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Journal Name

ARTICLE

Efficient Extraction of Sulfate from Water using a Zr-Metal-Organic Framework

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A Zr-based MOF, NU-1000, comprised of Zr_6 nodes and tetratopic pyrene-containing linkers is studied for adsorption and extraction of SO_4^{2-} from water. The adsorption capacity and uptake time of SO_4^{2-} in NU-1000 is determined at varying concentrations to give an overall maximum adsorption capacity of 56 mg SO_4^{2-}/g of MOF. Selective adsorption of SO_4^{2-} by NU-1000 in the presence of other anions as well as regeneration of the sorbent is also explored.

Introduction

The extraction of sulfate (SO_4^{2-}) from aqueous solutions containing competitive anions is a challenging problem that has a significant impact on the disposal of nuclear waste.[1] The United States has over 86 million gallons of high-level radioactive waste (HLW) stored at Idaho National Laboratory, the Hanford Site in Washington and the Savannah River Site in South Carolina.[2] The U.S. Department of Energy (DOE) has treated some of this waste by converting it to borosilicate glass, a process known as vitrification, which can then be stored safely in a geological repository.[2] Prior to vitrification, nuclear waste is subject to chemical pretreatment which typically involves the addition of sulfuric acid and sulfonated ion-exchange resins, which inevitably remain in the waste as SO_4^{2-}, the most oxidized form of sulfur.[3] While SO_4^{2-} does not pose the same risks as the radioactive components of nuclear waste, its low solubility in borosilicate glass interferes with the vitrification process which leads to significant complications in the safe storage and disposal of HLW.[4] As a consequence, the development of materials for the extraction of SO_4^{2-} from nuclear waste is extremely important.

Numerous techniques have been studied for the removal of SO_4^{2-} from aqueous solutions including but not limited to molecular recognition,[1] precipitation,[5] ion-exchange,[6] reverse osmosis,[7] and adsorption.[8] Yet to be developed, however, is a material or technology that is promising for large-scale implementation at nuclear waste sites. Metal-organic frameworks (MOFs) are promising candidates for the adsorption and removal of oxyanions from water[9] and there are a few examples of MOFs that have been studied for the extraction of SO_4^{2-} by selective crystallization and anion-exchange.[10] For a material to be considered for large-scale SO_4^{2-} extraction from nuclear waste, it should be (1) easy to synthesize, (2) stable in water – and ideally at somewhat alkaline pH, (3) selective for the extraction of SO_4^{2-} from other anions – particularly in the presence of high concentrations of nitrate, (4) reusable, and (5) economical in terms of volume required.

With these criteria in mind, we turn our attention to the Zr-based MOF, NU-1000. NU-1000 is composed of tetratopic pyrene-containing linkers (Figure 1a) and Zr_6-containing nodes (Figure 1b) resulting in a framework with 1D channels/apertures that are either 12 or 30 Å in diameter (Figure 1c).[11] The synthesis of NU-1000 is straightforward and amenable to large-scale production.[12] In addition, NU-1000 is highly stable in water[13] and demonstrates excellent chemical stability from pH 1 to 11.[14] Recently, we discovered that terminal water and hydroxyl ligands on the eight-connected Zr_6 node of NU-1000 (Figure 1b) are important for the adsorptive removal of selenate and selenite from water.[15] Given that zirconia has a known affinity for SO_4^{2-},[16] we reasoned that substitution chemistry similar to that observed with selenate[15] may occur where one doubly charged SO_4^{2-} anion can replace two singly charged terminal hydroxyl ligands on the Zr_6 nodes in the framework. Herein, we explore SO_4^{2-} extraction from water using NU-1000 including selective adsorption of SO_4^{2-} in the presence of other anions, competitive adsorption of SO_4^{2-} in the presence of high concentrations of nitrate, as well as recyclability.

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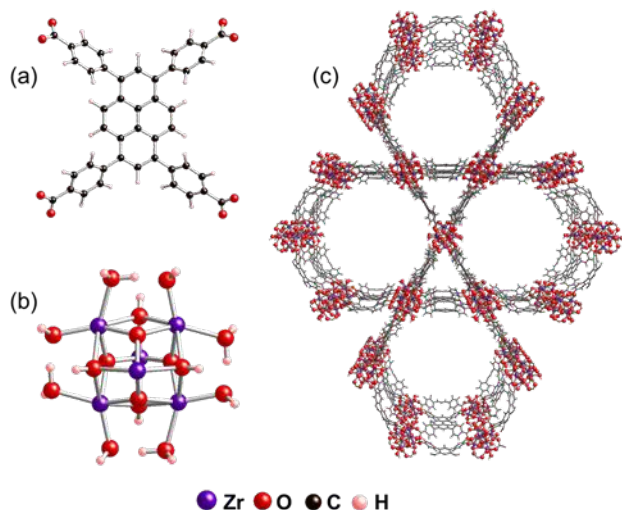[b.] Department of Chemistry, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia

Figure 1. (a) 1,3,6,8-tetrakis(p-benzoate)pyrene linker used to construct NU-1000 (b) Zr_6 node of NU-1000 and (c) structure of NU-1000

Figure 2. Amount adsorbed (q) vs. time with various starting concentrations of sulfate per node of NU-1000.

Results and Discussion

Adsorption Capacity. To determine if NU-1000 can effectively adsorb SO_4^{2-} from water, the MOF (5 mg) was exposed to 10 mL aqueous solutions of Na_2SO_4 with SO_4^{2-} concentrations ranging from 24 – 65 ppm, equivalent to an exposure level of 1 – 3 sulfate anions per Zr_6 node. The amount adsorbed (q) in mg of analyte per g of adsorbent was monitored as a function of time at 5 concentrations to construct a series of adsorption isotherms (Figure 2). Equation 1 was used to calculate q where C_i = initial concentration, C_f = final concentration, V = volume of solution exposed to NU-1000 and m = mass of NU-1000 in g. Using the Langmuir equation, the maximum adsorption capacity (Q) of NU-1000 for sulfate was determined to be 56 mg/g (Figure S1, Table S1). At all concentrations, NU-1000 reaches its maximum adsorption within 1 minute of exposure to the SO_4^{2-} solution, which is likely due to the large 30Å apertures of NU-1000 that facilitate diffusion of SO_4^{2-} throughout the framework. When 5 mg of NU-1000 is exposed to 5 mL of water containing SO_4^{2-} concentrations ranging from 36 – 126 ppm (equivalent to 2 – 7 SO_4^{2-}/Zr_6 node), the MOF was found to take up a maximum of 1.5 sulfates/node (Table S2), which is in agreement with the maximum adsorption capacity (Q) calculated above. The adsorption capacity of NU-1000 for sulfate is comparable to that of other materials that have been reported for sulfate extraction or adsorption (Table S3) but what sets NU-1000 apart from other materials, such as anion receptors or macrocycles, is the ease of synthesis[12] and fast rate of sulfate uptake (< 1 min).
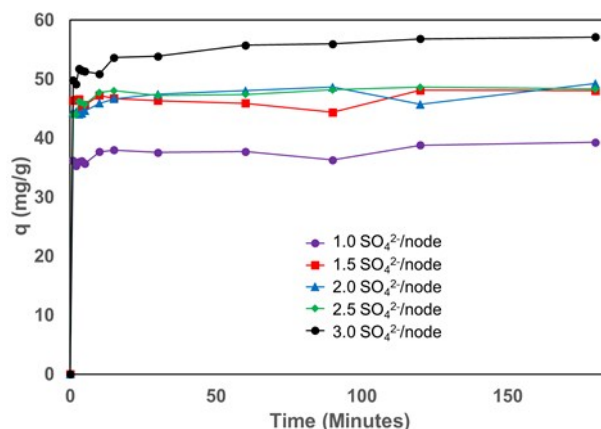
Equation 1
$$q_e = \frac{(C_i - C_f)V}{m}$$

Competitive Adsorption. Knowing that NU-1000 can efficiently adsorb sulfate anions from water, the next step was to probe how SO_4^{2-} adsorption is affected by the presence of other anions. Nuclear waste contains a variety of anions that may potentially compete with SO_4^{2-} adsorption including Cl^-, Br^-, I^- and NO_3^-.[17] NU-1000 was exposed to aqueous solutions containing SO_4^{2-} and equimolar amounts of Cl^-, Br^-, I^- or NO_3^-. Sulfate adsorption on NU-1000 was monitored as a function of time (Figure 3) and it was found in each case, that the amount of SO_4^{2-} adsorbed remains largely unaffected (< ± 4 mg/g difference) by the presence of other anions. In general, high concentrations of NO_3^- found in nuclear waste tend to have the most dramatic impact on SO_4^{2-} adsorption and/or extraction.[1] The concentration of NO_3^- in nuclear waste is often an order of magnitude higher than that of SO_4^{2-},[10a,17a] making it particularly challenging to selectively remove SO_4^{2-} from the mixture. To probe the effect of varying NO_3^- concentration on SO_4^{2-} adsorption in NU-1000, the MOF was exposed to solutions containing 15 ppm (0.1 mM) SO_4^{2-} with NO_3^- concentrations ranging from 10-50x higher (1 to 5 mM). The amount of SO_4^{2-} adsorbed by NU-1000 in the presence of NO_3^- was probed as a function of time (Figure S2) and it was found that the effect of NO_3^- on SO_4^{2-} adsorption was negligible with only a 1 mg/g decrease in SO_4^{2-} adsorption when exposed to 0 vs. 50x the molar concentration of NO_3^- (Figure 4). To gain further insight into the competitive adsorption of NO_3^- vs. SO_4^{2-} on NU-1000, the MOF was saturated with SO_4^{2-} (1.5 SO_4^{2-}/node) and then exposed to a 5 mM aqueous solution of NO_3^-. Leaching of SO_4^{2-} from NU-1000 in the presence of NO_3^- was monitored with time and compared to a control experiment where NU-1000-SO_4^{2-} was exposed to NO_3^--free water. While SO_4^{2-} leaching from NU-1000 was slightly higher in the presence of NO_3^- vs. NO_3^--free water, in all cases the leaching was essentially negligible (Figure S3).
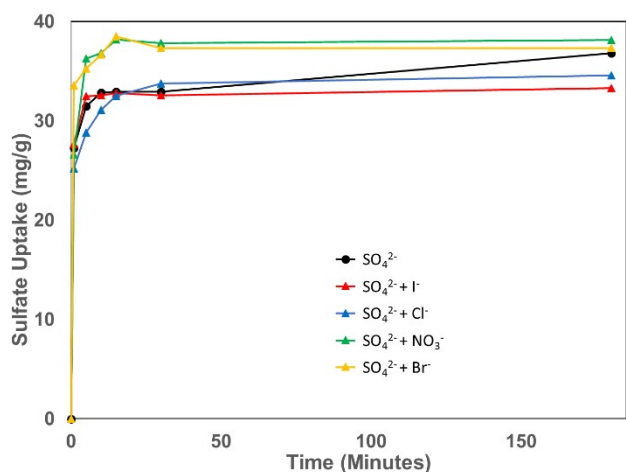
Figure 3. Sulfate adsorption in NU-1000 as a function of time in clean water and in the presence of I⁻, Cl⁻, NO₃⁻ and Br⁻ using 2 mg of NU-1000 and 10 mL of aqueous SO₄²⁻ at a concentration of 15 ppm (0.1 mM).
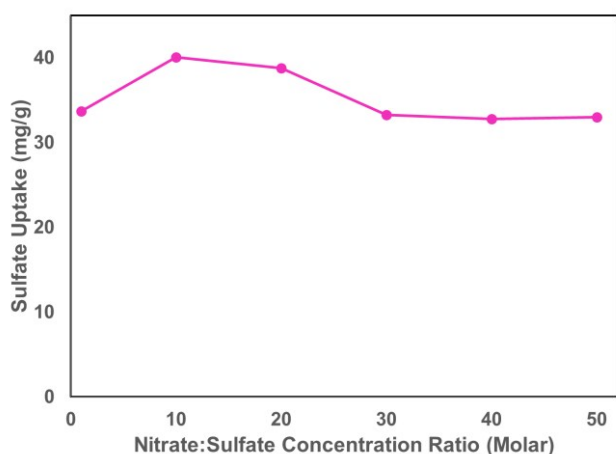

Figure 4. Sulfate uptake in NU-1000 in the presence of 1-50x the molar concentration of NO_3^- using 2 mg of NU-1000 and 10 mL of aqueous SO_4^{2-} at a concentration of 15 ppm (0.1 mM)

Post-Adsorption Characterization. Characterization of NU-1000 before and after adsorption of sulfate demonstrates that the framework remains intact after adsorption and no Zr leaching from the MOF into solution is observed. Powder X-ray diffraction (PXRD) patterns of NU-1000 and NU-1000-SO_4^{2-} are the same, implying that the bulk structure is unchanged (Figure S4). In addition, N_2 adsorption isotherms of NU-1000 pre- and post-adsorption of SO_4^{2-} are nearly identical (Figure S5) giving Brunauer-Emmett-Teller (BET) surface areas of 2130 ± 5 m²/g and 2045 ± 5 m²/g respectively. This slight drop in surface area is consistent with the addition of mass upon adding SO_4^{2-} to the framework and consistent with what we have seen after selenate extraction[15] or after installation of catalysts on the node of NU-1000 via atomic layer deposition or impregnation.[18]

Recycling. Another important feature of adsorbents designed for use on a large-scale is reusability. The ability to reuse and recycle a sorbent not only cuts down on cost but also reduces the carbon-footprint of the remediation process. The recyclability of NU-1000 was tested by placing 10 mg of the MOF

on an Anodisc™ filter membrane in a glass microanalysis vacuum filter apparatus equipped with a graduated cylinder. NU-1000 was then exposed to 10 mL of aqueous SO_4^{2-} at a concentration of 125 ppm (or 3.0 SO_4^{2-}/node). Using the vacuum filtration apparatus, all 10 mL of the SO_4^{2-} solution were passed through the MOF in less than 1 minute. Under these conditions, NU-1000 adsorbed 40 ppm (or 1.0 SO_4^{2-}/node) when first exposed to SO_4^{2-} (cycle 0 - Figure 5). NU-1000 was regenerated by washing the MOF with 5% HCl which was found to remove > 87 % of the initially adsorbed SO_4^{2-}. NU-1000 was then washed with 10 mL of water and exposed to an additional 10 mL of the aqueous SO_4^{2-} solution (cycle 1) and the MOF was found to take up more SO_4^{2-} (45 ppm or 1.1 SO_4^{2-}/node) than in the initial cycle. After two additional HCl washes followed by exposure to SO_4^{2-}, NU-1000 was found to consistently adsorb 45 ppm or 1.1 SO_4^{2-}/node (Figure 5).
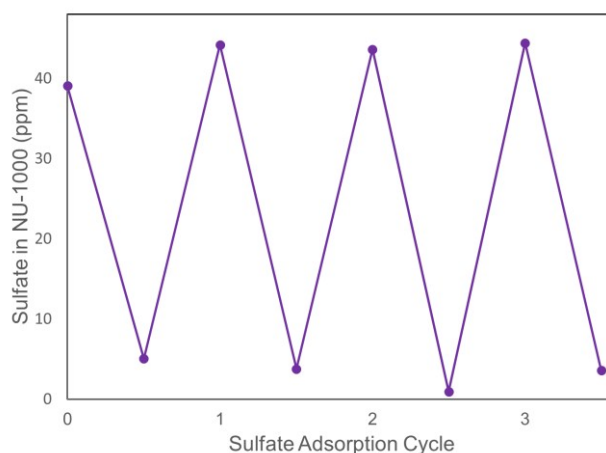

Figure 5. Recyclability of NU-1000. Cycle 0 refers to SO_4^{2-} adsorbed on fresh NU-1000. In between SO_4^{2-} exposure cycles 1-3, the MOF was washed with 5 % HCl and the amount of SO_4^{2-} remaining in NU-1000 (from the previous cycle-not additive) is plotted.

Conclusions

In summary, the adsorption of aqueous SO_4^{2-} using the water stable, Zr-based MOF NU-1000 was explored and the adsorption capacity of NU-1000 for SO_4^{2-} was found to be 56 mg/g. At varying concentrations, NU-1000 is shown to reach its maximum adsorption within the first minute of exposure to aqueous SO_4^{2-}. In addition, the presence of competitive anions such as Cl⁻, Br⁻, I⁻ and NO_3^- do not interfere with SO_4^{2-} adsorption including highly competitive concentrations of NO_3^- up to 50x higher than that of SO_4^{2-}. NU-1000 can also be regenerated by washing with dilute HCl, maintaining a consistent adsorption of 1.1 SO_4^{2-}/node throughout 3 cycles of washing followed by adsorption. The ease of synthesis, reusability and facile adsorption of SO_4^{2-} in NU-1000, particularly in the presence of competitive anions, makes this material a promising candidate in nuclear waste disposal applications where high concentrations of SO_4^{2-} interfere with the vitrification process and the safe storage of high-level radioactive waste.

Methods

General Experimental. NU-1000 was made according to a recently published, modified procedure.[19] Powder X-ray diffraction measurements were obtained using a Bruker MX IµS microsource with Cu-Kα radiation and an Apex II CCD detector. Measurements were made over a range of 2° < 2θ < 37°. N_2 adsorption and desorption isotherm measurements were performed on a Micromeritics Tristar II at 77K. Samples were activated by heating at 120 °C for 12 hours under high vacuum on a Micromeritics Smart VacPrep. All gases used were Ultra High Purity Grade 5 as obtained from Airgas Specialty Gases. ICP-OES data were collected on a Varian Vista MPX ICP Spectrometer. ICP standards were purchased from Fluka Analytical. The as-purchased S and Na ICP standards were 1000 mg/L in 2 % nitric acid, TraceCERT® and the Zr standard was 10 000 µg/mL in 4 wt% HCl. Standards for ICP-OES measurements (62.5 – 10 000 ppb) were prepared via serial dilution in 3 % HNO_3. Na_2SO_4, KBr, KI, KNO_3 and KCl were used to make aqueous solutions of the corresponding anions.

NU-1000 Maximum Uptake Per Node. The maximum uptake per node of NU-1000 was determined by exposing 5 mg of NU-1000 to 5 ml of an aqueous solution of sodium sulfate in a 15 ml polypropylene centrifuge tube with sulfate concentrations ranging from 36-126 ppm. These concentrations correspond to an exposure level of 2-7 analyte molecules per MOF node (i.e., Zr_6 cluster). The solutions were centrifuged for 1 minute to allow the MOF to settle to the bottom of the tube. Aliquots of the supernatant were removed and diluted to 5 mL in 3 % HNO_3 for analysis by ICP-OES. ICP-OES was used to determine the concentration of S, Na and Zr in each solution. Comparison of control solutions to those containing MOF was used to determine the number of sulfate anions adsorbed per node of NU-1000.

NU-1000 Adsorption Studies per Gram. The amount of sulfate adsorbed per gram of NU-1000 was determined by exposing 5 mg of NU-1000 to 10 mL of an aqueous solution of sodium sulfate in a 15 mL polypropylene centrifuge tube with concentrations ranging from 24-65 ppm. These concentrations correspond to an exposure level of 1.00-3.00 analyte molecules per Zr_6-node of NU-1000. The solutions were centrifuged for 30 seconds to allow the MOF to settle to the bottom of the tube. Aliquots of the supernatant were removed and diluted to 5 mL in 3 % HNO_3 at 1, 2, 3, 4, 5, 10, 15, 30, 60, 90, 120 and 180 minutes for analysis by ICP-OES. ICP-OES was used to determine the concentration of S, Na and Zr in each solution. Comparison of control solutions to those containing MOF was used to determine the amount of sulfate adsorbed (q) in mg/g of NU-1000 where $q = (C_i - C_f) \times V/m$, C_i = initial concentration, C_f = final concentration, V = volume of solution exposed to NU-1000 and m = mass of NU-1000 in g.

Competition Studies (1:1). Five different solutions were prepared with concentrations as follows: (1) 0.1 mM sulfate; (2) 0.1 mM sulfate and 0.1 mM iodide; (3) 0.1 mM sulfate and 0.1 mM chloride; (4) 0.1 mM sulfate and 0.1 mM nitrate and (5) 0.1 mM sulfate and 0.1 mM bromide. Five 2 mg samples of NU-1000 were exposed to 10 mL of each solution respectively in 15 mL polypropylene centrifuge tubes. The solutions were centrifuged for 30 seconds to allow the MOF to settle to the bottom of the tube. Aliquots of the supernatant were removed and diluted to 5 mL in 3 % HNO_3 at 1, 5, 10, 15, 30 and 180 minutes for analysis by ICP-OES. ICP-OES was used to determine the concentration of S, Na and Zr in each solution. Comparison of control solutions to those containing MOF was used to determine the amount of sulfate adsorbed (q) in mg/g of NU-1000.

Competition Studies (High concentrations of nitrate). Six different solutions were prepared with concentrations as follows: (1) 0.1 mM sulfate; (2) 0.1 mM sulfate and 1 mM nitrate; (3) 0.1 mM sulfate and 2 mM nitrate; (4) 0.1 mM sulfate and 3 mM nitrate; (5) 0.1 mM sulfate and 4 mM nitrate and (6) 0.1 mM sulfate and 5 mM nitrate. Six 2 mg samples of NU-1000 were exposed to 10 mL of each solution respectively in 15 mL polypropylene centrifuge tubes. The solutions were centrifuged for 30 seconds to allow the MOF to settle to the bottom of the tube. Aliquots of the supernatant were removed and diluted to 5 mL in 3 % HNO_3 at 1, 5, 10, 15, 30 and 180 minutes for analysis by ICP-OES. ICP-OES was used to determine the concentration of S, Na and Zr in each solution. Comparison of control solutions to those containing MOF was used to determine the amount of sulfate adsorbed (q) in mg/g of NU-1000.

Regeneration of NU-1000. A slurry of 10 mg of NU-1000 in ~ 10 mL of water was poured onto an Anodisc™ filter membrane in a glass microanalysis vacuum filter apparatus equipped with a graduated cylinder. Once the sample was dry, 10 mL of a 125 ppm aqueous solution of sulfate was added to the graduated cylinder with the flask under vacuum (all 10 mL were passed through the MOF within 1 minute). An aliquot of the filtrate was removed and diluted to 5 mL in 3 % HNO_3 for analysis by ICP-OES. The filter flask was dried and reassembled and while under vacuum, 10 mL of 5% HCl was passed through the MOF (again all 10 mL were passed through the MOF within 1 minute). An aliquot of the filtrate was removed and diluted to 5 mL in 3 % HNO_3 for analysis by ICP-OES. The filter flask was dried and reassembled and while under vacuum, 10 mL of water was passed through the MOF (again all 10 mL were passed through the MOF within 1 minute). The filter flask was dried and reassembled and while under vacuum, 10 mL of a 125 ppm aqueous solution of sulfate was passed through the MOF. This procedure was repeated for a total of 4 sulfate exposures and 4 HCl washes.

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Table of Contents Graphic A Zr-based metal-organic framework, NU-1000, is used to extract sulfate from aqueous solutions containing competitive anions. This is of interest for application in the safe disposal and storage of nuclear waste where sulfate anions are known to interfere with the waste vitrification process.

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