Functionalized Porous Organic Polymers as Uranium Nano-Traps for Efficient Recovery of Uranium from Seawater

Fuel Cycle Research and Development

Shengqian Ma
University of South Florida

Stephen Kung, Federal POC
Phil Britt, Technical POC
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Project Title:
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Principal Investigator:
Shengqian Ma
Department of Chemistry
University of South Florida, Tampa, FL 33620
Email: sqma@usf.edu

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Report Prepared by: Qi Sun and Shengqian Ma
I. Abstract

The long-term use of nuclear power for energy applications relies on the secure and economical supply of nuclear fuel. Among various natural sources of uranium for use in nuclear reactors, seawater is highly appealing given that the oceans contain about 4.5 billion tons of dissolved uranium, almost 1000 times that estimated for mineral reserves. Nonetheless, the concentration of uranium in seawater is extremely low (3-3.3 mg L\(^{-1}\) or 3-3.3 ppb); this, coupled with the presence of a relatively high concentration of other metal ions, makes uranium recovery from seawater a challenge that requires the development of efficient and effective separation processes. Various adsorbent technologies based upon synthetic organic polymers, biopolymers, inorganic materials, mesoporous silica materials, porous carbon-based adsorbents, and ionic liquids have been widely developed for the extraction of uranium from seawater. However, these benchmark sorbent materials suffer from a number of drawbacks such as low adsorption capacity (typically 0.1-3.2 mg-U g\(^{-1}\) adsorbent), poor selectivity, and slow kinetics. Given the extreme complexity and vast volume of seawater, as well as the very low concentration of uranium present, to attain this ambitious task demands the design of adsorbents with high affinity and fast kinetics.

The main objective of this project is to develop functional porous organic polymers (POPs) as a new type of adsorbent for mining uranium from seawater. This class of porous materials has quickly moved to the forefront of materials research due to their high internal surface areas, exceptional water/chemical stability, facile chemical tunability, and extraordinary capability to selectively adsorb large quantities of guest species. The potential to deploy POPs in uranium extraction is related to the ease with which their internal surfaces can be decorated with high densities of strong binding sites. Beyond introducing post-synthetic modification, the specific functionalities also can be used as building units to be incorporated into porous frameworks. Our approach to fulfill this task involves the custom-design of POP-based uranium “nano-traps” via a “crystal engineering” guided design followed by stepwise post-synthetic modification. Furthermore, to increase the density of chelating groups and to enhance their affinity towards uranyl ions, judiciously designed chelating systems were constructed into porous organic polymers. Moreover, to improve the accessibility of the chelating groups and thereby the utilization efficiency, we assembled the chelating groups into highly crystalline materials where they are aligned in periodic arrays on the open channels.
II. Scope and Aims of the Proposed Work

The overarching goal of this project is to deploy porous organic polymers as a designer platform for synthesis of high performance uranium scavengers. The modular nature of this type of material allows their chemical functionalities and pore geometries to be fine-tuned independently and thus enabling rigorous comparison between individual parameters, which can be leveraged to further tailor the outcomes for mining uranium from seawater. The project is divided into three main and interconnected tasks: 1) understand the effect of spatial continuity of chelating groups on the uranium binding fashions in the adsorbents; 2) understand how to improve the binding affinity of chelating moieties towards uranium; 3) understand how the pore structures of adsorbents affect the accessibility of chelating groups and thereby the utilization efficiency as well as the kinetics for uranium adsorption. The aim for these researches is the design of cost-effective and durable adsorbents with a high affinity, fast kinetics, and large capacity towards uranium. The fundamental scientific challenges which have to be overcome include enhancing the coordinative moieties’ binding affinity towards uranium species and thereby the selectivity and increase the density and accessibility of chelating groups and thus the efficiency and uptake capacity.

The aforementioned challenges were approached by understanding the structure-property relationships and the results were reported in peer-reviewed publications. The researches included custom-design of a POP-based uranium “nano-trap” via stepwise post-synthetic modification and understanding the coordination fashion of uranium species in it as well as unveiling the importance of spatial continuity of chelating groups to achieve cooperative binding (ACS Appl. Mater. Interfaces, 2017, 9, 12511-12517). Knowing this, to increase the density of binding sites and also to improve the uptake capacity of the porous adsorbents, the chelating units were designed to allow the synthesis of a high surface area material while conserving a sufficiently high density of binding sites. In addition, to enhance the binding moieties’ affinity towards uranyl ions, an assistant group was de novo introduced to reinforce the structure of the complex, thereby lowering the overall energy, reminiscent of biological systems (Nat. Commun. 2018, 9, 1644). Moreover, we delineated that the unique pore structure not only improved the accessibility of chelating groups, allowing significantly higher utilization efficiency, but also facilitated their cooperation, leading to a high affinity toward specific ions (Adv. Mater. 2018, 1705479).
III. Technical Summary of the Work Accomplished

A. Functionalized Porous Aromatic Framework for Efficient Uranium Adsorption from Aqueous Solutions


Compared with other types of porous materials, POPs feature robust covalent framework structures with high water and chemical stability, making them practically useful. Additionally, their pore walls can be decorated with functional organic groups to selectively capture targeted guest species, offering an opportunity for the development of new types of adsorbent materials for uranium extraction from water.

We showed the successful decoration of a POP with uranyl chelating groups. PAF-1 (cross-linked poly tetraphenylmethane) and the amidoxime group was the host material and chelating functionality of our choice, respectively. The amidoxime functionalized PAF-1 (PAF-1-CH$_2$AO) was synthesized by chloromethylation of PAF-1 followed by treatment with NaCN (PAF-1-CH$_2$CN), and then amidoximation using hydroxylamine (Figure 1).

![PAF-1 and PAF-1-CH$_2$AO](image)

Figure 1. Schematic illustration of the procedures for the preparation of PAF-1-CH$_2$AO. (a) AcOH, H$_3$PO$_4$, HCl; (b) NaCN; (c) NH$_2$OH.

The successful grafting of the amidoxime group onto PAF-1 was confirmed by elemental analysis, Fourier transform infrared spectroscopy (FT-IR), and solid-state $^{13}$C NMR. Elemental analysis reveals a nitrogen content of 2.38 wt.% of PAF-1-CH$_2$CN corresponding to 1.7 mmol·g$^{-1}$ CN groups in PAF-1-CH$_2$CN. The full conversion of cyano groups to amidoxime groups was evidenced by the IR spectra where the CN peak at 2251 cm$^{-1}$ disappeared along with the appearance of C=N (1638 cm$^{-1}$), C-N (1381 cm$^{-1}$), and N-O (933 cm$^{-1}$), characteristics of the amidoxime group (Figure 2a). To test the porosity of the materials, nitrogen sorption isotherms were collected at 77 K. As a result of the presence of amidoxime groups in the pores, the Brunauer-Emmett-Teller (BET) surface area was reduced to 855 m$^2$·g$^{-1}$ from 4715 m$^2$·g$^{-1}$ upon post-synthetic modification (Figure 2b).

After confirming the grafting of amidoxime groups and permanent porosity of PAF-1-CH$_2$AO, we assessed the overall capacity and an adsorption isotherm (Figure 3a) was collected. The resulting isotherm was well fitted with the Langmuir model, giving rise to a correlation coefficient R$^2 = 0.97$. The maximum
uranium uptake capacity was estimated to be 304 mg g⁻¹, which is among the highest reported values for uranium adsorbent materials reported at that time.⁴ Time-course adsorption measurements indicated that uranyl capture by PAF-1-CH₂AO is kinetically efficient (Figure 3b), as evidenced by reaching its 84.4% saturation capacity within 1 hour with an increase to 95.8% after 3 hours. After 12 h, PAF-1-CH₂AO gave rise to an adsorption capacity as high as 283 mg g⁻¹. More significantly, PAF-1-CH₂AO can readily be regenerated by treating it with Na₂CO₃ (1M) and it was demonstrated to retain its uranium uptake capacity for at least two consecutive cycles, affording a value of 271 mg g⁻¹, which is comparable to that of the fresh PAF-1-CH₂AO. Furthermore, we investigated the effectiveness of PAF-1-CH₂AO for removing UO₂²⁺ from aqueous solutions. In brief, 10 mg of PAF-1-CH₂AO was added to 200 mL of aqueous solution containing 4100 ppb UO₂²⁺. After 90 min of treatment, the residual concentration of UO₂²⁺ was reduced to 0.81 ppb, more than one order of magnitude lower than the acceptable limit of 30 ppb defined by the US EPA. We next tested the performance of PAF-1-CH₂AO in recovery of uranium from simulated seawater (7.05 ppm of uranium dissolved in 25.6 g L⁻¹ of NaCl and 0.198 g L⁻¹ of NaHCO₃ aqueous solution) and an uptake capacity of 40 mg g⁻¹ was achieved.
the equilibrium adsorption data with Langmuir adsorption model. (b) Adsorption kinetics of UO$_2^{2+}$ versus contact time in aqueous solution using PAF-1-CH$_2$AO.

To gain insight into the coordination environment of uranium in PAF-1-CH$_2$AO, we employed X-ray absorption fine structure (XAFS) spectroscopy. It was revealed that a uranyl ion was bound by 1.4 ± 0.3 amidoxime ligands in an η$_2$-motif, with the remaining equatorial plane filled with 0.5 ± 0.3 carbonate and 2.1 ± 0.8 coordinating water molecules.

In summary, we have demonstrated how porous organic polymers can be functionalized for efficient uranium adsorption from water as exemplified by decorating the highly porous and stable POP material, PAF-1 with the uranyl chelating amidoxime group. This work advanced functionalized POPs as a new type of adsorbent material for efficient uranium extraction from aqueous solutions.
B. Bio-Inspired Nano-Traps for Uranium Extraction from Seawater and Recovery from Nuclear Waste


Although POPs have shown to be a promising decorating platform for uranium capture via post-synthetic modification with chelating groups, there is still room for improvement when the following considerations are taken into account: i) multistep post-synthetic modification leading to a low overall efficiency; ii) blocked pores or partially blocked pores during the chemical modification as suggested by the drastically decreased surface area; and iii) due to the low grafting degree, the chelating groups being spatially separated in the adsorbent, which is unfavorable for their cooperative binding and thereby resulting in a low binding affinity.

With these in mind, to further enhance the affinity of chelating groups to uranyl ions without complicated ligand design, we were inspired by nature, where the affinity of amino acids involved in binding ions can be greatly enhanced by non-covalent interactions from the surrounding amino acids in the protein scaffold and even achieve femtomolar affinity. Therefore, we reasoned that the binding affinity of chelating sites towards specific ions can be improved by introducing an assistant group orientated in a suitable position. Given their cost effective synthesis, amidoxime polymers have been identified as the most promising platform for large-scale extraction of uranium species from seawater. Amidoxime typically has a low affinity and poor selectivity for uranyl in seawater conditions, as it binds nickel, cobalt, and iron present with greater affinity. To this end, we decided to introduce an assistant group to reinforce the coordinative binding between amidoxime and uranyl. Considering

Figure 4. Creating of Bio-Inspired Nano-Traps for Uranium Extraction.
the importance of spatial distribution to enhance their mutual cooperation, monomers containing an amino substituent with hydrogen bonding and electron donating capabilities in different positions relative to amidoxime were designed. Furthermore, these monomers were built into high surface area materials to conserve a sufficiently high density of chelating groups in the resultant adsorbents for achieving high uptake capacities (Figure 4).

Table 1 | Structure of building units and textural parameters of various amidoxime functionalized hierarchical porous polymers.

<table>
<thead>
<tr>
<th>POP</th>
<th>BET surface area (m$^2$ g$^{-1}$)</th>
<th>Pore volume (cm$^3$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POP-AO</td>
<td>696</td>
<td>0.52</td>
</tr>
<tr>
<td>POP-$p$NH$_2$-AO</td>
<td>397</td>
<td>0.22</td>
</tr>
<tr>
<td>POP-$o$NH$_2$-AO</td>
<td>415</td>
<td>0.22</td>
</tr>
</tbody>
</table>

In view of materials synthesis for practical applications, free-radical induced polymerization of vinyl-functionalized monomers holds great potential, on account of the monomer tunability together with the adapted and cost-effective synthesis. In this context, a family of vinyl-functionalized cyano compounds with different amine locations were designed for self-polymerization into highly porous materials followed by post-transformation of the cyano group into amidoxime (Table 1).

Figure 5. The kinetics of uranium adsorption for various adsorbents in simulated seawater solutions with an initial uranium concentration of 10.3 ppm (400 mL) and adsorbent material (3 mg).
Improvements towards uranium adsorption with the amidoxime-based sorbent are evident with the addition of an amino group together with its relative location. The porous framework bearing 2-aminobenzamidoxime is exceptional in sequestering high uranium concentrations with sufficient capacities from simulated seawater (290 mg g\(^{-1}\)) and trace quantities of uranium in real seawater (4.36 mg g\(^{-1}\), triple the benchmark), far outperforming those achieved by sorbents constructed by 4-aminobenzamidoxime (250 and 2.27 mg g\(^{-1}\)) and benzamidoxime (200 and 1.32 mg g\(^{-1}\), Figure 5). The underlying principles contributing to its superior performance were revealed by collaborative experiments including spectroscopic, crystallographic, and DFT calculation studies. It is revealed that the introduction of the amino group nearby the amidoxime not only alters the electron density of the complex to lower the overall charge on uranyl, but also provides an additional hydrogen binding site to align uranyl species in a favorable coordination mode and thereby increases its affinity (Figure 6). X-ray absorption fine structure (XAFS) spectroscopic studies revealed that each uranyl ion is bound exclusively by two amidoxime groups, further interpreting their excellent affinity.

![Figure 6](image-url) Crystal structures of uranyl complexes. (a) and (b) single crystal structures of UO\(_2\)(AO)\(_2\)(MeOH)\(_2\) and UO\(_2\)(oNH\(_2\)-AO)\(_2\)(MeOH)\(_2\), respectively. (c) DFT optimized structure of UO\(_2\)(AO)\(_2\)(MeOH)\(_2\) with dative U-O and U-N \(\sigma\)-bonds in UO\(_2\)(AO)\(_2\)(MeOH)\(_2\). (d) DFT optimized structure of UO\(_2\)(oNH\(_2\)-AO)\(_2\)(MeOH)\(_2\) with dative U-O and U-N \(\sigma\)-bonds along with second sphere hydrogen bonding interactions, characterized by overlap of the \(p\)-type amino lone pair and the methanol O-H \(\sigma^*\) orbital.

In summary, we have developed a promising strategy for the synthesis of highly efficient uranium adsorbent materials. This proof-of-concept study is important because it affords an amenable route to bridge natural and artificial systems. Moreover, this strategy is practically feasible and thus provides a new direction towards the development of adsorbents for uranium capture.
C. Covalent Organic Frameworks as a Decorating Platform for Utilization and Affinity Enhancement of Chelating Sites for Radionuclide Sequestration


Amorphous porous organic polymers (POPs) are potential candidates but their performance is often compromised by buried chelating sites stemmed from the small and irregular pores. In addition, their poorly defined structures complicate characterization and rational improvement. Therefore, porous materials that enable a deliberate and precise preparation are highly desirable.

Covalent organic frameworks (COFs) are an advanced class of porous crystalline material that enable the specific inclusion of various functionalized units into highly ordered periodic arrays. Their modular structure and extraordinarily broad chemical and reticular/topological variety can be translated into property tunability. We envision that COFs could offer an attractive alternative platform for uranium extraction, in particular, 2D COFs due to their unique structures. The layered sheets of these COFs typically adopt nearly eclipsed stacked structures, providing continuous nanometer-scale channels normal to the stacking direction, which provides a path for ions to the chelating groups that comprise the walls. Furthermore, the periodic arrays of aligned chelating groups in 2D COFs are expected to facilitate their cooperation in metal binding. Moreover, the crystallinity of these materials is beneficial in studying the relationship between structure and function. In this sense, we reason that incorporation of a specific ligand into 2D COF walls may provide a solution for the challenges encountered by other adsorbent materials, and a better system may be developed by integrating the intrinsic advantage of the chelating groups in selectivity and affinity with that of COFs in kinetics and capacity (Figure 7).

![Figure 7](image)

**Figure 7.** (a) Schematic illustration of chelating groups in COF materials. The uniform pore morphology of the COFs leads to the functionalized material with unrestricted access of ions to all of the chelating sites. (b) The functionalization of amorphous porous organic polymers, illustrating the blockage of narrow pore channels and bottlenecks. Pore-blocking is likely to impede access of metal ions to the functional sites in POPs.

To target the COF-based adsorbent material, a two-step synthesis was employed due to the
incompatibility of the amidoxime group during COF synthesis. A nitrile-functionalized COF was first obtained by condensing 2,5-diaminobenzonitrile (Db) with triformylphloroglucinol (Tp) under solvothermal conditions to yield COF-TpDb (Figure 8). The resultant COF was then amidoximated by treatment with hydroxylamine in methanol to afford the amidoxime-functionalized COF material (COF-TpDb-AO).

Figure 8. (a) Synthetic scheme of COF-TpDb through the condensation of Tp (black) and Db (blue) and corresponding chemical transformation from the cyano to amidoxime group, yielding COF-TpDb-AO. (b, c) Graphic view of the eclipsed AA stacking structure of COF-TpDb (blue, N; gray, C; red, O; hydrogen is omitted for clarity). (d) Graphic view of COF-TpDb-AO (blue, N; gray, C; red, O; hydrogen is omitted for clarity).

To study the post-synthetic conversion and the amidoxime formation, we carried out FT-IR and $^{13}$C MAS NMR spectroscopy. Successful amidoximation was indicated by the disappearance of the C≡N stretch (2213 cm$^{-1}$) and the appearance of C≡N (1646 cm$^{-1}$) and N-O (924 cm$^{-1}$), characteristic peaks of the amidoxime group in the FT-IR spectrum of COF-TpDb-AO. In addition, $^{13}$C MAS NMR analysis confirmed this efficient transformation, as indicated by the disappearance of the peak at 95 ppm that is related to CN groups together with the concomitant emergence of a peak at 169 ppm that is ascribed to open-chain
amidoxime groups. Moreover, the PXRD pattern of COF-TpDb-AO exhibits a diffraction pattern comparable to the one of COF-TpDb with an intense reflection at 4.8°. N₂ sorption measurements were conducted to verify pore accessibility after the post-synthetic conversion, affording isotherms similar to those of COF-TpDb. The BET surface area was calculated to be 826 m² g⁻¹, indicating the retention of porosity after the amidoximation process (Figure 9).

![Figure 9](image)

Figure 9. (a) PXRD profiles. (b) AA stacking mode of COF-TpDb. (c) AB stacking mode of COF-TpDb. (d,e) Nitrogen-sorption isotherm curves measured at 77 K for COF-TpDb and COF-TpDb-AO, respectively. (f) IR spectra. (g) Solid-state ¹³C NMR spectra.

To determine whether the long-range order pore structures of the adsorbents influence the sequestration performance, head-to-head comparisons were made with the amorphous analogue, POP-TpDb-AO (BET: 466 m² g⁻¹). This material was synthesized by condensation of triformylphloroglucinol with 2,5-diaminobenzonitrile and then amidoximated as described above. The amounts of uranium species enriched by these materials as a function of uranium concentration in the supernatant at the equilibrium state were determined by varying the initial concentrations. As shown in Figure 10, a continuous increase of uranium sorption with augmentation of the initial uranium concentrations was observed. The COF-based adsorbent showed superior performance in adsorption of uranium in terms of saturation adsorption capacity as compared to the amorphous porous polymer analogue, affording 408 and 355 mg g⁻¹, for COF-TpDb-AO and POP-TpDb-AO, respectively, suggesting a role of the material’s architecture. To further underscore the advantage of using COFs as a platform for the deployment of efficient adsorbent materials, adsorption kinetics between the COF-based sorbent and amorphous counterpart were compared. In relation to the COF-based adsorbent, the POP analogue displayed inferior adsorption kinetics. Under identical conditions, COF-TpDb-AO can reach 81% and 95% of its equilibrium adsorption capacity within 10 min and 30 min, respectively. However, it took 90 min for POP-TpDb-AO to accomplish around 95% of its equilibrium adsorption capacity.

Apart from the accessibility of binding sites, the pore architecture is assumed to result in different
orientations and distribution of the functionalities, which may affect their cooperation with each other, thereby leading to different binding strengths toward the guests. To evaluate the affinity of these materials to uranyl ions, the distribution coefficient values ($K_d$) were measured. Under the conditions of 5 ppm uranium at pH ~ 6.0 with a V/m of 10000 mL g$^{-1}$, the $K_d$ values for these samples were calculated and found to equal $3.6 \times 10^8$ (0.14 ppb) and $3.3 \times 10^7$ (1.51 ppb) for COF-TpDb-AO and POP-TpDb-AO, respectively (number given in parenthesis is the residual uranium concentration), with the COF showing more than an order of magnitude improvement in performance over its amorphous analogue.

Figure 10. (a) Uranium sorption isotherms for COF and POP based sorbents. The lines are fit with the Langmuir model; all the fits have $R^2$ values higher than 0.98. (b) Enlarged section of green rectangle in a. (c) The kinetics of uranium adsorption from aqueous solution with an initial concentration of 9.25 ppm (400 mL), at pH ~ 6, and adsorbent material (4.5 mg).

To further illustrate the benefit of COFs as an appealing functionality decorating platform for radionuclide sequestration, another amidoxime functionalized COF material (COF-TpAab-AO, Figure 11) and corresponding amorphous analogue (POP-TpAab-AO) were prepared for comparison. Again, the COF-based sorbent favored superior adsorption performance to that of its amorphous analogue in terms of both uranium uptake capacity and removal efficiency. Specifically, COF-TpAab-AO and POP-TpAab-AO afforded the uranium saturation uptake capacities of 305 and 256 mg g$^{-1}$, respectively. In addition, COF-TpAab-AO was three times faster than that of POP-TpAab-AO to reach their 95% equilibrium capacities. Furthermore, a pronounced improvement of affinity toward uranium was also observed, as demonstrated by a higher $K_d$ value of the COF in relation to that of the POP by a factor of 10 ($2.2 \times 10^8$ vs $1.8 \times 10^7$).

Figure 5. Synthetic scheme of COF-TpAab through the condensation of Tp (black) and Aab (green) and
corresponding chemical transformation from the cyano to amidoxime group, yielding COF-TpAab and COF-TpAab-AO, respectively.

Encouraged by the results described above, we were then motivated to evaluate its applicability in real water samples including potable water, well water, and river water, in which uranium was intentionally added at a dilute concentration (1000 ppb). A single treatment with COF-based materials reduced the uranium concentrations in these water samples to less than 0.1 ppb, which is two orders of magnitude lower than the U.S. Environmental Protection Agency elemental limits for hazardous wastes and even drinking water standards (30 ppb). Next, we examined its performance in seawater samples. The tests were performed using seawater samples spiked with 20 ppm uranium. COF-TpDb-AO showed high uptake capacities, giving rise to as high as 127 mg uranium per gram of adsorbent.

In summary, this work has demonstrated, using an example of radionuclide capture, the greatly improved accessibility and affinity of the binding sites towards guest ions in the adsorbents designed from well-defined channels, relative to those prepared from materials with disordered pore networks. This work thereby highlights new opportunities in using COFs as a novel platform for the deployment of adsorbent materials for environmental remediation by taking advantage of their amenability to design and unique structures.
IV. Summary of Major Achievements

The successful achievements and important findings are summarized below:

- Demonstration of porous organic polymers as an attractive platform for decorating chelating groups for uranium extraction.
- Demonstration of increase in the density of binding sites benefiting both uptake capacity and binding affinity by promoting the cooperative binding.
- Demonstration of the introduction of an assistant group boosting the binding moieties’ affinity towards uranyl ions.
- Demonstration of the effect of pore structure on the accessibility and orientation of chelating groups, thereby the uptake efficiency and binding affinity.

V. Publications


VI. Presentations

4. “Coordination Environment Control in Porous Organic Polymers to Enhance Uranium Adsorption,”
B. Aguila, Q. Sun, S. Ma, Posted by B. Aguila at International Conference on Seawater Uranium Recovery, University of Maryland, College Park, MD USA. July 19-22, 2016

VII. References