Porous Frameworks

Removal of Pertechnetate-Related Oxyanions from Solution Using Functionalized Hierarchical Porous Frameworks

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Abstract: Efficient and cost-effective removal of radioactive pertechnetate anions from nuclear waste is a key challenge to mitigate long-term nuclear waste storage issues. Traditional materials such as resins and layered double hydroxides (LDHs) were evaluated for their pertechnetate or perrhenate (the non-radioactive surrogate) removal capacity, but there is room for improvement in terms of capacity, selectivity and kinetics. A series of functionalized hierarchical porous frameworks were evaluated for their perrhenate removal capacity in the presence of other competing anions.

Although a trace amount of technetium is naturally present in the atmosphere because of the spontaneous fission of uranium isotopes, the major source of radioactive ^{99}Tc is the production of weapon grade plutonium (^{239}Pu) during irradiated uranium fuel cell reprocessing.[1] The so-formed ^{99}Tc can be found mainly as $^{99}TcO_4^-$ in legacy nuclear waste.[1a,d,f,g,2] The presence of large amounts of $^{99}TcO_4^-$ in stored nuclear waste is an environmental and public health concern mainly due to the long half-life ($t_{1/2} = 2.13 \times 10^5$ yr) and environmental mobility of $^{99}TcO_4^-$, as it has high water solubility (11.3 mol L^{-1} at 20 °C).[1a,g,3] Moreover, the high volatility of $^{99}TcO_4^-$ in the waste stream causes major operational inefficiencies during vitrifica-

tion (also called glassification, used for long-term storage purpose of nuclear waste) processes.[1d,f] Currently, it is possible to capture and remove TcO_4^- using a number of methods such as ion exchange, solvent extraction and gravity precipitation.[1a,d,f,g,3,4] Each of these processes has its own advantages and disadvantages, but $^{99}TcO_4^-$ removal by ion-exchange has received the most attention to date because of its ease of implementation and high recovery rate.[1a,b,f,4c,5] For example, commercial ion-exchange resins such as superLig-639 or Puro-lite-A-520E can remove $^{99}TcO_4^-$ from aqueous solutions, including simulated nuclear waste streams.[1f,6] Apart from these commercial ion-exchange resins, several other types of solid-state adsorbents, including layered double hydroxide (LDHs), purely inorganic and metal–organic hybrid materials were shown to be capable of removing TcO_4^- (or related oxyanions) from aqueous solutions.[7] Materials such as LDHs are inexpensive, but have very low selectivity in the presence of other competing anions such as chloride and carbonate.[7a] Moreover, a significant challenge exists for the recovery and reuse of these classes of materials. Other solid-state materials including nanostructured chalcogels and metalloborate were also studied but they have low selectivity and are radioactive, which makes their future application highly unlikely.[7b,d] Oliver and co-workers reported a series of cationic inorganic–organic hybrid materials such as [Ag$_2$(4,4′-bipyridine)$_2$·(O$_3$SCH$_2$CH$_2$SO$_3$)] [SLUG-21]; that can effectively capture oxyanions from solution in the presence or absence of competing anions by means of a structural transformation, but because of its unidimensional structure and presence of Ag–N coordination bonds, it lacks long term stability and recyclability.[7e] As such, room for improvement exists in terms of capacity, kinetics, and selectivity.[1a] Stable, hierarchical functionalized porous frameworks such as members of crystalline metal organic frameworks (MOFs), covalent organic frameworks (COFs) and amorphous porous aromatic frameworks (PAFs) offer several advantages over traditional ion-exchange materials, such as resins, including structural rigidity, modularity and functionalizable pore surfaces (Scheme 1).[1a,8] MOFs or PAFs with appropriate functional groups have shown excellent ion-exchange capacity, kinetics and selectivity for a range of industrially important ions. For example, Ghosh and co-workers recently reported rapid removal of environmentally toxic oxyanions, such as dichromate, using a water stable cationic MOF by an ion-exchange mechanism.[8n] Dichromate removal by a cationic MOF was also reported by Liu and co-workers that works by means of a single-

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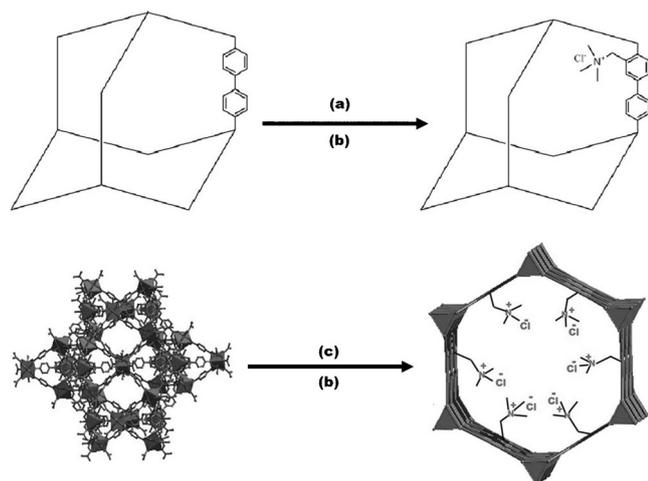
Scheme 1. Post-synthetic modification of hierarchical porous frameworks (a = CH₃COOH/HCl/H₃PO₄/HCHO, 363 K, 3 d, b = trimethylamine, ethanol, 353 K, 3 d, c = AlCl₃·6H₂O, nitromethane, methoxyacetyl chloride, reflux, 5 h.

crystal to a single crystal transformation process.[8m] Similarly, PAFs with appropriate functional groups exhibit fast, selective ion-exchange capacity with high overall capacity.[8j, 9] It is thus imperative to develop an ion-exchange system with a MOF or PAF backbone with appropriate functional groups of benchmark ion-exchange resins.[8j, 10] To avoid handling radioactive pertechnetate ions in a laboratory setup, perrhenate (ReO_4^-), a nonradioactive structural analogue of pertechnetate, was used to evaluate ion-exchange materials. In this work, we report the ReO_4^- uptake capacity and/or percent removal of two hierarchically porous framework materials in the presence and absence of competing anions, namely PAF-1 and MIL-101(Cr), post-functionalized with $NR_3^+X^-$ (R = alkyl group, X = OH^-, Cl^-) type functional groups resembling benchmark ion-exchange resins.

MIL-101(Cr) and PAF-1 were synthesized using previously reported procedures and duly characterized (Supporting Information, Figures S1–S4).[8k, 10, 11] MIL-101 and PAF-1 were specifically chosen because of their high surface area, large pore size (> 10 Å) and water stability. The large pore size enables facile post-synthetic functionalization even with a bulky functional group, while allowing sufficient access to the ion-exchange species. The as-synthesized MIL-101(Cr) and PAF-1 were post-synthetically functionalized with $-CH_2N^+(CH_3)_3X$ (X = OH^- for PAF-1, Cl^-) group based on a previously reported procedure (Supporting Information, Figure S5).[8j, 10] Such quaternary ammonium type functional groups are used in many benchmark anion exchanging (e.g., TcO_4^-) resins such as IRA-401, RO-02-119 and Purolite-A-520E and introduction of such groups in a high surface area adsorbent matrix such as MIL-101 and PAF-1 seems a logical choice. Both functionalized MIL-101 and PAF-1 (hereafter **MIL-101-F**, and **PAF-1-F** respectively) retain their permanent porosity and crystallinity (for MIL-101) as evident from BET surface area analysis and powder XRD (see the Supporting Information).

Once the functionalized materials were characterized, activated PAF-1-F and MIL-101-F were used to evaluate their

ReO_4^- adsorption capacity in the absence of competing anions and PAF-1-F was further evaluated in the presence of competing anions. The ion-exchange study was focused on three crucial parameters: uptake capacity, adsorption kinetics and selectivity. A high total uptake capacity is important as it will require less material for the ion-exchange, reducing large-scale synthesis and keeping process engineering costs to a minimum. Fast adsorption kinetics is required as the contact time will be relatively short during the exchange process in a commercial setup. Finally, it is anticipated that there will be a large excess of anions such as NO_3^-, SO_4^{2-} and PO_4^{3-} present in the nuclear waste medium, and the ion-exchange material has to be selective towards TcO_4^-. We first evaluated three materials, in their activated form, namely MIL-101(Cr), MIL-101-F and PAF-1-F for ReO_4^- adsorption from aqueous solution. To calculate the total uptake capacity of ReO_4^- within the framework a series of ReO_4^- (solution) and ion-exchange material (solid) mixtures, with ReO_4^-/MIL-101(Cr)/MIL-101-F/PAF-1-F molar ratios varying from 1:1 to 1:8, were analyzed (Figure 1). The ReO_4^- adsorption
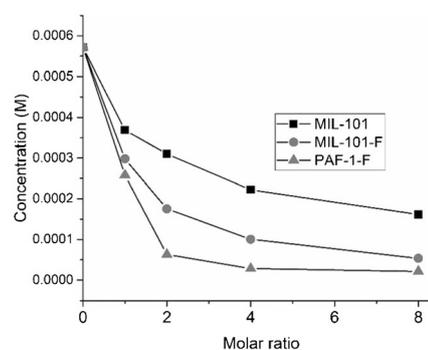
Figure 1. The ReO_4^- uptake of MIL-101(Cr) (black), MIL-101-F (red) and PAF-1-F (green) as a function of molar ratio. For the experiment, samples were kept within the ReO_4^- solution for 24 h.

was calculated by measuring its solution concentration, using ICP-OES, after a contact time of 24 h. Figure 1 shows the removal efficiency of ion-exchange materials as a function of molar ratio. Under these conditions (1:1 to 1:8 molar ratio and 24 h contact time; see the Supporting Information), the PAF-1-F is shown to have faster ReO_4^- uptake than MIL-101-F. This could be due to the presence of more number of readily exchangeable anion sites in PAF-1-F compared to MIL-101-F. Furthermore, the ion exchange is much slower in MIL-101 because of strongly bound -F in MIL-101. Figure 1 show that PAF-1-F with 1:2 molar ratios has significant ReO_4^- adsorption and further addition of PAF-1-F does not result in significant enhancement of ReO_4^- adsorption from the solution reaching saturation at 1:4 molar ratio. On the contrary, MIL-101(Cr) and MIL-101-F require a much higher molar ratio (1:8) to reach near saturation uptake. As expected, MIL-101-F has a higher uptake capacity than MIL-101(Cr), owing to the presence of labile anion exchanging $-CH_2N^+(CH_3)_3$ groups. Due to the presence of Fluorine ions (F^-) attached to Cr^{3+} sites, MIL-101(Cr) also exhibit ion-exchange properties to some extent by replacing F^- ions with ReO_4^- however such anion exchange is much slower be-

cause of strong metal–fluorine bond as exemplified in the ICP OES results (Figure 1). Overall, PAF-1-F shows a much higher ReO_4^- capacity at the same molar ratios than both MIL-101(Cr) and MIL-101-F. It is to be noted that in all cases, the percentage removal of the three materials, namely MIL-101(Cr), MIL-101-F and PAF-1-F is high, with MIL-101(Cr) showing the lowest percentage removal of 72% at 1:8 molar ratio after 24 h. The percentage removal for MIL-101-F (87%) and PAF-1-F (97%) is even higher (1:8 molar ratio). The total ReO_4^- capacity for PAF-1-F (at 1:2 molar ratio) is calculated to be 420 mg g^{-1}, higher than recently reported protonated MOF, UIO-66-NH$_3^+$ (159 mg g^{-1}), a super-tetrahedral cationic borate (250 mg g^{-1}) and traditional layered double hydroxide (80–120 mg g^{-1}).[7a, d, 12] However, for UIO-66-NH$_3^+$, ReO_4^- uptake can vary significantly from batch to batch depending on the number of anion exchange sites and the extent of conversion to NH$_3^+$Cl$^-$, whereas for PAF-1-F, we found that the uptake capacity (and percentage removal) is consistent. The difference in uptake capacity for MIL-101(Cr), MIL-101-F and PAF-1 can also be attributed to the fact that the number of ion-exchange sites per gram of PAF-1-F (molar mass −290 g mol^{-1}) is much higher than that of MIL-101(Cr) (molar mass −719 g mol^{-1}) and MIL-101-F (molar mass −790 g mol^{-1}). Based on this preliminary data set PAF-1-F was chosen for further studies in terms of kinetics and selectivity. In the kinetics study, both ICP-OES and UV/Vis spectroscopy were employed to determine the percentage ReO_4^- removal as a function of time (Figure 2). In a typical UV/Vis experiment, PAF-1-F was added to the standard solution of ReO_4^- and the UV/Vis signature of ReO_4^- was monitored as a function of time (see Supporting Information for more details). Complete removal of ReO_4^- was achieved within 24 h.
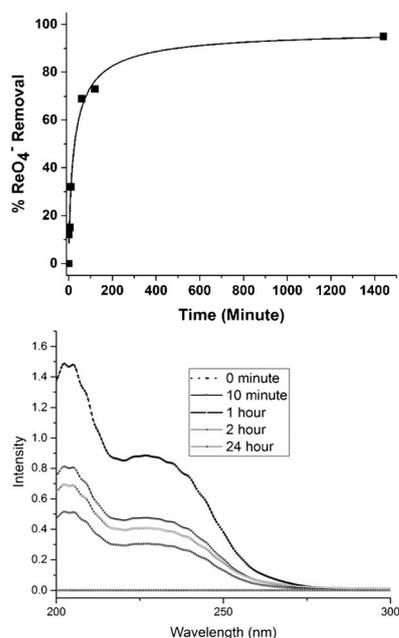
The UV/Vis data were fully consistent with the ICP-OES data. The percentage removal reached 97% after 24 h, with 80% removed in the first 150 min of adsorption. Based on this data, K_d (distribution coefficient) for PAF-1-F was calculated to be 2.55×10^4 mL g^{-1} (see Supporting Information for calculation details). Moreover, the uptake capacity and percent ReO_4^- removal of PAF-1-F was found to be better than benchmark anion exchange resins such as Purolite-530E, Purolite-532E and Dowex-1X8 (Supporting Information, Table S1).

Finally, the selectivity of PAF-1-F towards ReO_4^- in the presence of equimolar competing anions, such as SO_4^{2-} and PO_4^{3-}, was studied. SO_4^{2-} and PO_4^{3-} are chosen because they possess a higher negative charge and thus are expected to be favored in the ion-exchange processes in which columbic interactions play a major role. ICP–OES data showed that PAF-1-F can adsorb ReO_4^- even in the presence of PO_4^{3-} and SO_4^{2-}, but the percent ReO_4^- removal decreased from 97% to around 20% after 24 h at the 1:2 molar ratio (Supporting Information, Table S2). The result is surprising given the low charge density of the ReO_4^- anion with respect to PO_4^{3-} and SO_4^{2-}, but can be attributed to the steric factors due to the presence of partially solvated multivalent anions as well as the presence of mono-positive ion exchange sites.

In conclusion, we evaluated a series of -NR$_3^+$X$^-$ functionalized hierarchical porous frameworks (PAF-1-F) for ReO_4^- removal. Functionalized PAF-1, namely PAF-1-F showed the best uptake performance, with 97% ReO_4^- removal within the first 24 h. Such performance is significantly better than other reported materials including traditional inorganic materials and protonated UIO-66-NH$_2$. Although the current work demonstrates that post-functionalized hierarchical porous frameworks with appropriate functional groups can efficiently remove ReO_4^- from aqueous solution, the uptake performance of the material suffers when other competing anions are present. Future work in this direction will involve evaluation of other functionalized porous frameworks for the improved selectivity of perrhenate and eventually pertechnetate over other anions in simulated nuclear waste solutions.

Acknowledgements

Figure 2. UV/Vis spectra as a function of time (top). Percentage ReO_4^- removal as a function of time from ICP–OES (bottom), notice around 80% of removal achieved within 150 min (the molar ratio was kept constant at ReO_4^- : PAF-1-F 1:2).

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