Amidoxime-Engineered MOF for High-Performance Uranium Extraction from Seawater

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1. Introduction

Global energy consumption is escalating due to rapid population growth and the expanding adoption of energy-intensive technologies. Conventional energy sources such as coal, oil, and gas emit substantial CO_2, contributing to severe climate change. In contrast, renewable sources such as wind and solar are inherently intermittent and highly dependent on weather conditions, limiting their reliability for continuous power generation. Nuclear energy, however, offers the highest annual availability factor among major energy sources and delivers consistent, sustainable power with a minimal carbon footprint [1].

Rising global uranium (U) consumption for nuclear power generation is depleting its terrestrial reserves at an accelerating rate. Seawater holds vast U reserves (~4.5 billion tons) [2]. However, efficient and economically viable uranium extraction from seawater (UES) remains a major challenge due to the extremely low U concentration (~3.3 ppb), competing ions, and marine biofouling [3]. Over the years, numerous adsorbent materials have been developed for U recovery from seawater, including metal oxides, sulfides, and clay minerals. However, these materials often suffer from low adsorption capacity and slow uptake kinetics, limiting their practical application for UES [4]. Recently, Metal–organic frameworks (MOFs) have emerged as promising platforms for UES, owing to their high surface area, well-defined porous architectures, and tailorable chemical functionality, enabling efficient and rapid U capture.

Herein, we synthesized an amidoxime-grafted MOF-808 (MOF-808-AM) via a post-synthetic functionalization strategy to introduce high-affinity amidoxime coordination sites for rapid and efficient U capture.

2. Materials and Methods

2.1 Synthesis and characterization

MOF-808-AM was synthesized via a three-step route. MOF-808 was first prepared through a solvothermal reaction of zirconium(IV) oxychloride octahydrate and 1,3,5-benzenetricarboxylic acid in a DMF/formic acid mixture, followed by washing with DMF and acetone and subsequent drying. The resulting MOF-808 was then functionalized with diaminomaleonitrile (DAMN) under reflux in toluene, washed with ethanol and dried under vacuum to obtain DAMN-grafted MOF-808 (MOF-808-DM). Finally, MOF-808-DM was reacted with hydroxylamine hydrochloride and NaOH in an aqueous ethanol mixture under reflux; the resulting product was isolated by centrifugation, washed with DI water and ethanol, and dried at 60 °C to yield MOF-808-AM.

The structural, morphological, and chemical features of the synthesized MOFs were characterized using powder X-ray diffraction (XRD), scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS), and Fourier-transform infrared (FT-IR) spectroscopy. U concentrations were quantified by inductively coupled plasma mass spectrometry (ICP-MS).

2.2 Batch sorption test for U uptake

Batch sorption experiments were conducted at room temperature under optimized pH and contact time conditions. In a typical experiment, MOF-808-AM (0.1 g L^{-1}) was added to a polypropylene tube containing a U solution of known concentration. The suspensions were agitated for predetermined time intervals, filtered, and analyzed for U concentration by ICP-MS.

3. Results and Discussion

The XRD pattern of the amidoxime-functionalized MOF-808 was consistent with the simulated MOF-808-AM (Fig. 1). SEM analysis confirmed the uniform and well-defined octahedral morphology characteristic of pristine MOF-808, which was preserved after amidoximation. The FT-IR spectra of MOF-808 and MOF-808-AM exhibited characteristic asymmetric and symmetric stretching vibrations of carboxylate groups at 1565–1575 cm^{-1} and 1385 cm^{-1}, respectively. More importantly, a characteristic nitrile (–C≡N) stretching band at 2215 cm^{-1} appeared following DAMN functionalization and disappeared after amidoximation, confirming the successful conversion of MOF-808-DM into MOF-808-AM.

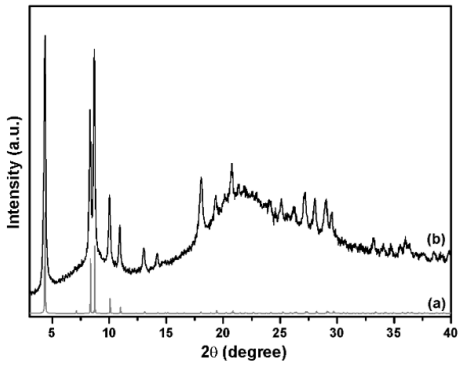


Fig. 1. X-ray diffraction patterns of (a) simulated MOF-808 and (b) MOF-808-AM.

Batch sorption experiments conducted across a pH range of 2.0–9.0 revealed maximum U uptake by MOF-808-AM at pH 7. Adsorption equilibrium was achieved within 90 min, with U uptake exceeding 95%, and the pseudo-second-order model provided the best fit to the kinetic data, indicating that chemisorption is the predominant rate-limiting mechanism.

4. Conclusions

Amidoxime-functionalized MOF-808 (MOF-808-AM) was successfully synthesized and structurally characterized by XRD, SEM, and FT-IR, confirming preservation of the parent MOF-808 framework following amidoxime functionalization and after uranium uptake. MOF-808-AM exhibited rapid sorption kinetics (equilibrium within 90 min) and a high uranium capture efficiency (>95%), demonstrating its strong affinity for uranium. These findings establish MOF-808-AM as a promising high-performance sorbent for efficient uranium recovery from seawater and uranium-containing waste streams.

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