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Selective removal of cesium and strontium using porous frameworks from high level nuclear waste†

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Efficient and cost-effective removal of radioactive ¹³⁷Cs and ⁹⁰Sr found in spent fuel is an important step for safe, long-term storage of nuclear waste. Solid-state materials such as resins and titanosilicate zeolites have been assessed for the removal of Cs and Sr from aqueous solutions, but there is room for improvement in terms of capacity and selectivity. Herein, we report the Cs⁺ and Sr²⁺ exchange potential of an ultra stable MOF, namely, MIL-101-SO₃H, as a function of different contact times, concentrations, pH levels, and in the presence of competing ions. Our preliminary results suggest that MOFs with suitable ion exchange groups can be promising alternate materials for cesium and strontium removal.

Among all the potential radioactive contamination in nuclear waste, radioactive ¹³⁷Cs and ⁹⁰Sr are of particular concern. ¹³⁷Cs ($t_{1/2} = 30.17$ years) is a strong beta–gamma emitter and ⁹⁰Sr ($t_{1/2} = 28.8$ years) is a beta emitter and a large source of radiation.¹ These two elements are major contributors to radioactivity and heat load (radiation), which create a major hurdle for long term storage of nuclear waste. ¹³⁷Cs, in particular, dominates the radioactivity of the waste due to its solubility. Therefore, there is an urgent need to develop an efficient and economical process for the removal of ¹³⁷Cs and ⁹⁰Sr from the waste streams before their intended long-term storage. Several types of methods, including liquid–liquid extraction and ion-exchange by using solid-state adsorbent materials have been applied with varying degrees of success.^{1–9} Although the extraction method is preferable for systems with a high concentration of target ions, ion-exchange performs better in terms of capacity and selectivity where the target ion concentration is low.¹ The amount of ¹³⁷Cs and ⁹⁰Sr in nuclear waste streams is estimated to be ~4.2 wt%, with much of the rest being bulk

non-radioactive components.¹ As a result, selective capture of these ions in the presence of other competing ions or molecules is a significant challenge. Solid-state materials such as ion-exchange resins (*e.g.* resorcinol-formaldehyde^{3,4}) and titanosilicate zeolites (*e.g.* crystalline silicotitanate⁵) were tested so far for effective removal of ¹³⁷Cs and ⁹⁰Sr from aqueous solutions, but there is room for improvement in terms of the total capacity, kinetics and selectivity. Among the new generation solid-state materials, metal organic frameworks (MOFs) or porous coordination polymers (PCPs)^{10,11} and covalent organic frameworks (COFs)¹² are viable candidates because of their structural diversity and chemical tunability. In particular, MOFs have been successfully utilized for a diverse set of ion-exchange experiments under different experimental conditions.^{11,13–19} With the advent of ultra-stable, easy to synthesize MOFs (*e.g.* UIO, UIO = University of Oslo,²⁰ MIL series, MIL = material of lavoisier²¹) it is fairly evident that these MOFs can be utilized under ‘real-life’ ion-exchange conditions. Herein, we report the Cs⁺ and Sr²⁺ ion exchange ability of a stable, highly porous MOF, namely MIL-101-SO₃H, in aqueous solutions. The removal capabilities were tested at varying contact times, concentrations, pH levels, and in the presence of competing ions. We found that MIL-101-SO₃H has a high Cs⁺ and Sr²⁺ uptake both in the presence and absence of competing ions.

MIL-101-SO₃H was synthesized using a previously reported method and the phase purity and surface area were confirmed by powder XRD and BET surface area measurement, respectively (Fig. S1 and S2, ESI†).²² MIL-101-SO₃H possesses a three-dimensional MTN type zeolite architecture with two types of similar mesoporous cages.²¹ The sulfonic acid groups are uniformly distributed throughout the MOF making them readily accessible for cation exchange without altering the structure of the MOF.²² We hypothesize that cation exchange will occur between the proton in the –SO₃H groups and Cs⁺ and Sr²⁺ in aqueous solutions.

A preliminary study was done on the sorption amount of Cs⁺ at increasing contact times. Fig. 1 depicts the sorption amount as a function of time. It is evident from the graph that the sorption amount plateaus and reaches its maximum in 1440 minutes

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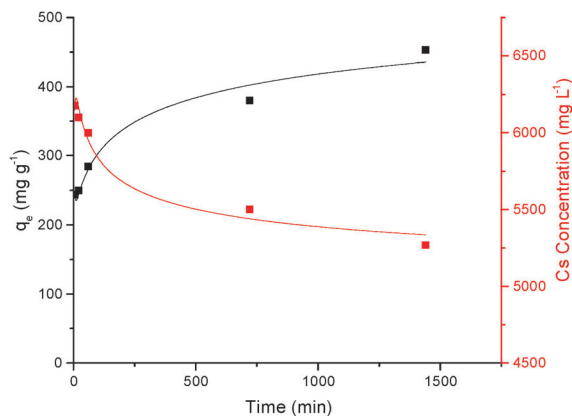


Fig. 1 Sorption amount (q_e) (black) and Cs concentration (red) as a function of time.

(24 hours) with a value of 453 mg g^{-1} . Fig. 1 also depicts the decreasing Cs concentration as a function of time. The concentration of Cs^+ ions in solution was decreased by 1397 mg L^{-1} after a contact time of 24 hours. The MOF also shows structural stability after ion-exchange. Powder XRD was used to analyze the sample after 24 hours in solution and the MOF retained the same peaks as the activated sample (Fig. S2, ESI[†]). To achieve maximum removal, all further experiments were done at a contact time of 24 hours.

The optimum molar ratio of MIL-101-SO₃H required for Cs^+ and Sr^{2+} removal was also studied. Fig. 2 shows that at a molar ratio of 4:1 (sorbent to Cs/Sr solution) Cs had 99.99% and Sr had 98.92% removal. This gives a particularly high K_d value of $22938.2 \text{ mL g}^{-1}$ for Sr. The amount of Cs left in solution was undetectable thus giving us almost 99.999% removal and an incalculable K_d value. The lower saturation ratio of MIL-101-SO₃H:Cs/Sr means that a lower amount of ion-exchange material is needed to achieve maximal adsorption, which is very cost effective in the long run. With these results all further experiments were performed at this molar ratio. With knowledge of the best conditions for MIL-101-SO₃H to remove Cs and Sr from aqueous solutions, some real life application studies were then performed.

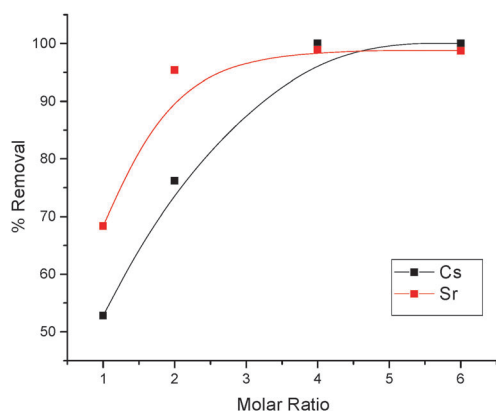


Fig. 2 Percent removal of Cs and Sr with increasing amounts of sorbent (time = 24 hours).

To test the effects of pH on the removal of Cs^+ ions, standard solutions were prepared with a pH of 3 and 10, respectively, and compared with the removal efficiencies obtained at neutral pH. Even with changes in pH, the percent removal of Cs was still relatively high, around 79% at pH 10 and 88% at pH 3, as shown in Table 1. Due to the alkalinity of the nuclear waste tanks, it is important to have a material that can withstand a high pH level. The lower uptake capacity at pH 10 can be attributed to NH_4OH used to alter the solution pH. While a negligible amount was used, NH_4^+ ions could have still competed in the ion-exchange process, inhibiting the amount of Cs^+ that would have been removed. Although the q_e and K_d values are lower, MIL-101-SO₃H proves to be stable in a wide range of pH levels while still retaining Cs removal capabilities.

Experiments were then conducted to test the Cs and Sr removal capabilities of MIL-101-SO₃H in the presence of competing ions, such as Na^+ and K^+ , both of which are present in large excess in nuclear waste streams. Experiment A involved only Cs^+ removal in the presence of Na^+ and K^+ . Experiment B tested only Sr^{2+} removal in the presence of Na^+ and K^+ . Experiment C then tested all four ions simultaneously, to see which cation MIL-101-SO₃H was most selective for (Tables S6–S8, ESI[†]). It is evident from Fig. 3 that MIL-101-SO₃H is much more selective towards Cs^+ or Sr^{2+} . For Experiments A and B the percent removal of Cs^+ and Sr^{2+} are both around 17%, while those of Na^+ and K^+ are less than 3%. The K_d values follow a similar trend, with Cs^+ and Sr^{2+} both having around 50 mL g^{-1} , while, Na^+ and K^+ fall under 10 mL g^{-1} . When all four ions are present, Experiment C, Sr^{2+} easily surpasses the other ions in percent removal and K_d values. Many ions are present in the nuclear waste tanks, therefore, the selectivity for Cs^+ and Sr^{2+} ions over others is imperative for the material to be effective. Compared to the resorcinol-formaldehyde resin, which has a Cs uptake of $0.06\text{--}0.08 \text{ mg g}^{-1}$,^{3,4} MIL-101-SO₃H has a much

Table 1 Effect of solution pH on Cs removal

pH	% Removal	q_e (mg g^{-1})	K_d (mL g^{-1})
3	88.35	23.43	1896.04
6	100.00	36.47	—
10	79.26	29.17	955.37

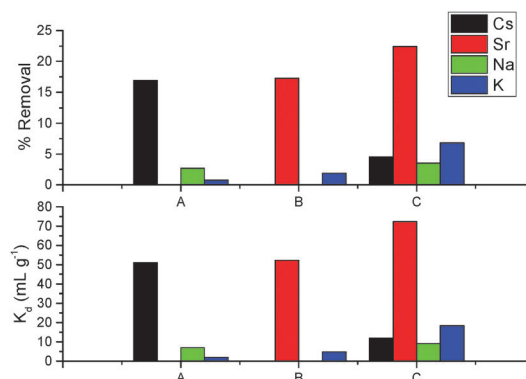


Fig. 3 Percent removal and K_d values of all ions in experiments A, B, and C.

higher uptake of 0.835 mg g^{-1} for Cs^+ and 7.548 mg g^{-1} for Sr^{2+} under similar experimental conditions.

To conclude, we used a high surface area porous framework, MIL-101- SO_3H , to capture Cs^+ and Sr^{2+} ions from aqueous solutions. MIL-101- SO_3H was easily synthesized in bulk quantity and the structure was confirmed by XRD and the N_2 sorption isotherm. MIL-101- SO_3H was found to remove Cs^+ and Sr^{2+} ions optimally at a contact time of 24 hours and at a molar ratio of 4:1 (sorbent to Cs/Sr solution). The MOF still upheld removal capabilities at varied pH levels and in the presence of competing ions. This work demonstrates that MOFs are sorbent materials worth investigating for nuclear waste remediation. Future work will be done to enhance the removal in the presence of competing ions and to explore other MOFs that can withstand highly alkaline solutions and are selective for Cs^+ and Sr^{2+} ions.

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Notes and References

- 1 T. A. Todd, T. A. Batcheller, J. D. Law and R. S. Herbst, *Cesium and Strontium Separation Technologies Literature Review*, Idaho National Laboratory, 2004.
- 2 M. R. Awwal, S. Suzuki, T. Taguchi, H. Shiwaku, Y. Okamoto and T. Yaita, *Chem. Eng. J.*, 2014, **242**, 127.
- 3 M. R. Duignan and C. A. Nash, *Sep. Sci. Technol.*, 2010, **45**, 1828.
- 4 N. M. Hassan and K. Adu-Wusu, *Solvent Extr. Ion Exch.*, 2005, **23**, 375.
- 5 A. J. Celestian, J. D. Kubicki, J. Hanson, A. Clearfield and J. B. Parise, *J. Am. Chem. Soc.*, 2008, **130**, 11689.
- 6 M. V. Balarama Krishna, S. V. Rao, J. Arunachalam, M. S. Murali, S. Kumar and V. K. Manchanda, *Sep. Purif. Technol.*, 2004, **38**, 149.
- 7 H. Kazemian, H. Zakeri and M. S. Rabbani, *J. Radioanal. Nucl. Chem.*, 2006, **268**, 231.
- 8 S. Sarina, A. Bo, D. Liu, H. Liu, D. Yang, C. Zhou, N. Maes, S. Komarneni and H. Zhu, *Chem. Mater.*, 2014, **26**, 4788.
- 9 W. R. Wilmarth, G. J. Lumetta, M. E. Johnson, M. R. Poirier, M. C. Thompson, P. C. Suggs and N. P. Machara, *Solvent Extr. Ion Exch.*, 2011, **29**, 1.
- 10 S. Kitagawa, R. Kitaura and S.-i. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334.
- 11 H.-C. Zhou, J. R. Long and O. M. Yaghi, *Chem. Rev.*, 2012, **112**, 673.
- 12 X. Feng, X. Ding and D. Jiang, *Chem. Soc. Rev.*, 2012, **41**, 6010.
- 13 S. Yang, X. Lin, A. J. Blake, G. S. Walker, P. Hubberstey, N. R. Champness and M. Schröder, *Nat. Chem.*, 2009, **1**, 487.
- 14 S. R. J. Oliver, *Chem. Soc. Rev.*, 2009, **38**, 1868.
- 15 K. L. Mulfort and J. T. Hupp, *Inorg. Chem.*, 2008, **47**, 7936.
- 16 W.-G. Lu, L. Jiang, X.-L. Feng and T.-B. Lu, *Inorg. Chem.*, 2009, **48**, 6997.
- 17 H. Fei, D. L. Rogow and S. R. J. Oliver, *J. Am. Chem. Soc.*, 2010, **132**, 7202.
- 18 S. Dang, E. Ma, Z.-M. Sun and H. Zhang, *J. Mater. Chem.*, 2012, **22**, 16920.
- 19 R. Custelcean and B. A. Moyer, *Eur. J. Inorg. Chem.*, 2007, 1321.
- 20 J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, **130**, 13850.
- 21 G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, **309**, 2040.
- 22 Y.-X. Zhou, Y.-Z. Chen, Y. Hu, G. Huang, S.-H. Yu and H.-L. Jiang, *Chem. – Eur. J.*, 2014, **20**, 14976.