Peroxide-Treated Metal-Organic Framework Templated Adsorbents for Remediation of High Level Nuclear Waste

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ABSTRACT

Remediation of legacy nuclear waste is one of the greatest challenges faced by the US Department of Energy, with projected cleanup efforts requiring over five decades and hundreds of billions of dollars. New materials are necessary to accelerate waste processing, achieving time and financial savings. Herein we report a peroxide treatment to a Ti metal-organic framework (MOF) and related MOF-templated adsorbents. The resulting materials displayed exceptional affinity for Am(III), achieving distribution coefficients in excess of 10^5 mL/g, and out-performing state-of-the-art benchmarks monosodium titanate (MST) and peroxo-treated modified MST (mMST) for removal of ^{85}Sr(II) and $^{239, 240}$Pu(IV) from legacy nuclear waste simulant.

1. Introduction

A tremendous need exists for innovative new materials capable of expediting the processing and decontamination of nuclear waste.[1, 2] Over 705 thousand tons of spent nuclear fuel await processing globally, while more than 340 million liters of legacy waste awaits processing in the United States.[3] Generation of new approaches and materials for high efficiency separations are essential to reduce the waste processing footprint, decrease secondary waste generation, reduce technical risk, and decrease processing time. At the Savannah River Site (SRS), the current disposal path involves multiple engineering processes to separate the high activity supernatant from sludge, followed by removal of the most radioactive components through application of an inorganic sorbent and a solvent extraction process.[4] The state of the art material, monosodium titanate (MST), is a spherical particle composed of an amorphous titanate core with a fibrous crystalline surface.[5-12] Despite displaying excellent affinity for a wide variety of metal ions over a broad pH range, the MST also constitutes the current bottleneck in waste processing.[1] The modest Ti solubility in the final waste form, a vitrified borosilicate glass log, restricts the maximum loading that can be safely achieved. Deployment of a material capable of more efficient radionuclide removal would reduce the overall volume of waste requiring long term storage in a geological repository.

While several different approaches, such as in situ formation of mixed iron oxide[13-15] or precipitation through caustic adjustments with addition of strontium nitrate and sodium permanganate[16-18] have been proposed for accelerating removal of radioactive Sr and transuranics, another interesting approach is the improvement of MST properties through treatment with hydrogen peroxide.[11, 12, 19, 20] So-called modified MST (mMST) is prepared through direct synthesis with peroxide in water or isopropyl alcohol, as well as through post-synthetic peroxide treatment of MST.[19] Although performance varies between mMST synthetic variants, they nevertheless display universally improved metal uptake compared to traditional MST for removal of Sr and actinides in legacy waste simulant.[19]

We recently reported a wet-treatment method for transforming sacrificial metal-organic framework (MOF) templates into porous inorganic adsorbents through a thermodynamically-driven ligand exchange process.[21, 22] Composed of metal cluster nodes and organic bridging ligands, MOFs are porous coordination polymers which possess high surface areas and well-defined long-range ordering. MOFs have been investigated as solid phase extractants for the removal of various metals, displaying promise due high loading of site isolated metal-chelating functionalities in conjunction with rapid mass transport facilitated by their extensive porosity. Unfortunately, due to their construction from labile metal-ligand coordination bonds, they are inherently unstable under harsh conditions, such as the highly caustic and radioactive environment that defines legacy nuclear waste. However, these weak coordination bonds can be eliminated through substitution with a strongly binding inorganic species, as readily identified through inspection of K_{sp} values. The resulting materials are thermodynamically stable, resisting decomposition at temperatures above 600 °C, yet retain significant porosity and in some instances surpass the volumetric surface area of their MOF precursor.

Part of our previous work entailed investigation of several MOF-templated adsorbents for radionuclide removal from legacy nuclear waste.[21] When added at as little as 25% the concentration as MST (with respect to metal, the limiting parameter for waste disposal), a Zr-derived MOF-templated material achieved a decontamination factor 3× greater than MST for Sr-removal, affording a net 12× improvement in performance. The same material displayed a 50% improvement in Pu uptake and a 60% improvement in U extraction, in all instances rivaling or surpassing results obtained previously for mMST.[19] Nevertheless, inspired by the improvements afforded by the straightforward transformation of MST to mMST, we hypothesized similar peroxide treatments could further improve our MOF-templated adsorbents. In this work we report two avenues for the generation of peroxo-modified MOF-templated materials and characterize their performance for the removal of Sr and Pu from nuclear waste simulant, as well as Am and Eu from an aqueous solution.

2. Experimental

2.1 Materials

All chemicals were obtained from commercial vendors except where specified. Chemicals and solvents were used without further purification, with the exception of $Ti(^iPrO)_4$ which was distilled. Radioactive components were obtained from the following sources: ^{85}Sr radiotracer from Perkin Elmer Life Sciences, Boston, MA; nitric acid solutions of Pu(IV) were derived from Pu production operations at Savannah River Site; ^{241}Am radiotracer was obtained from the Radiochemical and Engineering Research and Development Center (REDC) of Oak Ridge National Laboratory; $^{152,\,154}Eu$ radiotracer was obtained from Isotope Products, Burbank CA. The MST used for comparison in sorption testing was provided by Harrell Industries, Inc. (Rock Hill, SC).

2.2 Synthesis

Peroxo-treated adsorbents were prepared from MIL-125(Ti) MOF precursors, synthesized as reported previously.[21, 23] For one adsorbent material, the MIL-125(Ti) was treated with aqueous NaOH to generate TiOx, as articulated in prior work,[21] followed by post-synthetic treatment with three equivalents of H_2O_2 in water (Figure 1). Specifically, 90 mg TiOx (55 wt% Ti; 1 mmol Ti) was transferred in 5 mL DI water to a glass beaker. The pH of the solution was adjusted with 2 M HNO_3 to a final pH of 2.4, and the solution was transferred to a round bottom flask with stir bar. While stirring, 316 µL of 30% H_2O_2 in water was added (3 mmol H_2O_2; 3 eq. with respect to Ti). The white solution immediately displayed an abrupt color change to bright yellow, indicative of protonated or hydrated Ti-peroxo species (Figure S1). The flask was capped with a rubber septum, vented with a needle to prevent pressure buildup, and the mixture was stirred for 24 h. The yellow solid was collected by centrifugation, washed two times with DI water, and suspended in 5 mL DI water. 57 mg H_2O_2-TiOx was achieved (48 wt% Ti), affording an approximate yield of 55%. Experiments using dry H_2O_2-TiOx involved an additional wash with methanol, followed by drying under vacuum to afford a dry solid yellow product.

In contrast to the aforementioned post-synthetic approach, the second adsorbent material was prepared by direct treatment of the MIL-125(Ti) MOF with 75 equivalents of H_2O_2, generating a yellow solid. Specifically, 100 mg MIL-125 (24.5 wt% Ti; 0.51 mmol Ti) was suspended in 10 mL DI water and transferred to 20-mL glass scintillation vial. 3 mL of 30% H_2O_2 in water was slowly added to the MOF suspension, affording a light yellow solid. The scintillation vial was capped with a septum, vented with a needle, and the solution was gently agitated on a plate shaker overnight. The light yellow solid was collected by centrifugation, washed three times with DMSO, then two times with DI water. The final material was stored in 4 mL DI water. 33 mg H_2O_2-MOF was obtained (48 wt% Ti), affording an approximate yield of 65%. Experiments using dry H_2O_2-MOF involved an additional wash with methanol, followed by drying under vacuum to afford a dark orange product.

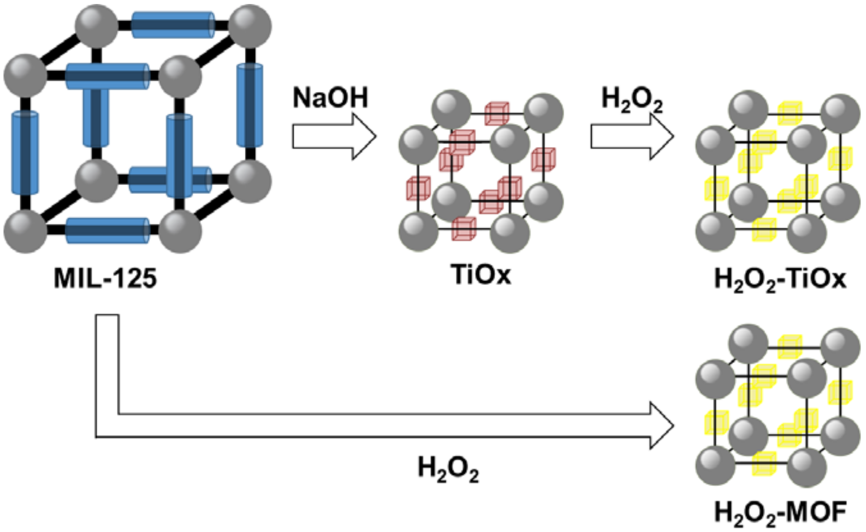

Figure 1. Synthetic approaches for preparation of MOF-templated adsorbents used in this study. The MOF precursor, MIL-125, is displayed on the left. The MOF-templated TiOx is in the middle. The peroxo-treated material is displayed on the right. H_2O_2-TiOx is prepared through the top path where a TiOx intermediate is obtained followed by a post-synthetic treatment of TiOx with H_2O_2. H_2O_2-MOF is prepared through the bottom path by treating the MIL-125 directly with H_2O_2.

2.3 Am/Eu Removal Experiments

In each experiment, 5 mg adsorbent was contacted with 1 mL of Am, Eu aqueous solution containing 1.85×10^4 Bq/mL (0.5 μCi/mL) of each radiotracer. Solutions were mixed on a rotating wheel for 2 h at a rotational velocity of 60 rpm and a temperature of 25 ± 0.2 °C. After contact, the samples were centrifuged at 3000 rpm for 5 min; 100 μL of supernatant was aliquoted from each sample and placed into capped polypropylene tubes. The amount of ^{241}Am and $^{152, 154}$Eu in each sample was determined by a Canberra High-Purity Germanium Detector (HPGe) Gamma Analyst, with a count time of 30 minutes for each sample. Blanks were analyzed to confirm background subtraction was not necessary, and quality assurance calibration was performed prior to testing. All separations were performed in duplicate, with average results reported and error determined by calculation of the standard deviation.

2.4 High Level Waste Decontamination Experiments

Sr and Pu removal testing was performed from high level waste simulant (see Table 2 for composition), with all adsorbents contacted at Ti concentrations of 2 mM. Samples of MST and mMST were also run to provide a direct benchmark against state of the art materials currently in use. Samples were shaken at 175 rpm in a shaker oven at 25 °C, with sampling performed at 1, 6, and 24 h. Before sampling, the bottles were manually agitated to ensure a representative aliquot of both solids and solution were removed. Aliquots were subsequently filtered through 0.10-µm polyvinylidene fluoride membrane syringe filters, with a measured quantity of filtrate acidified with an equal volume of 5 M nitric acid, thoroughly mixed, and allowed to stand for a minimum of 2 h prior to radiochemical analysis. ^{85}Sr activity was determined by gamma spectroscopy, while $^{239, 240}$Pu content was quantified by plutonium thenoyltrifluoroacetone scintillation (PuTTA) analysis.

3. Results and Discussion

Similar to TiOx and other MOF-templated adsorbents, both H_2O_2-TiOx and H_2O_2-MOF were structurally amorphous. Powder X-ray diffraction data (not shown) collected on the H_2O_2-treated samples were absent of any peaks or features and dominated by random noise, indicating the substitution of bridging ligands destroys the crystallographic order of the MOF precursor. SEM imaging (Figure S2) displays no obvious difference in bulk or surface morphology between H_2O_2-TiOx and H_2O_2-MOF, but due to the requirement for dehydration prior to imaging we cannot rule out differences when the adsorbents are wetted. The images display individual adsorbent particles which resemble the block-shaped morphology of the MOF precursors. Closer inspection reveals significant surface texturing, similar to previously published images of MST and mMST. Comparison of thermogravimetric analysis (TGA) data reveal comparable weight loss at 600 °C for both H_2O_2-treated materials, similar to other peroxide-modified titanates,[19, 24] as well as the non-treated TiOx adsorbent (Figure 2a). In contrast, the MIL-125 MOF precursor displays catastrophic weight loss from 300 – 450 °C, due to the combustion of the organic bridging ligand. The absence of such behavior in any of the templated materials supports the complete removal of the bridging ligand during the various treatment processes, as was also demonstrated previously.[21] However, differences in weight loss profiles exist at low temperature for both H_2O_2-TiOx and H_2O_2-MOF, with the former displaying a profile similar to the TiOx precursor. The variety in low temperature TGA data for the peroxide-treated materials we attribute to the differences in solvent evaporation due to different material morphology and porosity. This result may also suggest peroxo modification of the TiOx occurs primarily on the surface, whereas complete removal of the bridging ligand by H_2O_2 affords a different atomic structure in the final material. As a result, decomposition of differing surface functionalities is also believed to influence the low temperature TGA results.

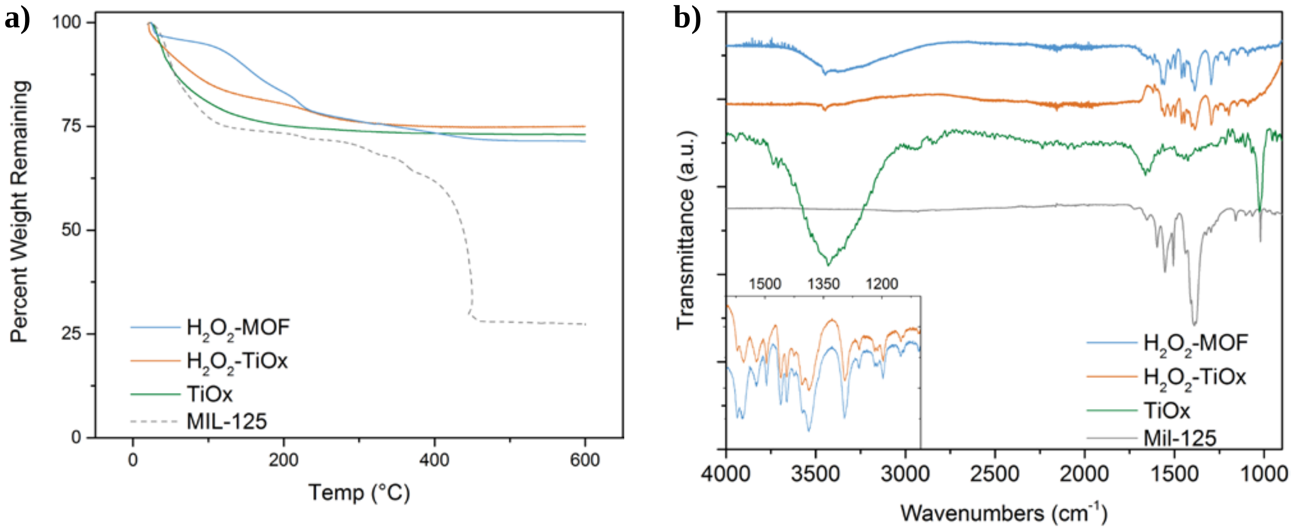

Figure 2. (a) TGA data of the MIL-125 precursor, TiOx, and peroxo-treated adsorbents. (b) IR spectra for peroxo-treated MOF-templated adsorbents and precursors. Remarkable similarities in low energy IR features are observed between H_2O_2-TiOx and H_2O_2-MOF, displayed in the inset, despite their preparation from different precursor materials.

Analysis of the IR spectra reveals marked similarities between both peroxo-treated materials, and distinct differences from MIL-125(Ti) and TiOx precursors (Figure 2b). Metal peroxide literature reveals characteristic IR peaks predominantly occur at frequencies from 500-900 cm^{-1}, which is outside of the range of analysis for our spectrometer. However, M-OOH frequencies occur above 1000 cm^{-1}, as is the case for a $K_3[Co(CN)_5OOH]$ salt (1264 cm^{-1}),[25] and is consistent with the IR spectra of our peroxide-treated materials. Sharp, intense features slightly above 1000 cm^{-1} are observed for MIL-125 and TiOx, which can likely be attributed to Ti-O stretching vibrations.[25, 26] While we cannot precisely define the peaks, the strong similarity between peroxo-treated adsorbents confirms a common structure and is useful for a rudimentary fingerprinting-type analysis. Moreover, while the MIL-125 displays several peaks in low wavenumbers, they do not align with those in the peroxo-treated adsorbents, corroborated by

TGA data confirming the complete removal of all organic species from the MOF template. Hydrogen bonding in metal hydroxides is known to afford an absorption band around 3000 – 3600 cm^{-1}, as is obvious in the TiOx and also visible in the H_2O_2-MOF,[26] yet remarkably subtle in the H_2O_2-TiOx. Perhaps most importantly, fine features are observed at low wavenumbers in both H_2O_2-treated materials, consistent with titanium oxygen polyhedra observed in titanates[26, 27] and not observed in either TiOx or MIL-125 precursors.

Separation of trivalent actinides from lanthanides is a major research focus for closing the nuclear fuel cycle.[28] Accordingly, we initially screened the MOF-templated adsorbents for separation of Am and Eu from an aqueous solution, with the results summarized in Table 1. Samples were kept in slurry form from initial MOF synthesis until contact with the radionuclide solution, as initial screening studies revealed a 25 – 50% reduction in metal removal for materials which had been dried and redispersed in solution. The peroxo-treated materials displayed exceptional affinity for Am and Eu, extracting approximately 95 – 100% of all metals from the nitric acid solution and achieving distribution coefficients (K_d) approaching 2×10^5 mL/g. K_d values are defined by equation 1:

$$K_d = \frac{(C_0 - C_e)}{C_e} \times \frac{V}{m} \tag{1}$$

where C_0 and C_e refer to the metal concentration originally and at equilibrium, V is volume of contact solution (in mL) and m is mass of adsorbent (in g). Higher K_d values equate to more effective adsorbent materials, with values in excess of 1×10^5 mL/g considered exceptional.[29, 30] While high K_d values were demonstrated by both materials, no appreciable selectivity was observed for Am or Eu, attesting to its utility as a broad-spectrum, albeit non-selective, adsorbent.

In contrast to the peroxide-treated materials, the precursor MOF and TiOx displayed some selectivity towards Am over Eu, with both materials removing approximately 88% and 74%, respectively. The performance of the precursors was analyzed primarily as a control experiment, nevertheless this is a noteworthy, if serendipitous, observation. We hypothesize the origins of the observed selectivity are attributable to the porosity of the MOF and TiOx materials, combined with surface functionalities possessing lower affinity for Am and Eu than their peroxide-treated products. It is possible that the slightly greater radius of Eu over Am promotes the slight selectivity based on the decrease in mass transport through pore architectures. Nevertheless, further investigation into this phenomenon is needed before any definitive conclusions can be obtained.

Table 1. Effect of peroxo-treatment on Am / Eu removal by MOF-templated adsorbents.

	MOF	**TiOx**	**H_2O_2-MOF**	**H_2O_2-TiOx**
% Am Removed	87.6 ± 1.2	88.3 ± 0.8	99.9 ± 0.0	94.8 ± 0.6
% Eu Removed	74.6 ± 2.4	73.0 ± 1.8	99.9 ± 0.0	94.8 ± 0.6
K_d Am ($\times 10^5$ mL/g)	1.753 ± 0.023	1.766 ± 0.016	1.999 ± 0.000	1.897 ± 0.012
K_d Eu ($\times 10^5$ mL/g)	1.493 ± 0.049	1.460 ± 0.037	1.999 ± 0.000	1.896 ± 0.013
SF Am/Eu	1.17 ± 0.02	1.21 ± 0.02	1.00 ± 0.000	1.00 ± 0.00

All measurements were performed in duplicate. Errors are the standard deviation of two replicates.

Informed by the Am / Eu separation study, we tested the post-synthetically peroxo-treated material, H_2O_2-TiOx, against MST and mMST for removal of Sr and Pu from legacy nuclear waste simulant (Table 2). Results are reported in Figure 3 as decontamination factors (DFs), which are the ratio of metal in solution before and after adsorbent contact, i.e. DF = M_i/M_f. Rearranging the expression for DF reveals 1/DF is equal to the percent of M_i remaining, and allows the percent of metal removed from solution to be calculated by equation 2:

$$\% \, M \; Removed \; = \; 1 - \frac{1}{(DF)} \tag{2}$$

While the directly-prepared H_2O_2-MOF displayed slightly superior performance to the H_2O_2-TiOx in the Am / Eu extraction study, it was also fragile and required delicate handling. These attributes are unsuitable for industrial-scale waste processing, so H_2O_2-MOF was thus down-selected from further testing.

Table 2. Composition of High-Level Waste Simulant.

Component	**Concentration**
$NaNO_3$	2.35 M
NaOH	1.27 M
Na_2SO_4	0.531 M
$NaAl(OH)_4$	0.389 M
$NaNO_2$	0.127 M
$NaCO_3$	0.0302 M
$Sr(NO_3)_2$	7.72×10^{-6} M
^{85}Sr	30,000 dpm/mL (target)
$CsNO_3$	1.4×10^{-4} M
^{137}Cs	123,000 dpm/mL
Total Pu	0.128 mg/L
^{237}Np	0.463 mg/L
Total U	10.1 mg/L

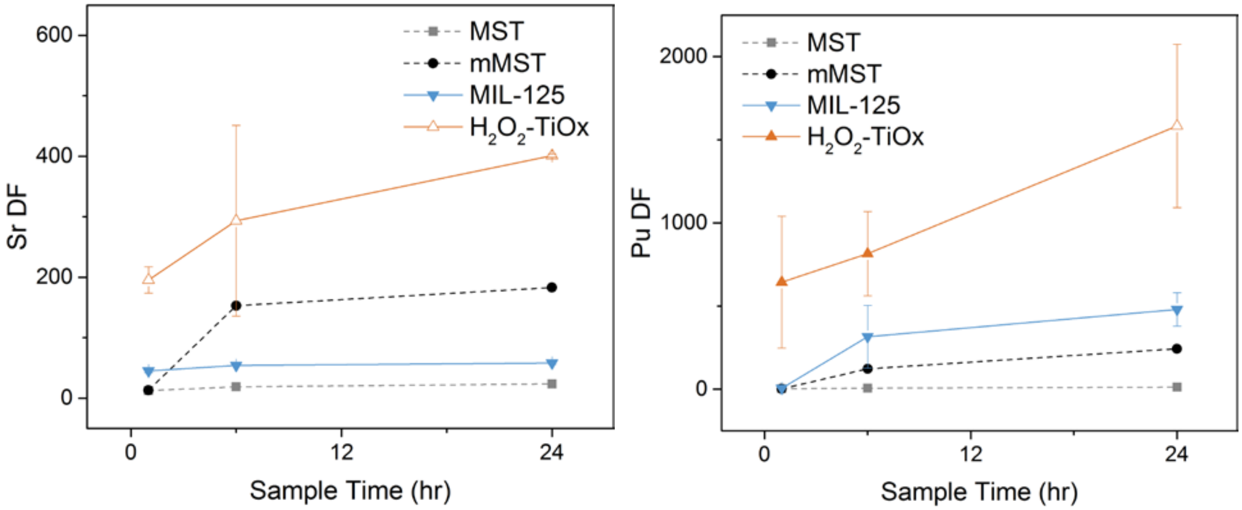

Figure 3. Performance of peroxo-treated adsorbents, MST, and mMST for removal of Sr and Pu from legacy nuclear waste simulant. All samples are added at a concentration of 2 mM Ti. Samples with the greatest decontamination factor (DF) are desired as they would enable the greatest amount of radionuclide to be irreversibly bound in the final borosilicate glass waste form. MIL-125 and H_2O_2-TiOx samples were measured in duplicate. While data for MST and mMST have only one replicate, the performance can be compared with other results in the literature.[10, 12, 20, 21] Open points indicate the limit of quantification was surpassed during analysis of metal in the waste simulant.

Inspection of the decontamination results reveal H_2O_2-TiOx to be a superior adsorbent compared to MST, mMST, or the TiOx precursor.[21] For Sr removal, the H_2O_2-TiOx more than doubles the performance of mMST and is approximately 8× superior to the original MOF template. Interestingly, our previous investigation of non-peroxo-treated TiOx revealed little inherent affinity for Sr, and displayed negligible uptake under identical conditions.[21] Pu removal performance was also dramatically enhanced following peroxide treatment, with previous DF values < 10 reported for the non-peroxide-treated TiOx over 24 hours of contact,[21] compared to DF values > 1500 for H_2O_2-TiOx. From these results we conclude the observed performance improvement for the TiOx materials is solely attributable to the post-synthetic peroxide treatment. H_2O_2-TiOx out-performed mMST by approximately 6× and MST by > 10×, revealing remarkable potential to expedite waste processing throughput if assimilated into operations at the Salt Waste Processing Facility.

4. Conclusions

In conclusion, we report the post-synthetic peroxide treatment of MOF-templated adsorbent materials, resulting in orders of magnitude performance gains over non-treated precursors or state of the art solid phase adsorbents MST and mMST. Peroxo-treated MOF-templated adsorbents were prepared in two ways, through direct treatment with H_2O_2 as well as by treatment of the TiOx adsorbent with H_2O_2. Both materials displayed exceptional performance for the removal of Am and Eu from a nitric acid solution, though no appreciable selectivity was observed, and the H_2O_2-TiOx material achieved the best performance in the open literature for removal of Sr and Pu from high level waste. Extension of this generalized post-treatment to Zr-based MOF-templated materials, which out-performed the first generation of Ti-materials, or other promising titanates like titanate nanotubes[31-33] is expected to result in unprecedented performance in next-generation materials for radiological waste decontamination.

ASSOCIATED CONTENT

Supporting Information. The following files are available free of charge: synthetic procedures for preparation of MIL-125, TiOx, and mMST.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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ABBREVIATIONS

DF, Decontamination Factor; K_d, Distribution Coefficient; mMST, Modified Monosodium Titanate; MOF, Metal-Organic Framework; MST, Monosodium Titanate; TGA, Thermogravimetric Analysis.

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