profiles substantiated the inherent porosity with an uptake of 64 mLg⁻¹ for *i*POP-3 and 49 mLg⁻¹ for *i*POP-4. Additionally, the chemically robust nature of these iPOPs were further substantiated from its outstanding performance upon exposure to various chemical environments. A minimal loss in residual weight % (Figure S12) was observed when both of the compounds were immersed in a wide array of solutions advocating for its highly stable nature.

Such physiochemical stability along with cationic nature of both compounds propelled us to evaluate its potential towards toxic oxo-anion trapping from water. Depending upon the pH of the medium, hexavalent chromium oxo-anions, i.e. chromate (CrO_4^{2-}) and dichromate $(Cr_2O_7^{2-})$, primarily remain in interconvertible equilibrium. Hence, we further performed the capture experiments with chromate in this work. Initially, we dipped 5 mg of both iPOP-3 and iPOP-4 in a 5 mL 2 mM aqueous CrO₄²⁻ solution individually and monitored the trapping process via both naked eye color change and UV-Vis spectroscopy. A gradual color change from yellow to almost colorless for both the solutions was observed within just 1 h illustrating rapid capture of CrO_4^{2-} by both the compounds (Figures 3a-c). Enthused from such fast kinetics, we have carried out in situ titration of CrO₄²⁻ capture in water for both *i*POPs and monitored via UV-Vis spectroscopy where 2 mL 0.5 mM aqueous solution of CrO₄²⁻ was added to 1 mg of both compounds individually and the absorption maxima (λ_{max}) at 372 nm for CrO₄²⁻ ion was monitored (Figures 4a and d). The diminishing trend in UV-Vis spectra at 372 nm with increment of time affirmed trapping of CrO₄²⁻ anions in case of both compounds. As was observed, the anion trapping took place in a rapid manner with almost ~60% and ~55% removal of CrO_4^{2-} ions were observed within just 2 min while almost ~90% and ~80% 0 min

10 min

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Figure 3. Visual color change of aqueous solution of ${\rm CrO_4^{2-}}$ and corresponding iPOPs (a) upon addition of iPOP-3, (b) upon addition of iPOP-4, (c) decrease in concentration of CrO₄²⁻ with increment of time upon addition of iPOP-3.

20 min

30 min 40 min 60 min

removal was achieved within 60 min using 1 mg of iPOP-3 and iPOP-4 respectively (Figures 4a and d). The percentage removal vs. time study corroborated with the fast kinetics of the capture process by both iPOP-3 and iPOP-4 (Figure S31, S33). In addition, the saturation uptake capacity of CrO₄²⁻ evidenced from UV-vis spectroscopy are 170 mgg^{-1} and 141 mgg^{-1} for iPOP-3 and iPOP-4 respectively (Figure S35–S36). It is noteworthy to mention that these saturation uptake capacities are accounted among the highest values reported in the literature of porous materials (Table S1). The differential efficiency toward pollutant capture performance of iPOP-4 in comparison with iPOP-3 may be attributed to a combination of reduced porosity as well as enhanced hydrophobicity (Figure S8, S65). Furthermore, the post-capture phases were characterized by SS NMR, solid state UV-vis analysis, FTIR analysis, EDX and elemental analysis studies. The SS NMR confirmed retention of the characteristic peaks for both iPOPs in post-capture phases (Figure S19–S20). FTIR analysis confirmed presence of all characteristic peaks along with emergence of a new peak at ~894 cm⁻¹ correlated with the CrO_4^{2-} anions validating the retention of the network integrity (Figure S23-S24). In addition, homogeneous distribution of chromium in EDX and elemental spectra analysis confirmed the incorporation of chromate anions inside the pores of both the compounds (Figure S25-S30).

Along the same line, pertechnetate (TcO₄⁻) is another lethal oxo-anion on account of being radioactive while ⁹⁹Tc is β emitting in nature. Due to radioactivity of TcO₄⁻, we have used a non-radioactive surrogate viz. ReO₄⁻, that have similar sizecharge distribution. Further, we have performed in situ titration studies for ReO₄⁻ anions under UV-vis spectroscopy by monitoring the intensity maxima (λ_{max}) at 208 nm with increase in time intervals. Notably, both compounds exhibited similar rapid kinetics as almost ~75% and ~55% of ReO_4^- anions were found to be trapped within just 2 min by iPOP-3 and iPOP-4 respectively (Figures 4b and e). The percentage removal vs. time studies further corroborated with the rapid kinetics of the capture processes (Figure S41, S43). In addition, the saturation uptake capacities of ReO₄⁻ ions evidenced from UV-Vis spectroscopy are 515.5 mg g^{-1} and 350.3 mg g^{-1} for *i*POP-3 and *i*POP-4 respectively (Figure S41, S42), among which iPOP-3 was found to stand tall among the highest values reported in the regime of porous materials (Table S2). ¹³C NMR data of post pollutant capture phase corroborated well with the pristine compound while FTIR spectra revealed the presence of characteristic peaks for both the compounds with a new peak at ~918 cm⁻¹ corresponding to the ReO₄⁻ anions (Figure S19–S20, S23–S24). Additionally, a homogeneous distribution of rhenium along with the other elements in EDX and elemental spectra analysis confirmed the incorporation of perrhenate anions inside the pores of both the compounds (Figure S37-S40). Keeping in mind the real time applicability of our materials, we were prompted to test the competency of these compounds when subject to harsh chemical environments. To validate this, we have performed the oxo-anion capture experiments with both iPOP-3 and iPOP-4 after they were exposed to 1(N) HCl and 1(N) NaOH respectively. To our delight, both iPOPs exhibited almost intact efficiency with the acid treated phases: 99% (iPOP-3), 95% (iPOP-4) for CrO_4^{2-} and 98% (iPOP-3), 96% (iPOP-4) for ReO_4^- whereas with base treated phases: 100% (*i*POP-3), 94% (iPOP-4) towards CrO₄²⁻ capture and 99% (iPOP-3), 95% (iPOP-4) towards ReO₄⁻ anions (Figure 4i). Such results indeed underscore the utility of these iPOPs in treatment of real-world wastewater. Moreover, anion trapping by both the iPOPs followed pseudo-second-order kinetics as the time dependent uptake capacity fitting profile revealed that all the capture processes were exclusively dependent upon the quantity of adsorbent and the adsorbate used (Figure 4c, 4f, S47, S48). The correlation coefficient (R^2) values for *i*POP-3 were found to be 0.999 and 0.997 for CrO_4^{2-} and ReO_4^{-} ions respectively. On the other hand, R² values of *i*POP-4 were found to be 0.995 and 0.999 for CrO_4^{2-} and ReO_4^{-} anions respectively. The rate constant (k₂) values were found to be 0.00728 mg/g min (CrO_4^{2-}) and 0.00621 mg/g min (ReO_4^{-}) in case of *i*POP-3 and 0.00938 mg/g min (CrO_4^{2-}) and 0.00735 mg/g min (ReO_4^-) in case of iPOP-4. Further, to substantiate the potential of these iPOPs towards removal of such oxo-anions in very low concentration, we have performed CrO₄²⁻ removal experiments with both iPOPs in a very low concentration range (10-100 ppm). To our delight, both iPOPs have recorded almost 100% removal efficiency toward CrO₄²⁻ anions even in lower concentration of 10 ppm (Figure S49–S50).

Enthused by their impressive uptake capacities, we were motivated to investigate the selectivity of these iPOPs as real wastewater effluents contain several interfering anions (such as SO₄²⁻, Br⁻, Cl⁻, NO₃⁻ etc.) that coexists along with the targeted oxo-anions. The competing studies were carried out in presence of various coexisting interfering anions in a 1:1 mixture of both CrO₄²⁻ and ReO₄⁻ oxo-anions individually. Both *i*POPs exhibited



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Figure 4. (a) UV-Vis spectra in presence of iPOP-3 for CrO₄²⁻, (b) UV-Vis spectra in presence of iPOP-3 for ReO₄⁻⁻, (c) Kinetic study of CrO₄²⁻ ion capture with iPOP-3, (d) UV-Vis spectra in presence of iPOP-4 for CrO₄²⁻, (e) UV-Vis spectra in presence of iPOP-4 for ReO₄⁻, (f) Kinetic study of ReO₄⁻ ion capture with iPOP-3, (g) Bar diagram for CrO₄²⁻ removal efficiency of *i*POP-3 in presence of Br⁻, Cl⁻, NO₃⁻ and SO₄²⁻ ions, (h) Bar diagram for ReO₄⁻ removal efficiency of *i*POP-3 in presence of Br⁻, Cl⁻, NO₃⁻ and SO₄²⁻ ions, (i) Removal efficiency of acid and base treated phases of *iPOP-3* and *iPOP-4*.

excellent selectivity towards CrO_4^{2-} and ReO_4^{-} as the removal performance remained almost unaltered (>90%) in each case confirming very high affinity of both the iPOPs toward such oxo-anions (Figures 4g-h, S51, S52). Further, to strengthen and verify our results regarding the selectivity of iPOPs, we have performed Density Functional Theory (DFT studies) which successfully validated our experimental findings (discussed in details later).

Reusability of the sorbent material is one of the major aspect in real-time water pollutant sequestration processes. In this regard, we have carried out reversibility experiments with both *i*POPs in which we dipped 5 mg of each oxo-anion (CrO₄²⁻ and ReO₄⁻) occluded phase of iPOP-3 (iPOP-3@CrO₄²⁻, iPOP- $3@ReO_4^-$) and *i*POP-4 (*i*POP-4@CrO_4^2^-, *i*POP-4@ReO_4^-) in 2 M aqueous solution of tetrabutylammonium bromide. A gradual color change upon release of trapped CrO₄²⁻ anions from colorless to yellow was observed for both iPOPs while the

compounds went back to their initial off-white color. Further, the concentration of the released oxo-anions were verified via UV-vis spectroscopy. The kinetics for release profile was noted to be moderate but both the iPOPs were able to release almost all CrO₄²⁻ anions within 24 h (Figure S53–S54, S63). The slow kinetics indicate that both iPOP frameworks possess very high affinity as well as favorable binding sites toward the oxo-anions in comparison to Br⁻ anion, which was further confirmed by the theoretical DFT calculations. Similar results were obtained for the release of perrhenate anions by the *i*POPs. Notably, both compounds exhibited almost same efficiency in first two cycles of recyclability and it reduced to ~85% in 3rd cycle for both iPOPs (Figure S53, S54). To get more insights about such excellent selectivity and affinity of both iPOPs toward these oxo-anions, we have executed DFT calculations using Discovery Studio software package (Supporting Information contains more simulation details). According to the experimental param-

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eters a monomeric unit of *i*POP-3 and *i*POP-4 was constructed, consisting of triazine rings along with imidazole and benzimida-



Figure 5. Monomer unit of *i*POP-3 and *i*POP-4 showing the electrostatic potential isosurface (isodensity = 0.001 a.u.) calculated using DFT-DMOL3-B3LYP (a) and (c) represent top view of *i*POP-3 and *i*POP-4 respectively, (b) and (d) represent top view ESP diagram of *i*POP-3 and *i*POP-4 respectively.

zole respectively. The electrostatic potential (ESP) distribution profile of monomers corroborated well with the uniform delocalization of negative and positive charges surrounding imidazole, benzene and triazine rings which further serve as the preferential recognition sites for the incoming oxo-anions, having lower charge density (Figure 5).

Theoretical DFT calculations provided valuable information regarding several favorable binding sites for CrO₄²⁻ and ReO₄⁻ over other anions that is directly reflected in the binding energy values. The binding energies of CrO₄²⁻ with the building units of iPOP-3 and iPOP-4 were found to be -304.45 kJ/mol and -544.45 kJ/mol respectively, which are much higher than the binding energies of other anions (Figures 6a-f, S64). Similarly, the binding energies of ReO₄⁻ anion with the building units of iPOP-3 and iPOP-4 were found to be as high as -413.12 kJ/mol and -603.12 kJ/mol respectively, which indicate strong interactions as well as high affinity of both the iPOPs for ReO₄⁻ anions. The binding energies for Br⁻ ion with the *i*POPs building units were found to be -69.72 kJ/mol and -74.82 kJ/mol, which are much lower than the corresponding binding energies of the target analytes aiding both these materials in kinetics, capture efficiency and selectivity as observed in the experimental studies.

Conclusions

In conclusion, two new chemically stable cationic porous organic polymers, namely *iPOP-3* and *iPOP-4*, were synthesized



Figure 6. Optimized structures of monomeric unit of *i*POP-3 with different binding anions and the corresponding binding energies calculated based on DFT-DMOL3-B3LYP, (a) *i*POP-3-(ReQ₄⁻), (b) *i*POP-3-(CrQ₄²⁻), (c) *i*POP-3-(SQ₄²⁻), (c) *i*POP-3-(NO₃⁻), (e) *i*POP-3-(Cl⁻), (f) *i*POP-3-(Br⁻).

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and thereupon utilized for sequestration of toxic oxo-anions (CrO₄²⁻ and ReO₄⁻) from water. Both compounds performed remarkably well in terms of rapid kinetics, high uptake efficiency and superior selectivity toward these oxo-anions. The uptake capacities of *i*POP-3 for both CrO₄²⁻ and ReO₄⁻ are among the highest reported values in the arena of overall porous materials. Furthermore, the theoretical calculations along with DFT analysis brings forth insights regarding potential recognition sites for oxo-anions as well as the emergence of the exceptional selectivity and efficiency of both the iPOPs. In addition, both compounds showed reusability up to three cycles for the oxo-anions, advocating as potential candidates for real-time utilization in such oxo-anion sequestration applications. The experimental findings of this work highlights that iPOPs can serve as potent adsorbents toward wastewater remediation with facile synthesis, exceptional removal efficiency and high adsorption capacity.

Experimental

Synthesis of tris-(4-bromomethyl-phenyl)-[1,3,5]triazine: This compound was synthesized by following a reported protocol with little modifications (Scheme S1).^[18]

Synthesis of iPOP-3: This compound was also synthesized following a previously reported protocol with slight modifications (Scheme S2).^[19] Imidazole (20.83 mg, 0.306 mmol) was refluxed along with potassium carbonate (K₂CO₃) (0.306 mmol, 42.28 mg) in 10 mL dry acetonitrile for 3 h. Subsequently, Tris-(4-bromomethylphenyl)-[1,3,5] triazine (0.17 mmol, 100 mg) was taken in 6 mL dry THF and was added dropwise very slowly to the refluxing reaction mixture which was further refluxed for 24 h under inert conditions. Then the obtained white solid product was collected and washed thoroughly with different solvents (DMF, DMSO, THF, Toluene, MeOH, acetone and water) for several times to ensure the removal of any unreacted substrates and oligomers within the pores of iPOP-3. Further, the as-obtained solids were soaked in a combination of solvents of DCM, THF and acetonitrile (1:1:1) for 72 h and subsequently heated at 90 °C under vacuum for 24 h to obtain the desolvated phase of the compound (Scheme S2).

Synthesis of iPOP-4: This compound was synthesized by following the similar protocol by using benzimidazole instead of imidazole (Scheme S3). Benzimidazole (36.15 mg, 0.306 mmol) was refluxed along with potassium carbonate (K_2CO_3) (42.28 mg, 0.306 mmol) in 10 mL dry Acetonitrile for 3 h. Thereafter, Tris-(4-bromomethyl-phenyl)-[1,3,5]triazine (100 mg, 0.17 mmol) was taken in 60 mL dry THF and was added dropwise very slowly to the refluxing reaction mixture which was further refluxed for 24 h under inert conditions (Scheme S3).

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Conflict of Interest

The authors declare no conflict of interest.

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FULL PAPER

An example of utilization of imidazole-functionalized chemically robust cationic porous organic polymers (POPs) for rapid and efficient capture of hazardous dual oxo-anionic pollutants from water. The study will enrich the concept of designing new efficient cationic polymeric materials to tackle the problems based on water pollution, one of the most important threats towards the initiative for a green and clean environment.



Toxic Oxo-pollutants trapping by ionic POPs

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Imidazolium-Functionalized Chemically Robust Ionic Porous Organic Polymers (*i*POPs) toward Toxic Oxo-Pollutants Capture from Water