Letter to the Editor

Facile Synthesis of the Magnetic Metal Organic Framework Fe_3O_4@UiO-66-NH_2 for Separation of Strontium*

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A magnetic metal organic framework (MMOF) was synthesized and used to separate Sr^{2+} in aqueous solution. The shape and structure of prepared Fe_3O_4@UiO-66-NH_2 were characterized, and the absorbed concentration of strontium was determined through inductively coupled plasma mass spectrometry. The results indicated that Fe_3O_4 and UiO-66-NH_2 combined through chemical bonding. The experimental adsorption results for separation of Sr^{2+} in aqueous solution indicated that the adsorption of Sr^{2+} to Fe_3O_4@UiO-66-NH_2 increased drastically from pH 11 to pH 13. The adsorption isotherm model indicated that the adsorption of Sr^{2+} conformed to the Freundlich isotherm model (R^2 = 0.9919). The MMOF thus inherited the superior qualities of magnetic composites and metal organic frameworks, and can easily be separated under an external magnetic field. This MMOF thus has potential applications as a magnetic adsorbent for low level radionuclide ^{90}Sr.

Key words: Magnetic metal organic framework (MMOF); Fe_3O_4@UiO-66-NH_2; Radioactivity; Strontium; Adsorbents

Strontium-90, one of the most important long-lived radionuclides, emits high energy β rays as fission products of ^{235}U and ^{239}Pu. Its chemical characteristics are very similar to those of calcium, and it accumulates mainly in the bones and teeth, and damages blood-producing cells in humans[1]. Therefore, the ability to precisely detect low level ^{90}Sr in environmental and biological samples is essential for environmental protection and health and safety. Numerous techniques for removing strontium from radioactive wastewater have been developed[2-5]. Adsorption is regarded as an efficient technology to remove Sr^{2+} from aqueous solutions, concerning its good adsorption capacity, low cost, and simplicity of use.

Metal organic frameworks (MOFs) have exceptionally high surface areas and porosity, and have been used for penetration, accumulation and separation of various species, such as heavy metals, radionuclides, and other toxic chemicals from both gas and liquid phases[6-11]. Since the magnetic properties of the sorbent aid in rapid and easy separation of the new solid phase from solution, introducing additional functionality via magnetic nanoparticles can be achieved by synthesizing magnetic framework composites.In our study, facile preparation of magnetic metal organic framework (Fe_3O_4@UiO-66-NH_2) was achieved, and the magnetic metal organic framework (MMOF) was applied as a sorbent for the extraction of Sr^{2+} ions from liquid. This sorbent was characterized by X-ray diffraction (XRD), vibrating sample magnetometry (VSM), fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Brunauer-Emmett-Teller analysis (BET), and elemental analysis. The magnetic properties of the sorbent allowed for rapid and easy isolation of the solid phase from a solution. Fe_3O_4@UiO-66-NH_2 exhibited both magnetic characteristics and high porosity, thus making it an excellent sorbent for wastewater treatment.

All reagents were of analytical grade. Strontium standard [GBW(E) 080242] solution was obtained from the National Research Center for Certified Reference Materials, Beijing, China.

An ICP-MS Element 2 (Thermo Fisher Scientific, Waltham, Mass., USA) mass spectrometer was used for determination of Sr^{2+}. SEM images of the prepared materials were captured on a S4800

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electron microscope (Hitachi, Tokyo, Japan). High angle X-ray diffraction patterns were obtained on a RAPID IP diffractometer with Cu Kα radiation (Rigaku, Japan). The magnetic properties of the materials were characterized with a PPMS-9 vibrating sample magnetometer (Quantom, USA). Thermodynamic investigation was performed with a synchronous thermal analyzer under nitrogen with a heating rate of 5 °C/min (STA449c, Netzsch). A Fourier transform infrared spectrometer (Jasco FT/IR-660 plus, Germany) was also used.

Fe_3O_4 nanoparticles were prepared through the conventional coprecipitation method with some modifications[12]. $FeCl_3·6H_2O$ (23.6 g) and $FeCl_2·4H_2O$ (8.6 g) were dissolved in 500 mL deionized water under nitrogen gas with vigorous stirring at 80 °C. $NH_3·H_2O$ (25 mL, 25 wt.%) was added to the solution. The magnetic precipitates (Fe_3O_4 magnetic nanoparticles) were isolated from the solvent through magnetic decantation. The precipitates were washed with deionized water three times. Then Fe_3O_4 nanoparticles were initially functionalized with Mercaptoacetic acid (MAA)[11]. Fe_3O_4 (0.10 g) was added to 20 mL of an ethanol solution of MAA (0.58 mmol/L) with shaking for 24 h. The product was collected under an external magnetic field and washed several times with deionized water and ethanol under ultrasonication, then dispersed in a mixture containing 15 mL DMF, 0.12 g $ZrCl_4$, and 0.09 g 2-aminoterephthalic acid under oscillation for 30 min to ensure uniform dispersion. The mixture was transferred into an autoclave, sealed and maintained for 24 h at 120 °C. After being cooled to room temperature, the precipitate was collected with a magnet and washed with N,N-dimethylformamide.

Portions of strontium standard solution (100 mg/L) and appropriate volumes of ultrapure water were mixed in 10 mL test tubes, and then 5 mg of Fe_3O_4@UiO-66-NH_2 was added during mixing; the total volume of the suspension was then adjusted to 5.0 mL. The mixed solutions were then shaken at room temperature for 60 min to ensure complete adsorption of Sr^{2+} onto the sorbent. Subsequently, the magnetic sorbent with adsorbed Sr^{2+} was separated from the suspension with a permanent magnet. The concentration of strontium was determined through inductively coupled plasma mass spectrometry with a calibration curve prepared by dilution of the strontium standard solution with 2% (v/v) HNO_3. All experiments were performed twice, and mean values were used in data analysis. Control experiments without sorbent were carried out to determine the degree of strontium removal in test tubes.

The XRD patterns of Fe_3O_4, UiO-66-NH_2, and Fe_3O_4@UiO-66-NH_2 are shown in Figure 1A. The diffraction peaks of the synthesized microspheres showed that the MOF crystal and Fe_3O_4 were well-retained, because all characteristic peaks of the magnetic microspheres were readily indexed to Fe_3O_4 and UiO-66-NH_2. The magnetic properties of the samples are shown in Figure 1B. The magnetic hysteresis loop showed no remanence or coercivity at room temperature, thus suggesting that the particles had superparamagnetic character, such that no magnetization remained when the applied magnetic field was removed. The magnetic Fe_3O_4 and Fe_3O_4@UiO-66-NH_2 particles had magnetic saturation (MS) values of approximately 60.4 and 7.5 emu/g, respectively. The lower MS value of Fe_3O_4@UiO-66-NH_2 particles was due to the dielectric property of the UiO-66-NH_2. Owing to the paramagnetic quality of the MMOF, the particles could be easily separated from aqueous solution after adsorption of Sr^{2+} nuclides by using an external magnetic field. To investigate the surface morphology of the Fe_3O_4-MAA, MOF and MMOF nanocomposite, samples were characterized by TEM and SEM. As illustrated in Figure 1C, D, E, Fe_3O_4 nanoparticles were functionalized with MAA, and the size of Fe_3O_4-MAA particles was approximately 10 nm. The original UiO-66-NH_2 crystals had smooth surfaces and an average size of 100 nm. However, the surface of the MMOF tended to be rougher after immobilization with MAA-Fe_3O_4.

The FT-IR spectra of Fe_3O_4, UiO-66-NH_2, and Fe_3O_4@ UiO-66-NH_2 are presented in Figure 2A, B. In the FT-IR spectra of Fe_3O_4, the peaks observed at 586 cm^{-1} were due to Fe-O vibration. In the FT-IR spectra of UiO-66-NH_2, a triplet at 767, 665, and 484 cm^{-1} was ascribed to Zr-O_2[13]. The intensities of peaks at 3,475 and 3,356 cm^{-1} were attributed to symmetric and asymmetric stretching of primary amines[14], respectively. In the spectra of Fe_3O_4@UiO-66-NH_2, the MMOF had an infrared absorption similar to that of UiO-66-NH_2, but the corresponding absorption shifted slightly from 665 cm^{-1} to 661 cm^{-1} and increased because of the Fe-O vibration. At 1,625 cm^{-1}, new absorption associated with vibration of carboxylic iron was found, and the bands around 1,018 and 894 cm^{-1} observed in Fe_3O_4@UiO-66-NH_2 were attributed to C-S vibration. N_2 adsorption-desorption analysis was also performed to investigate