

Reaction: Porous Organic Polymers for Uranium Capture

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As clearly stated by Kushwaha and Patel,¹ uranium recovery from seawater is largely a game of economics and scale because of the elevated costs of sorbents and labor. For example, extracting 1 g of uranium requires that 300 tons of seawater be processed. Not to mention less than 1% of natural uranium is fissile, and therefore the theoretical energy potential is just equivalent to 15~20 kg of dirt-cheap coal.

In fact, the process of treating large amounts of caustic ocean water is no small task and requires corrosion-resistant equipment and oxidation-proof adsorbents that can also withstand immense pressure from the pumped brine. These unforgiving conditions necessitate robust adsorbent materials. Among porous materials developed thus far, porous organic polymers (POPs) offer the best of both worlds: porosity and stability. This is why there has been a surge in studies of uranium capture by POPs,^{2,3} which reach capacities of 13.0 mg g⁻¹ from natural seawater.^{1,2}

The challenges in uranium capture, however, are not just limited to scale

or stability; solving uranyl (UO₂²⁺) selectivity over vanadyl (VO²⁺) ions is quite difficult.¹ It is no coincidence that only a few of the literature reports report uranyl/vanadyl selectivity.

Another downplayed problem is pH. It turns out that amidoximes, the most popular functional group for uranyl binding,^{3,4} capture uranium far better when solutions are strongly acidic (e.g., pH < 5). We attempted to address this issue by bubbling CO₂ into ocean water to bring down the pH,³ but the logistics and environmental impact of such processes are not attractive.

And yet another, never truly addressed problem is the wettability of the adsorbents. Uranyl ions are dissolved in water, and the kinetics of adsorption will depend squarely on the efficient mass transport of seawater within a porous framework. Unfortunately, hydrophobicity is often used to make porous materials water resistant. Covalent frameworks of POPs, however, do not require such preventive measures

and can be tuned with chemical grafting.

In addition to the challenges above, practical seawater testing for uranium adsorbents often necessitates polymer fibers.⁴ This is for easy processing and deployment, because otherwise adsorbent powders would need enclosures such as "teabags." Many porous materials are not easily made into fibers, and monolithic design efforts backfire with a heavy loss in porosity.

A subset of POPs that can address all these requirements are called polymers of intrinsic microporosity (PIMs). PIMs are linear ladder polymers that feature covalently locked curvatures enabling permanent porosity while providing handling just like any other polymer fiber. We have previously shown an amidoxime-PIM-1 enhancing the kinetics of uranium capture.³ Our investigations continue in this direction because we believe an optimized PIM would check all the boxes for a commercial uranium-capture operation.

There is still a lot of hope in pursuing the development of uranium-adsorbing POPs. One clear advantage of the exceptional stability of POPs, compared with other emerging porous materials, is that they can be cast in the ocean for months without any loss of activity and harvested periodically for sustained uranium production. And because they're fully organic, regeneration and single use are both

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<https://doi.org/10.1016/j.chempr.2021.01.011>



feasible given the budgets of the operator.

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Reaction: Goal-Oriented PAF Design for Uranium Extraction from Seawater

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The utilization of nuclear power is a mature technology with a high capacity factor and persistent energy output. Therefore, it is considered one of the top contenders for clean energy sources. Power generation by worldwide nuclear plants has kept a steady pace in the past two decades, and robust growth is expected in the future. In China, nuclear energy has made great contributions to domestic electricity production; its current power-generating capacity is 49 GW, and its target is 150 GW by 2035.¹

The main fuel resource for nuclear plants is uranium, and its supply is one of the key dominating factors in energy production. However, terrestrial uranium reserves are far from satisfying the increasing demands of global energy consumption. Under the circumstances, uranium extraction from seawater (UES) is becoming a potential process to supply sufficient nuclear

fuels for durative energy production because the total uranium content in seawater is 1,000 times more than in terrestrial uranium reserves. However, uranium exists in seawater at an extremely low concentration of ca. 3.3 parts per billion (ppb), whereas many other metal cations are at much higher concentrations and would severely affect uranium extraction by competitive adsorption. In their *Catalysis* piece,² Kushwaha and Patel have given insight into the UES progress and discussed the criteria for adsorbent design. Uranium-extracting performance is closely associated with multiple factors and their synergy, including the property and accessibility of uranium-capturing sites, the porosity of adsorbents, the tolerance of adsorbents to seawater, and the extrinsic driving forces that speed up uranium diffusion. In order to achieve high UES capacity, the rational design of uranium adsorbents should be carried out with

three key goals, namely (1) high selectivity to uranium over abundant competing metals, (2) fast mass transport of uranium species within adsorbents, and (3) the availability and reliability of adsorbents.

Porous aromatic frameworks (PAFs) are a family of nanoporous solids with extended networks. Typically, they are constructed from carbon-carbon-linked rigid building units.³ Because of the insufficient stacking of rigid building units, PAFs exhibit surface area comparable to that of other porous material series, such as covalent organic frameworks and metal-organic frameworks. Meanwhile, the robust carbon-carbon linkages between the building units give PAFs exceptional stability toward the severe conditions of chemical treatment or harsh hydrolytic environments. Diverse functionalities of PAFs are readily obtained either by direct synthesis from designed building units or by post-modification to introduce desired active sites. The rational design of PAFs has provided opportunities to achieve the key UES goals.

Goal 1: Improve Uranium Selectivity

The majority of UES adsorbents interact with uranium through coordinating groups, especially oximes and

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<https://doi.org/10.1016/j.chempr.2021.01.012>

