Porous Frameworks

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


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 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). Moreover, the high volatility of $^{99}$TcO$_4^-$ in the waste stream causes major operational inefficiencies during vitrification (also called classification, used for long-term storage purpose of nuclear waste) processes.[1a,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, 1] 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,d,f,g, 1] For example, commercial ion-exchange resins such as superLig-639 or PuroLite-A-520E can remove $^{99}$TcO$_4^-$ from aqueous solutions, including simulated nuclear waste streams.[1c,d] 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.[1i] Materials such as LDHs are inexpensive, but have very low selectivity in the presence of other competing anions such as chloride and carbonate.[1j] 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.[1k] Oliver and co-workers reported a series of cationic inorganic–organic hybrid materials such as [Ag$_4$(4,4’-bipyridine)$_2$(O,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.[1l] As such, room for improvement exists in terms of capacity, kinetics, and selectivity.[1m] 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).[1n] 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.[1o] 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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Similarly, however such anion exchange is much slower be-
2016 adsorption and fur-
sites, MIL-101(Cr) also exhibit
MIL-101 and PAF-1 were specific-
adsorption = for T
uptake from aqueous solution. T oc alculate the total
a
To avoid handling radioactive
and PO
ions
+ 
respectively) retain their
solution for 24 h.
It is thus
MIL-101-F
uptake capacity in the absence of competing anions
uptake than MIL-101-F.T his
uptake capacity and/or percent removal of
Post-synthetic modificationo fh ierarchicalp orousf rameworks
within the framework as eries of
uptake of MIL-101(Cr)( black), MIL-101-F( red)a nd PAF-
Such quaternary am-
(R
47x98 vated PAF-1-F and MIL-101-F were used to evaluate their
porting Information).
from BETs urfacea rea analysisa nd powder XRD (see the Sup-
permanent porosity andc rystallinity (for MIL-101)a se vident
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10
molar ratio. Under thesec onditions (1:1 to 1:8m olarr atio and
moval efficiency of ion-exchangem aterials as af unction of
was calculated by measuring its solution concentration, using
ICP-OES, after a contact time of 24 h. Figure 1 shows the re-
moval 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
uptake than MIL-101-F. This
could be due to the presence of more number of readily ex-
changeable anion sites in PAF-1-F compared to MIL-101-F. Fur-
thermore, 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
adsorption and fur-
ther addition of PAF-1-F does not result in significant enhance-
ment of ReO
adsorption from the solution reaching satura-
tion 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 sat-
uration uptake. As expected, MIL-101-F has a higher uptake ca-
pacity than MIL-101(Cr), owing to the presence of labile anion
exchanging -CH, N
(CH, ) groups. Due to the presence of Fluoro-ine ions (F ) attached to Cr
sites, MIL-101(Cr) also exhibit
ion-exchange properties to some extent by replacing F ions
with ReO
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$^{-1}$). 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 $\sim$290 g mol$^{-1}$) is much higher than that of MIL-101(Cr) (molar mass $\sim$719 g mol$^{-1}$) and MIL-101-F (molar mass $\sim$790 g mol$^{-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 $\times$ 10$^{10}$ 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-S30E, Purolite-S32E 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 -NH$_3^+$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$_3^+$. 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.

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