Preview

Radioactive Strontium Removal from Seawater by a MOF via Two-Step Ion Exchange

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Radioactive waste, such as ^{90}Sr, ^{134}Cs, and ^{131}I, from the Fukushima nuclear spill highlighted the need to find effective adsorbents for scrubbing radioactive ions from seawater. In this issue of *Chem*, Wang and colleagues report a remarkably ^{90}Sr-selective metal-organic framework (SZ-4) that operates with a two-step ion-exchange mechanism and at a wide pH range while being active and intact when tested in actual seawater.

Even after 8 years, the Fukushima nuclear waste spill into the Pacific Ocean is still an issue given that the cleanup methods require elemental selectivity, particularly to common ions, such as Cs^+, I^-, and Sr^{2+}.[1–5] Considering that oceans contain large amounts of competing ions, such as Na^+ and Cl^-, and solutes diffuse quite rapidly (reaching North American shores within a year), non-trivial adsorbents are essential. But then, the separations at industrial scales require precision and stability, both of which could be best achieved by chemical tuning of porous materials. For example, in natural gas sweetening, H_2S-stable CO_2-capturing adsorbents are key for long-term applications.[6,7] Water harvesting from air demands rapid cycling and low regeneration energies.[8]

In this issue of *Chem*, Shuao Wang and his team tackle an outstanding radioactive contamination problem by employing a target-oriented approach (Figure 1). Given that removing an earth alkali metal has to include selectivity over more strongly binding transition metals, they knew that traditional adsorptive media wouldn't work. Ion exchange, they determined, would at least give them selectivity over weakly binding, abundant cations. But the

more challenging task was to specifically favor strontium. For that, they turned to crystal engineering of metal-organic frameworks (MOFs), where one could pinpoint functionalities without yielding mass transfer features.

The only problem for such a MOF design is stability. For that, they used zirconium MOFs, where zirconium-based frameworks are known to be stable in a wide variety of conditions. They started with the complexation of $ZrOCl_2 \cdot 8H_2O$ and methylenediphosphonic acid with *N,N*-dimethylacetamide in a solvothermal method full of acids, which resulted in the single crystal of anionic, layered coordination polymers (CPs) of SZ-4, $[(CH_3)_2NH_2][ZrCH_2(PO_3)_2F]$.[9] The single-crystal analysis revealed that SZ-4 crystallizes in the triclinic space group P-1. The asymmetric unit of SZ-4 contained one Zr^{4+} ion, one F atom, one methylenediphosphonate ligand, and one protonated dimethylamine (DMAH$^+$). This was particularly attractive because the DMAH$^+$ cations in the channels of SZ-4 could enhance the ion-exchange mechanism, mainly with the Sr^{2+} ion. These zirconium fluorophosphonate layers feasibly propagated along the b axis with interlayer distances of 3.6 Å each. The octahedral ZrO_5F unit in coordina-

tion with diphosphonate ligands predominantly formed these layers. The shorter distances of $N\cdots F$ (2.797 Å) and $N\cdots O$ (2.856 Å) were the main driving forces for the layered packing structure, which would eventually help the exclusive ion-exchange mechanism.

Stability was the first to be checked. Powder X-ray diffraction (PXRD) patterns confirmed the structural integrity of crystalline SZ-4 in water and, most importantly, seawater; surprisingly, the authors found that SZ-4 could resist the radiation even at large doses up to 200 kGy of ^{60}Co γ and β irradiation. Then, SZ-4 was found to withstand a wide pH range from 3 to 11. At pH over 12, crystals dissolved in solution and lost structural integrity. But when the pH went down to 0, SZ-4 crystals remained intact throughout the entire course of the pH, making it possible to determine single crystal structures. It is important to note that only a handful of reported MOFs show such remarkable stability.

At pH 2, SZ-4 transformed into a crystalline phase of $[(CH_3)_2NH_2]_{0.5}[ZrCH_2(PO_3)(PO_3H_{0.5})F]$ (SZ-4-a). The single crystals of SZ-4-a exhibited the same space group as SZ-4 with an anionic layered structure. As a result of a partial substitution of DMAH$^+$ with H_3O^+, the interlayer distance shrunk from 3.6 to 2.7 Å. When the pH was further lowered down to 0, SZ-4-a morphed into another crystalline phase of $Zr_2F_{0.5}(NO_3)_{1.5}[CH_2(PO_3)(PO_3H)]_2 \cdot 1.5H_2O$ (SZ-4-b) with the same space group and 2D layered topology. With a further increase in acidity (pH < 0), asymmetric units changed upon removal of DMA by water. At the same time, partial substitution of

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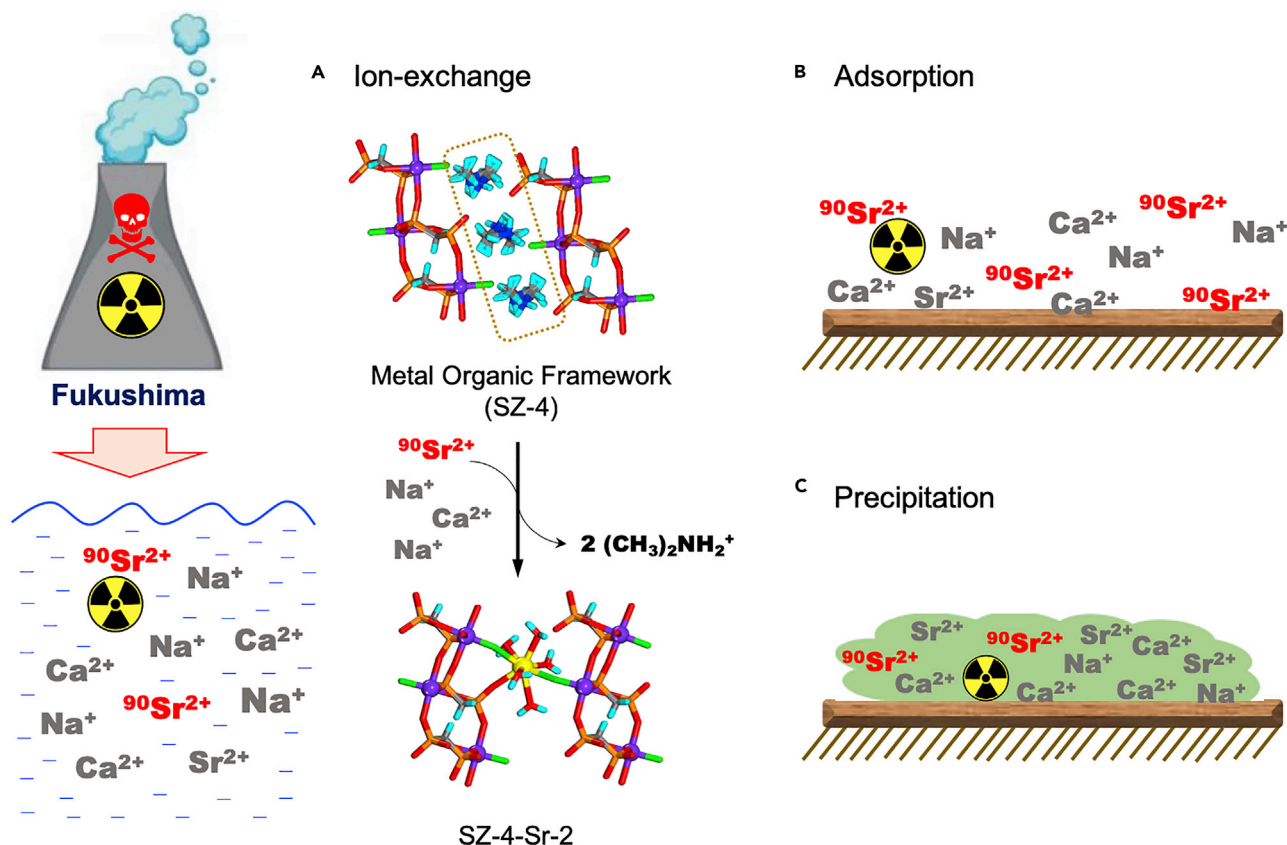
Figure 1. Radioactive Strontium-90 Ions Are Commonly Found in Oceans after Nuclear Accidents, and Selective Uptake Is Required for Effective Cleanup
(A) Ion-exchange mechanism for selective $^{90}Sr^{2+}$ uptake by the MOF SZ-4.
(B) Conventional adsorption techniques don't have high selectivity.
(C) Precipitation has the least selectivity but is effective in long-term storage.

F^- occurred by NO_3^- exchange, and the phosphonate ligand was partially protonated to form a neutral layer without any ion-exchange capability.

Once the stability was in the right place, SZ-4 was put to good use. To date, conventional techniques (adsorption, ion exchange, and precipitation) have mostly been used for wastewater treatment (Figure 1). Among them, adsorption is usually the most effective because of the strong binding, chemical stability, and heterogeneous practices. Precipitation is the ultimate cleanup method, but only if you can let go of the selectivity. Ion exchange offers the most targeted option and is used mostly for specific capture purposes, such as in household water filters.

In toxic and radioactive wastewater treatment, ion exchange works the best given that we're always after a certain ion. Capacity might not be as high as adsorption, but the kinetics of the exchange make up for the losses. For example, we reported that the nanoporous amidoxime PIM-1 showed high uranium uptake capacity from seawater with fast kinetics ($K_d = 8.02 \times 10^3$ mL/g).[10] SZ-4 showed a fast and efficient uptake capacity for $^{90}Sr^{2+}$ in comparison with other ion-exchange materials, even in very acidic conditions ($K_d = 4.06 \times 10^6$ mL/g). It is normally very challenging for adsorptive media because of the competition with H^+ ions.

In a wide range of pH and in the presence of competing cations, SZ-4 removes 90% of $^{90}Sr^{2+}$ from waste-water as quickly as within 20 min. The uptake capacity at pH 2 is 121 mg/g, very close to the theoretical capacity (133 mg/g), and is almost four times larger than that of KMS-1 (ca. 23 mg/g) under the same conditions.[1] In addition, SZ-4 captures 59.6 mg/g at pH 1. It's important to note that no such activity at highly acidic media has ever been reported before. Real seawater samples also showed very high selectivity for Sr^{2+}, another first to be reported.

Because SZ-4 is a single crystal, *in situ* Sr^{2+} ion exchange could be visualized by single-crystal-to-single-crystal (SCSC) transformation, which illustrates a unique two-step intercalation mechanism and exclusive soft cation (Sr^{2+}) uptake

selectivity. This is particularly useful because it is critical to know what exactly is taking place when such remarkable selectivities are observed. After interacting with Sr^{2+} for 12 h, parent crystal SZ-4 formed an intermediate complex $[((CH_3)_2NH)Sr(H_2O)_3]_{0.5}[ZrCH_2(PO_3)_2F]\cdot0.5H_2O$, (SZ-4-Sr-1). SZ-4-Sr-1 maintained the parent crystal's space group. The single-crystal analysis revealed that polyhedral Sr^{2+} coordinated with basic $[ZrCH_2(PO_3)_2F]^-$ anionic layers and showed a significant contraction of the interlayer from 3.6 Å in SZ-4 to 2.9 Å in SZ-4-Sr-1. As a result of the incorporation of Sr^{2+} in SZ-4, $DMAH^+$ molecules were deprotonated via the ion-exchange mechanism, a thermodynamically stable process that can prove the selective Sr^{2+} uptake under lower pH value. A lower Sr–N bond distance (2.69 Å) indicates a strong interaction between Sr^{2+} and DMA in SZ-4-Sr-1. This, in turn, supports uptake selectivity toward soft Sr^{2+} over the hard divalent cations according to Pearson hard and soft acid-base theory. After 24 h of ion exchange, DMA molecules were fully removed, but SZ-4-Sr-2 was still crystallized with the same space group. Its interlayer distance expanded again (3.8 Å) close to the parent crystal. Each Sr^{2+} cation was surrounded by one O atom from the p=O bond, two F atoms, and five coordinated water molecules, suggesting that Sr^{2+} is thermodynamically stable in SZ-4-Sr-2. Time-dependent PXRD analysis proved the Sr^{2+} uptake phenomenon through observed peak shifting. In addition, density functional theory calculations confirmed the dynamic structural changes.

Lastly, the pH of nuclear waste and contaminated ground water can vary from strongly acidic to extremely alkaline. Adsorption capacities are mainly studied in a wide range of pH. One of the best-performing adsorbents, the non-oxidic inorganic KMS-1, shows high selectivity at pH 12.8 because of its soft negatively charged sulfide layers. Biomineral-based GO–HAp (hydroxyapatite) nanocomposites are capable of 90% Sr^{2+} uptake in a wide pH range (5–11), and 76% Sr^{2+} was adsorbed at low pH (pH 2–4). But still, SZ-4 shows faster sorption kinetics, better performance under acidic conditions, increased refinement depth over a wide pH range, and upgraded Sr^{2+} remediation efficiency from wastewater. As a bonus, single crystals of SZ-4 allow *in situ* studies, which could reveal more adsorptive mechanisms of other important ions and lead to effective sorbents for economical seawater mining of valuable resources such as uranium.

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