



Synthesis of UiO-66-OH zirconium metal-organic framework and its application for selective extraction and trace determination of thorium in water samples by spectrophotometry

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ABSTRACT

In this study, a zirconium-based metal-organic framework (Zr-MOF), named UiO-66-OH, was synthesized by the solvo-thermal method and characterized by Fourier transform-infrared spectroscopy (FTIR), powder X-ray diffraction (PXRD), and scanning electron microscopy (SEM). This Zr-MOF was then employed as a sorbent for selective extraction and preconcentration of thorium ions after their complexation with 2 (2,4 dihydroxyphenyl) 3,5,7 trihydroxychromen 4 one (morin) from environmental water samples prior to its spectrophotometrical determination. The experimental parameters affecting extraction, such as pH of sample solution, amount of Zr-MOF, type and volume of eluting solvent, adsorption and desorption time, and concentration of complexing agent were evaluated and optimized. Under the optimized conditions, an enrichment factor of 250 was achieved. The limit of detection was calculated to be $0.35 \mu\text{g} \cdot \text{L}^{-1}$ with a linear range between 10 and $2000 \mu\text{g} \cdot \text{L}^{-1}$ of thorium. The maximum sorption capacity of MOF toward thorium was found to be $47.5 \text{ mg} \cdot \text{g}^{-1}$. The proposed procedure was successfully applied to the analysis of real water samples.

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1. Introduction

Thorium, as one of the nuclear power sources, is found in plants, sand, soil, rocks, and water [1]. Moreover, this radioactive element is used in gas mantles and kerosene lamps to produce bright white light when heated [2]. Thus, people can be exposed to thorium through air, food and water. Studies have been shown that continuous exposure of thorium can cause cancer in various forms [3]. According to World Health Organization, acceptable thorium concentration in drinking water is normally $<20 \mu\text{g} \cdot \text{L}^{-1}$ [4]. Thus, determination of thorium in environmental samples is of importance. So far, several methods such as, ion chromatography (IC) [5], inductively coupled plasma-optical emission spectrometry (ICP-OES) [6], flow injection analysis (FIA) [7], inductively coupled plasma-mass spectrometry (ICP-MS) [8], capillary zone electrophoresis (CZE) [9], fluorimetry [10], and electrochemical techniques [11] have been used for the determination of thorium. Spectrophotometry represents an attractive common technique due to its high precision and accuracy in measurement associated with its lower cost compared to the above mentioned techniques. But there are disadvantages of the technique including low sensitivity and impossibility of direct determination without sample preparation [12].

Nowadays, solid-phase extraction (SPE) is one of the most extensive and most efficient method for the separation and pre-concentration of trace elements in environmental samples, food and water samples, benefiting from its high enrichment factor, high repeatability, low need for organic solvents, saving cost and time, and ease of automation. In SPE, solid adsorbents have been shown great potential for improving the extraction, sensitivity, and accuracy [13–15].

Metal-organic frameworks (MOFs), are three-dimensional crystalline porous materials having various geometries and functional groups within the channels/cavities, which are synthesized by mixing organic linkers and metal salts, often under hydrothermal or solvothermal conditions. Adjustable pore-sizes and controllable structural properties, extra ordinarily large porosity, low density, and very high surface areas are the unique characteristics of the hybrid solids. As a result, MOFs have been considered as promising candidate materials for various applications such as adsorption [16–18], sensing [19], catalysis [20], separation [21], gas storage [22], luminescence [23], drug delivery [24], conductivity [25], removal of toxic materials [26,27], nuclear waste partitioning [28–31] and radioactive remediation [32–35]. Zirconium(^{IV})-based metal organic frameworks show an exceptional thermal stability (up to 550 °C) and the chemical stability in water and organic solvents. UiO-66-OH, as a Zr-based MOF, has the formula of $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{O}_2\text{C}-\text{C}_4\text{H}_3(\text{OH})-\text{CO}_2)_6$ in which rigid $\text{Zr}_6\text{O}_4(\text{OH})_4$ octahedral connected together by twelve carboxylate groups from

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2 hydroxyterephthalic acid linkers (Scheme 1). The solvo-thermal synthesis of the MOF using hydrochloric acid results in missing-linker defects [36,37] in the framework, leading to enhanced porosity, hydroxyl groups and zirconium open metal sites, thus, causing to increase of the adsorption, substrate uptake, and catalytic efficiency.

These finding motivated us to prepare and apply the UiO-66-OH MOF as sorbent for the extraction of Th(IV) ions after its chelating with morin. The experimental parameters such as pH of sample solution, amount of Zr-based MOF, type and volume of eluting solvent, adsorption and desorption time, and concentration of complexing agent were investigated.

2. Experimental

2.1. Chemicals

Reagent grade $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ and nitrate or chloride salts of other cations were obtained from Merck (Germany) and used as received. Zirconium tetrachloride (ZrCl_4), 2 hydroxyterephthalic acid and *N,N'* dimethyl formamide (DMF) were obtained from Sigma-Aldrich (MO, USA). A stock standard solution of thorium ($1000 \text{ mg} \cdot \text{L}^{-1}$) was prepared by dissolving 2.38 g of thorium nitrate in 1000 mL of double distilled water. Working standard solutions were prepared by serial dilutions of the stock solution prior to analysis. 1 g of morin was dissolved in 1000 mL of double distilled water ($1000 \text{ mg} \cdot \text{L}^{-1}$) for determination of thorium and was used as a ligand to react with Th(IV).

2.2. Instrumentation

Absorption measurements were carried out with a UV-Vis spectrophotometer (UV-2100 RAYLEIGH, Beijing, China) by monitoring the absorbance at maximum wavelength of 410 nm. All experiments were performed in triplicate at least and the mean values were used for optimization. A Metrohm (Switzerland) model 630 pH meter was used for pH measurements. Powder X-ray diffraction (PXRD) patterns were recorded on a Philips X'pert diffractometer (Netherlands) with

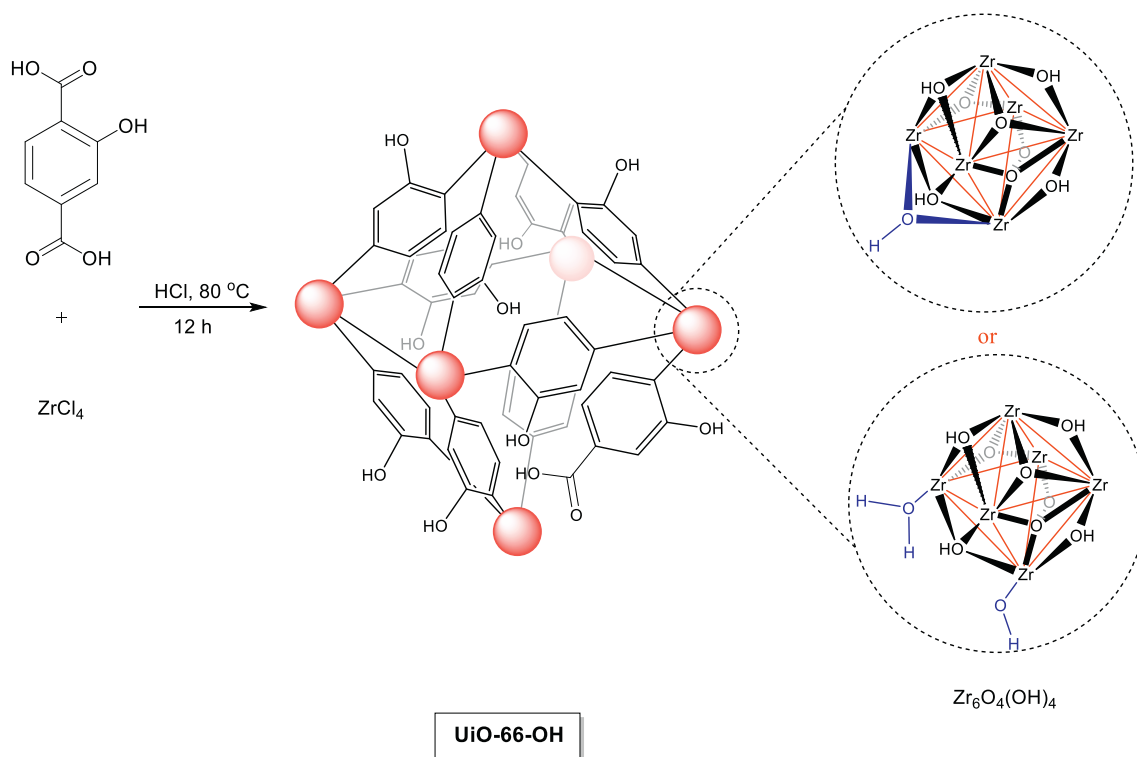
monochromated Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at a range of $5^\circ < 2\theta < 50^\circ$. Fourier transformed infrared (FTIR) spectra were recorded in the range of $4000\text{--}500 \text{ cm}^{-1}$ using KBr pellets on a Perkin Elmer Spectrum-FTIR, version 10.01.00 (USA). The morphology and chemical composition of the sample was characterized using scanning electron microscopy (SEM, MIRA3 TESCAN, Czech Republic).

2.3. Synthesis of UiO-66-OH

The synthesis of UiO-66-OH Zr-based MOF was based on the method suggested by Katz et al. [36]. In a 30 mL vial, ZrCl_4 (125 mg, 0.54 mmol), 5 mL dimethyl formamide (DMF) and 1 mL of concentrated HCl were loaded and sonicated for 10 min until all solids fully dissolved. Then, 2 hydroxyterephthalic acid (135 mg, 0.75 mmol) and 10 mL DMF were added to the solution and sonicated for more 20 min. The obtained mixture was placed in an oven and heated at 80°C for 12 h. After cooling down to room temperature, the resulting solid was filtered, repeatedly washed several times with DMF and then with ethanol. Finally, it was dried at 120°C under vacuum to give the MOF.

2.4. SPE Procedure

For optimization of the extraction parameters, the sorption experiments were performed according to a batch method: a 10 mL measuring flask was loaded with $20 \mu\text{L}$ of the $1000 \text{ mg} \cdot \text{L}^{-1}$ standard solution of $\text{Th}(\text{IV})$ (0.008 mmol) then $20 \mu\text{L}$ of morin solution (0.006 mmol) was added. The mixture was made up to the mark with double distilled water then was transferred to a beaker and the pH was adjusted to 2.0 by drop-wise addition of HCl 0.15 M. 10 mg of UiO-66-OH adsorbent was added to the solutions and was shake on a shaker for 30 min to facilitate adsorption of Th-morin complexes onto the sorbent. The MOF solid was then isolated by centrifugation (1000 rpm, 2 min). The aqueous phase was easily decanted by simply inverting the tube. 1 mL of HNO_3 $0.2 \text{ mol} \cdot \text{L}^{-1}$ solution was added as eluent to the precipitate and was shaken for 30 min. Finally, UiO-66-OH was separated by



Scheme 1. Proposed structure of UiO-66-OH with missing-linker defects.

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