

Efficient Capture of Perrhenate and Pertechnetate by a Mesoporous Metal–Organic Framework and Crystallographic Examination of Binding Motifs

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INTRODUCTION

During World War II and the Cold War, the nuclear weapons industry in the United States saw the production of 100 tons of plutonium and the generation of over 100 million gallons of hazardous liquid waste.¹ The Hanford Site in southeastern Washington state once operated nine nuclear reactors and produced two thirds of the nation's plutonium supply. The U.S. Department of Energy is preparing to treat 56 million gallons of legacy waste currently stored in the site's 177 underground tanks.²

Technetium-99 is a high yield, long-lived fission product.^{3, 4} In the oxidizing environment of the waste storage tanks, Tc-99 is present as the pertechnetate ion (TcO_4^-), a highly soluble, environmentally mobile, and volatile species.^{3, 4} The current legacy waste treatment plan includes separation of waste into high level and low activity waste streams followed by vitrification to immobilize the radioactive species in borosilicate glass. The volatility of pertechnetate at the high operating temperatures of the melters hinders its retention in the glass waste form.⁵⁻⁷ Additionally, pertechnetate's high solubility makes it dangerously environmentally mobile.⁸ Development of an effective strategy for pertechnetate removal from nuclear waste prior to vitrification is critical.

Various methods have been reported for pertechnetate capture and the most promising strategies utilize ion exchange processes.⁸ Unfortunately, a sorbent with high uptake capacity, fast kinetics, and selectivity is yet to be realized. Metal–organic frameworks (MOFs) are comprised of inorganic metal oxide nodes connected by multitopic organic linkers through coordination bonds.⁹ Given the variety of nodes and linkers available, MOFs have been tailored toward numerous applications¹⁰ including gas storage and delivery,^{11, 12} catalysis,¹³ and water remediation.¹⁴⁻¹⁶ Given the strength of Zr(IV)–O bonds, Zr₆-based MOFs are stable in aqueous media over a wide range of pH.¹⁷ A number of connectivities displayed by Zr₆-nodes contain terminal nonstructural labile ligands i.e. –OH/–OH₂ pairs. These spatially oriented Zr–OH sites have been utilized to capture oxyanions in a charge balancing manner.^{18, 19} Here,

we utilize the labile hydroxyl ligands at the node of NU-1000 to capture perrhenate (ReO_4^-), a TcO_4^- simulant, and capitalize on the MOF's permanent crystallinity to crystallographically identify the anion's binding motif.

NU-1000 is comprised of 8-connected Zr₆-nodes and 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene (H_4TBAPy) linkers (Fig. 1). The framework is characterized by 1D triangular (~12 Å) and hexagonal (~30 Å) channels with adjacent channels connected by small pores (~8 Å). NU-1000 is stable in aqueous media over a large range of pH (1-11).^{20, 21} Our group has shown that the terminal hydroxyl groups on the Zr₆-node of NU-1000 can be substituted by hazardous oxyanions such as selenate/selenite¹⁸ and sulfate.¹⁹ We hypothesized that NU-1000 would similarly capture perrhenate (ReO_4^-). Here, we highlight our findings from our effort to determine NU-1000's maximum perrhenate uptake capacity, its perrhenate selectivity in the presence of competing anions, and stability to the adsorption process. Furthermore, we briefly investigate pertechnetate capture and the suitability of perrhenate as a surrogate. Finally, we elucidate the various binding motifs of perrhenate at the Zr₆-node via single-crystal X-ray diffraction.

RESULTS

Maximum Uptake Per Node

To investigate the affinity of NU-1000 for perrhenate (ReO_4^-), MOF samples were exposed to aqueous sodium perrhenate solutions with Re concentrations corresponding to 2 – 7 ReO_4^- per Zr₆-node. After an exposure time of 26 h, NU-1000 was found to capture between 1.2 and 2.0 ReO_4^- ions per node when exposed to 2 and 7 ReO_4^- per node, respectively.²² These results suggested that NU-1000 might be an effective sorbent for perrhenate.

Adsorption Per Gram

Effective sorbents must exhibit high uptake capacity and rapid uptake kinetics. To quantify the maximum ReO_4^- capacity of NU-1000 and study the associated kinetics, MOF

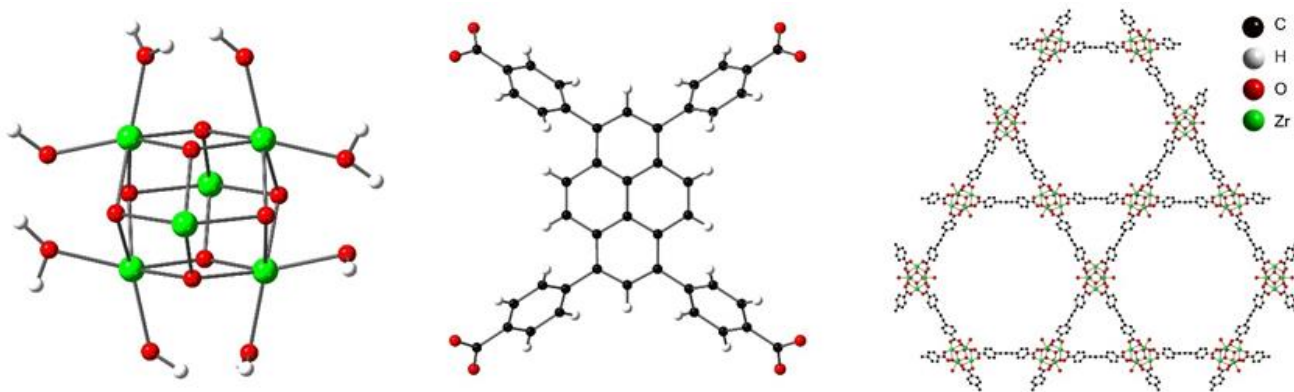


Fig. 1. (a) Structure of Zr_6 -node in NU-1000. (b) Structure of the tetratopic pyrene-based linker H_4TBAPy . (c) Structure of NU-1000 containing ~ 30 Å hexagonal mesopores and ~ 12 Å triangular micropores.

samples were exposed to aqueous sodium perrhenate solutions with Re concentrations corresponding to 1.0 – 3.0 ReO_4^- ions per MOF node. The amount adsorbed q in mg of ReO_4^- per gram of NU-1000 was determined using eqn (1)

$$q = \frac{(C_i - C_f) \times V}{m} \quad (1)$$

where C_i = initial concentration (mg/L), C_f = final concentration (mg/L), V = volume of solution exposed to NU-1000 (L), and m = mass of NU-1000 (g). Adsorption isotherms, constructed by monitoring q as a function of time (Fig. 2), reveal that NU-1000 saturates within 5 min of exposure likely due to framework's large diffusion-facilitating pores. According to a Langmuir Type I fit, the maximum perrhenate adsorption capacity of NU-1000 was determined to be 210 mg/g placing NU-1000 among the best sorbents reported to date.²²

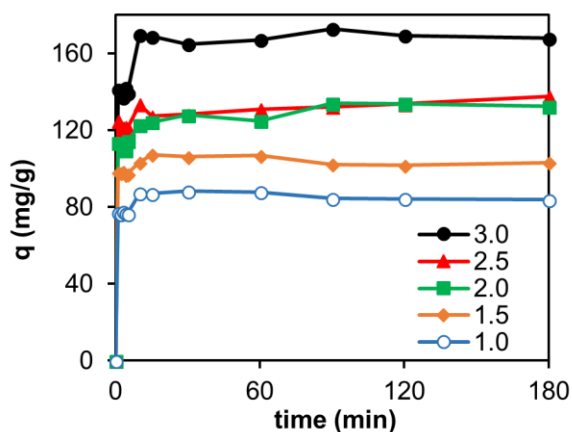


Fig. 2. Amount ReO_4^- adsorbed (q) vs time at various exposure concentrations of perrhenate per node of NU-1000.

Competition

Selectivity in the presence of competing anions is an important metric for evaluating sorbent applicability. The waste streams at Hanford include not only perrhenate but

also halides, nitrate, and sulfate. Therefore, to evaluate if NU-1000 retains its perrhenate affinity in the presence of competing anions, MOF samples were exposed to equimolar aqueous solutions of perrhenate and one of the following: chloride, bromide, iodide, nitrate, or sulfate. Uptake isotherms indicate that NU-1000 maintains its original uptake capacity and uptake kinetics even in the presence of equimolar amounts of halides and nitrate. The perrhenate uptake is slightly reduced in an equimolar solution of sulfate likely due to stronger electrostatic interactions between the NU-1000 node and the doubly-charged sulfate anion. It is worth noting that despite the higher negative charge on the sulfate and similar molecular geometry to perrhenate, more than 86% of the original perrhenate uptake is maintained.

Regeneration

The economic feasibility of implementing a waste remediation method significantly increases when a sorbent is recyclable. The reusability of NU-1000 was probed using a glass microanalysis vacuum filtration apparatus equipped with an Anodisc™ filter membrane. MOF samples were exposed to an aqueous perrhenate solution with a Re concentration of ~ 255 ppm (equivalent to an exposure of 3.0 ReO_4^- ions per Zr_6 -node). Under weak vacuum, the solution was passed through the MOF within one minute. The MOF captured ~ 1.9 ReO_4^- ions/node during the first exposure. NU-1000 was regenerated by washing with a 5% HCl solution which was found to completely remove the captured perrhenate. After washing with water, the same MOF sample was exposed to another aliquot of the perrhenate solution. The uptake of this second trial was found to be ~ 1.8 ions/node. Again, the 5% HCl wash entirely removed the captured perrhenate. The MOF was similarly washed with water to prepare for the next cycle. Over three additional cycles of exposure, acid washing, and water washing, NU-1000 sustained a steady uptake of ~ 1.8 ReO_4^- ions per node. Therefore, captured perrhenate is efficiently removed from NU-1000 by washing with dilute hydrochloric acid, and NU-

1000 consistently captures at least 1.8 ReO_4^- ions per node through 5 cycles of exposure and regeneration.

Single-Crystal X-Ray Diffraction

Few sorbents have the advantage of containing well-defined binding sites and analyte binding motifs that can be characterized crystallographically. To directly investigate the perrhenate binding motifs, single crystals of NU-1000 were exposed to an aqueous sodium perrhenate solution and examined via single-crystal X-ray diffraction analysis. Structure refinement reveals that there are both chelating and non-chelating, or terminal, perrhenate binding modes in both the small pore and the mesopore of NU-1000 (Fig. 3). Residual electron density plots ($F_o - F_c$ contoured maps) of the structure without rhenium atoms indicate that hydroxyl ($-\text{OH}$) and water ($-\text{OH}_2$) groups at the node are displaced by perrhenate via a pseudo-ion exchange mechanism. Therefore, both an $-\text{OH}$ and an $-\text{OH}_2$ group are displaced by perrhenate when the analyte is bound via a chelating motif. Similarly, a single $-\text{OH}$ group is exchanged when perrhenate is bound in a non-chelating manner.

The chelating sites directed into the small pore and the mesopore are each disordered between two equivalent positions. The non-chelating perrhenate ions were found to be disordered over 3 positions surrounding each terminal $-\text{OH}$ group on the Zr_6 -node, with two crystallographically nonequivalent positions in both the small pore and the mesopore. Due to the highly disordered structure and the surrounding solvent, the terminal oxygen positions of the non-chelating perrhenate ions could not be resolved. The number of crystallographically determined perrhenate was *ca.* 0.7 and 2.2 per Zr_6 -node for the chelating and non-chelating motifs, respectively, which indicates that at room temperature, the non-chelating coordination mode contributes heavily to the capture of perrhenate by NU-1000.

Post-Adsorption Characterization

To confirm the retention of bulk crystallinity and porosity throughout the adsorption process, full post-adsorption characterization of NU-1000 was performed. Powder X-ray diffraction patterns support that NU-1000 remains crystalline throughout adsorption. Additionally, N_2 isotherms before and after adsorption are nearly identical in shape with Brunauer-Emmett-Teller (BET) surface areas of $2140 \pm 5 \text{ m}^2 \text{ g}^{-1}$ ($1010 \pm 5 \text{ m}^2 \text{ cm}^{-3}$) and $1640 \pm 5 \text{ m}^2 \text{ g}^{-1}$ ($1040 \pm 5 \text{ m}^2 \text{ cm}^{-3}$), respectively. The decrease in gravimetric surface area is consistent with the increase in mass due to adding perrhenate to the framework. The associated pore size distributions further corroborate the existence of binding motifs within both pores as shown by the SCXRD data.

In conclusion, NU-1000 was found to have a perrhenate adsorption capacity of 210 mg/g. Over a range of concentrations, NU-1000 reached its maximum capacity within five minutes of exposure, presumably due to its large

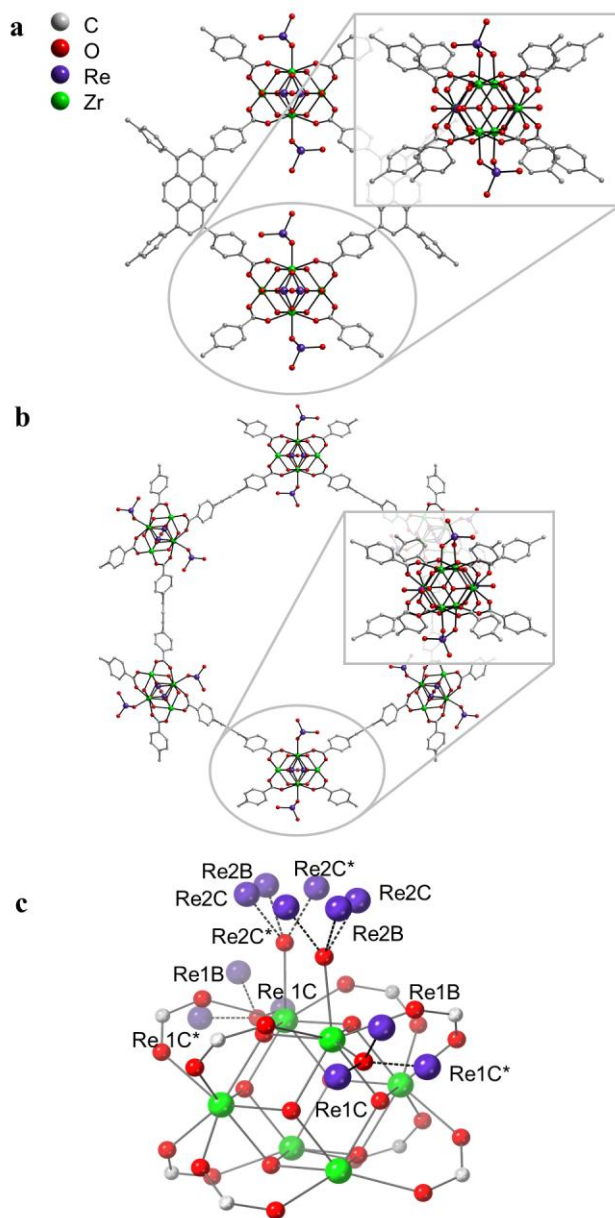


Fig. 3. The crystal structure of NU-1000 after ReO_4^- ion capture. Chelating perrhenate binding motifs pointing into the (a) small pore (Re1A) and (b) mesopore (Re2A). (c) Disorder of non-chelating perrhenate ions bound to the node of NU-1000 at the terminal $-\text{OH}$ group positions. At each position, there are two crystallographically unique positions (B and C) with one mode disordered between two positions (C and C*).

pores that facilitate diffusion and the accessible and substitutionally labile $\text{Zr}-\text{OH}$ sites on the nodes. Importantly, screening with pertechnetate further indicated that NU-1000 is an effective sorbent and supports that perrhenate is a suitable surrogate. Additionally, the presence of competing anions such as halides and nitrate did not inhibit the

adsorption of ReO_4^- ; while sulfate slightly reduced ReO_4^- adsorption. Furthermore, washing with dilute HCl can easily regenerate NU-1000 and the MOF consistently adsorbs 1.8 ReO_4^- ions per node through 5 cycles of exposure and washing. Single-crystal X-ray diffraction studies demonstrated that ReO_4^- binds at the node via a unique chelating mode in both the small pore and the mesopore, and two additional unique non-chelating modes in each pore. The facile, large scale synthesis of NU-1000, the framework's properties, and our recently garnered understanding of perrhenate binding at the node make this material a promising candidate for pertechnetate remediation.

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