

## Earth and Environmental Sciences

Special Topic: Nuclear Environment Advances

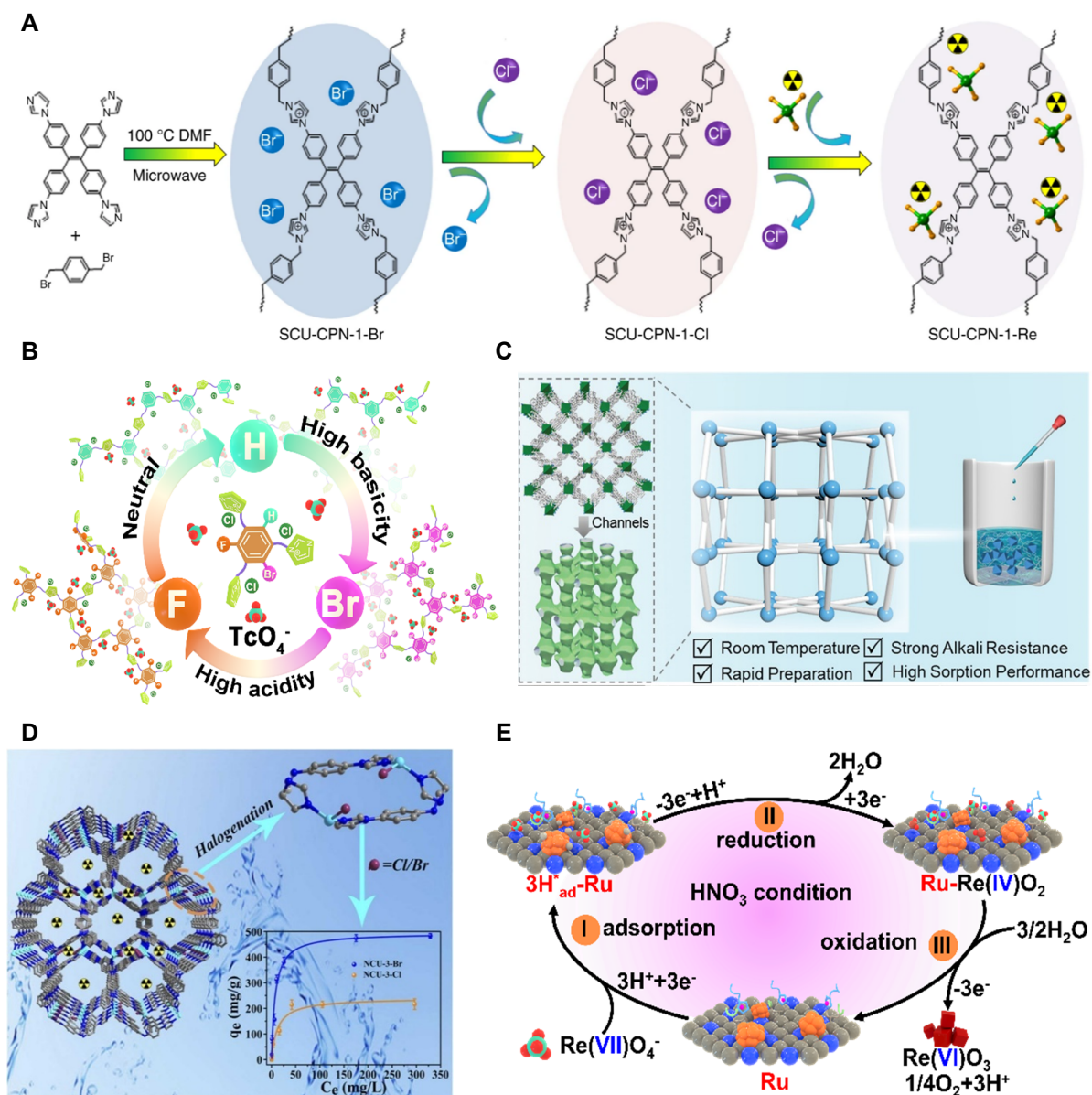
**Promising porous materials for  $^{99}\text{TcO}_4^-$  removal from nuclear wastes**Xinyue Zhang<sup>1,2</sup>, Mengjie Hao<sup>2</sup>, Xinyi Yang<sup>2</sup>, Zhongshan Chen<sup>2</sup>, Suhua Wang<sup>1</sup>, Hui Yang<sup>2,\*</sup> & Xiangke Wang<sup>2,\*</sup><sup>1</sup>School of Environmental Science and Engineering, Guangdong University of Petrochemical Technology, Maoming 525000, China;<sup>2</sup>College of Environmental Science and Engineering, North China Electric Power University, Beijing 102206, China\*Corresponding authors (emails: [h.yang@ncepu.edu.cn](mailto:h.yang@ncepu.edu.cn) (Hui Yang); [xkwang@ncepu.edu.cn](mailto:xkwang@ncepu.edu.cn) (Xiangke Wang))

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As a kind of green and clean energy resource, nuclear energy has attracted extensive attention and utilization [1]. Technetium-99 ( $^{99}\text{Tc}$ ) is a byproduct of  $^{235}\text{U}$ , which exists extensively in the spent fuel and radioactive waste generated during nuclear energy production (about 6%) [2]. The volatile  $^{99}\text{Tc}$  can escape during the vitrification process of nuclear waste, posing the risk of leakage [3].  $^{99}\text{Tc}$  usually occurs in the form of pertechnetate anion ( $^{99}\text{TcO}_4^-$ ), under neutral, oxidative or even slightly reducing conditions. Due to characteristics of non-complexing and high water-solubility,  $^{99}\text{TcO}_4^-$  can diffuse into ecological systems easily, resulting in difficult separation during the treatment of contaminants. The  $^{99}\text{TcO}_4^-$  removal is complex from nuclear waste due to the high alkaline environment at Harford and locations like Savannah River, the strong acidic and various coexisting ions of highly radioactive liquid wastes [4]. Hence, the development of materials and techniques for  $^{99}\text{TcO}_4^-$  removal under practical conditions remains a significant challenge.

So far, a variety of materials have been developed for  $^{99}\text{TcO}_4^-$  removal, including layered double hydroxides (LDHs), anion exchange resins, inorganic composites (Sn(II)-based materials, Fe(II)-based materials, and so on), and others [5]. Among them, resins and LDHs are used for ion exchange, and some inorganic composites could convert Tc(VII) into insoluble Tc(IV). However, these inorganic materials have drawbacks such as poor acid or alkali resistance, low removal rate, and poor regeneration. Recently, porous materials have been considered as potential candidates for  $^{99}\text{TcO}_4^-$  removal and  $\text{ReO}_4^-$  (as a nonradioactive surrogate for  $^{99}\text{TcO}_4^-$ ) by ion exchange, such as covalent organic frameworks (COFs), metal-organic frameworks (MOFs), and organic polymers [5]. It is promising that these porous materials can overcome the limitations mentioned earlier, which also present some challenges during ion exchange, including (1) reducing costs and improving product yields in the preparation process of materials; (2) maintaining high stability and radiation resistance of materials under practical applications; (3) improving reuse and economic efficiency.

Ionic polymers have moved to the forefront of materials research because of their predictable structure type, tunable pore diameter, and flexible functionalization. Li *et al.* reported that SCU-CPN-1 (Figure 1A) has excellent radiation resistance and hydrolytic stability, which can reach the adsorption capacity of



**Figure 1** Schematic showing (A) synthesis route of SCU-CPN-1 and its anion-exchange applications [6]; (B) the <sup>99</sup>TcO<sub>4</sub><sup>-</sup> removal by iCOPs under different conditions [9]; (C) the synthesis of Ag-TPPE through directly mixing raw materials [12]; (D) the application of NCU-3-X (X = Cl, Br) on ReO<sub>4</sub><sup>-</sup>/TcO<sub>4</sub><sup>-</sup> removal [13]; (E) the reaction mechanisms for the Ru@HNCC-R catalyzed extraction of ReO<sub>4</sub><sup>-</sup> during the adsorption-electrocatalysis [14].

876 mg/g for ReO<sub>4</sub><sup>-</sup>. Meanwhile, SCU-CPN-1 exhibited cost-effective and practical application potential due to its decent radiation resistance and reusability [6]. Then, Li *et al.* prepared SCU-CPN-2 [7] and SCU-CPN-4 [8] for the uptake of <sup>99</sup>TcO<sub>4</sub><sup>-</sup> in nuclear waste. SCU-CPN-2 exhibited a high uptake capacity of 1467 mg/g for ReO<sub>4</sub><sup>-</sup>, and SCU-CPN-4 showed fast removal kinetics and excellent uptake selectivity from the simulated SRS (Savannah River Site) solutions. Yang *et al.* utilized imidazolium-N<sup>+</sup> nanotraps by tuning the surrounding environments via a halogenation strategy, which realized a high <sup>99</sup>TcO<sub>4</sub><sup>-</sup> adsorption capacity of 1434.1±24.6 mg/g, fast kinetics and excellent selectivity. The XPS, X-ray absorption fine structure (XAFS),

and molecular dynamics (MD) simulations demonstrated the mechanism of ion exchange and the relationship between the functional structure (imidazolium-N<sup>+</sup> sites assisted by halogen) and adsorption performance (Figure 1B) [9]. Overall, due to their simplicity, low cost, and highly efficient properties, the ionic polymer materials show promising application potential for <sup>99</sup>TcO<sub>4</sub><sup>-</sup> removal from nuclear wastes.

COFs have increasingly attracted attention for <sup>99</sup>TcO<sub>4</sub><sup>-</sup>/ReO<sub>4</sub><sup>-</sup> and target radionuclide removal due to their high crystallinity, porosity, multi-functionality, pore space adjusting and stability properties [10]. For instance, Hao *et al.* reported a cationic pyridinium salt-based COF (PS-COF-1) with a specific surface area of around 2703 m<sup>2</sup>/g, exhibiting fast kinetics and high removal capacity towards ReO<sub>4</sub><sup>-</sup> (1262 mg/g)/<sup>99</sup>TcO<sub>4</sub><sup>-</sup>. Mechanism study showed that the saturation adsorption was attributed to ion exchange between ReO<sub>4</sub><sup>-</sup>/<sup>99</sup>TcO<sub>4</sub><sup>-</sup> and Cl<sup>-</sup> on the pyridine N(+) sites [11]. This work demonstrated the function of the pyridinium salt group and the possibility of COFs for environment remediation by virtue of radiation resistance, ordered pore structure and chemical stability.

Benefitting from the advantages of high specific surface area, high porosity, tunable shapes, and facile functionalization, MOFs have also received much attention for ReO<sub>4</sub><sup>-</sup>/<sup>99</sup>TcO<sub>4</sub><sup>-</sup> removal from aqueous solutions. Kang *et al.* synthesized a fourfold interpenetrated cationic MOF (Ag-TPPE) (Figure 1C) with structural stability under extreme conditions (8M NaOH). Ag-TPPE could selectively remove <sup>99</sup>TcO<sub>4</sub><sup>-</sup> in the presence of excess SO<sub>4</sub><sup>2-</sup> or NO<sub>3</sub><sup>-</sup>. The removal percentages remained above 99% when the molar ratio of SO<sub>4</sub><sup>2-</sup>:ReO<sub>4</sub><sup>-</sup> was 1000:1. In addition, the simulated potential of mean force (PMF) results revealed the molecular mechanism of ion exchange [12]. Furthermore, the introduction of halogen atoms (such as Br and Cl) into MOF skeletons can facilitate the adsorption process. Hu *et al.* regulated different halogen atoms to construct two isostructural MOFs, NCU-3-X (X=Br, Cl), in which NCU-3-Br exhibited a maximum capacity of 483 mg/g towards ReO<sub>4</sub><sup>-</sup> (Figure 1D). The excellent performance could be attributed to the synergy of the halogen bond (between ReO<sub>4</sub><sup>-</sup> and bromine atoms) and the interaction (between imidazole groups and ReO<sub>4</sub><sup>-</sup>) [13].

In addition to these materials, carbon-based materials have also been studied extensively. Liu *et al.* reported hollow porous N-doped carbon capsules loaded with ruthenium cluster that was modified with the cationic polymeric networks (Ru@HNCC-R), which reached the removal capacity of 449 mg/g in 3M HNO<sub>3</sub> for ReO<sub>4</sub><sup>-</sup> via the adsorption-electrocatalytic method (Figure 1E) [14]. The generation of the insoluble Re(VI)O<sub>3</sub> through electrocatalytic redox promoted the removal efficiency, which offered a new idea for ReO<sub>4</sub><sup>-</sup>/<sup>99</sup>TcO<sub>4</sub><sup>-</sup> removal from aqueous solutions. The developed Ru@HNCC-R represented good durability.

In recent years, significant progress has been made for <sup>99</sup>TcO<sub>4</sub><sup>-</sup> removal by porous materials both in adsorption capacity and selectivity, especially in the face of extreme conditions of nuclear waste environment. Although many effective adsorbents and promising adsorption/catalytic pathways have been reported, most investigations were conducted under laboratory conditions. The practicality, effectiveness, and stability of the material should be further approved through practical applications under nuclear waste environments. In addition, given the economic feasibility, the cost of the materials and the conditions for synthesis should also be taken a reasonable consideration. Improving the reuse of materials also dramatically reduces costs, especially for powdered materials. Therefore, it is particularly vital to develop materials with scalable, low-cost, efficient, and recyclable properties, which will benefit the disposal of nuclear waste and the sustainable development of the future nuclear energy industry. At the same time, compliance with environmental safety standards and government policies is the basis for ensuring the smooth conduct of all experiments.

## Data availability

The original data are available from corresponding authors upon reasonable request.

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## Author contributions

Z.C., S.W., H.Y. and X.W. supervised the project. X.Z., M.H. and X.Y. wrote the manuscript. All authors reviewed and edited the manuscript.

## Conflict of interest

The authors declare no conflict of interest.

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