Simultaneously Remove and Visually Detect Ce^{4+} Based On Nanocomposite of UiO-66- NH_2 /CPA-MA

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Abstract

Effective strategies to deal with rare earth pollution are urgently needed due to the overexploitation of rare earths resource. In this study, a novel nanocomposite of UiO-66-NH₂/CPA-MA denoted as UA was successfully synthesized, which can simultaneously remove and detect Ce⁴⁺ in water. The hybrid consists of UiO-66-NH₂ and CPA-MA. Based on the high adsorption performance of UiO-66-NH₂, it can remove Ce⁴⁺ with high capacity by adsorption. Moreover, it can change its color from olive drab to light cyan depending on the adsorbed Ce⁴⁺ concentration, and the chroma is linearly related to the Ce⁴⁺ concentration. So UA can be used to qualitatively and quantitatively detect Ce⁴⁺ by its color changing. The kinetics of adsorption course were investigated in details. The anti-inference ability of the nanocomposite in co-existing systems were carefully evaluated. The results indicate that UiO-66-NH₂/CPA-MA is highly potential to deal with Ce⁴⁺ pollutions due to its bi-functionality.

1. Introduction

Rare earths are important strategic resources, which are eagerly required in many areas of modern industry. However, overexploitation of rare earth has also brought about serious ecological and environmental problems, especially in those countries with vast reserves while relatively low exploitation techniques of rare earth. The effective strategies for dealing with rare earth pollution are urgently needed. Detection and removal are two important aspects for the treatments of pollution. Several techniques have been applied to detect rare earth element (REE) in water, including spectrophotometric method, INAA, MAA, ICP-MS, ICP-AES and EXAFS. However, most of them require expensive instruments and skilled operators, and usually are hard to be used on site. As to the removal of REE in water, sorption is one of the most widely applied techniques because of its cheapness and facile operation [1].

In the previous studies, detection and removal were usually the two independent procedures, resulting toilsome steps and enhancing cost. If these two functions can be incorporated into one material and work simultaneously, the treating efficiency would be highly enhanced.

Metal organic frameworks (MOFs) is a kind of novel materials developing fast in the recent years. They have been widely applied in gas storage and separation, contaminant migration and catalysis [2]. UiO-66-NH₂ is a Zr based MOF which has attracted increasing attention because of its high stability, high adsorption ability and easy modification. In this study, UiO-66-NH₂ was incorporated with Chlorophosphonazo-MA (CPA-MA) to construct a novel bifunctional nanocomposite denoted as UA. CPA-MA is a typical spectrophotometric reagent for REE based on its distinctive color changing property as capture REE [3]. The chemical structures of UiO-66-NH₂ and CPA-MA are shown in Scheme S1. Based on the high adsorption property of UiO-66-NH₂ and the distinctive color changing property of CPA-MA, this hybrid UA can not only effectively adsorb REE, but also can significantly change its color when captures the certain REE. The certain color and different chrominances appearing at different REE concentrations can be used to qualitatively and quantitatively detect the certain REE.

A common REE of Ce^{4+} was used as the model contaminant in this study due to its wide distribution and high hazardousness. UA shows high adsorption capacity toward Ce^{4+} . Furthermore, UA exhibits two different color changing phenomenons in different Ce^{4+} concentration ranges, which could be used to qualitatively and quantitatively detect Ce^{4+} even via naked eyes in rough level, while the precise measurement can be fulfilled by an inexpensive visible-light spectrophotometer. The present study provides a novel effective method to deal with rare earth pollution.

2. Experimental

2.1 Materials

2-amino terephthalic acid ($\text{NH}_2\text{-BDC}$) was bought from Shanghai Macklin Biotechnology Company, China. Cerium sulfate ($\text{Ce}(\text{SO}_4)_2$) was obtained from Shanghai Yuanye Biotechnology Company, China. Chlorophosphonazo-mA (CPA-MA) was bought from Sinopharm Chemical Reagent Co., Ltd, China. Zirconium tetrachloride (ZrCl_4) was bought from Dongguan Waxi Chemical Company, China. Other chemicals are all commercial. All materials are directly used without further purification with their analytical grade.

2.2 Experiments

2.2.1 Preparation of UiO-66-NH_2

In a typical preparation, 0.2332 g ZrCl_4 (1.0 mmol) and 0.1812 g 2- NH_2 -benzenedicarboxylate (1.0 mmol) were dissolved in 50 mL N, N-dimethyl formamide (DMF) with magnetic stirring for 30 min to produce uniform dispersion. Then the mixture was placed into a 100 mL Teflon-lined stainless steel autoclave. It was reacted at 393 K for 48 h. After cooled in air to room temperature, the yellow powder was recovered from the mixture by centrifugation, and then washed with DMF and anhydrous ethanol for several rounds. In the end, the powder was dried at 353 K for 12 h to get UiO-66-NH_2 .

2.2.2 Synthesis of $\text{UiO-66-NH}_2/\text{CPA-MA}$

The hybrid of $\text{UiO-66-NH}_2/\text{CPA-MA}$ was synthesized by following procedure: 10 mg CPA-MA were dissolved in 40 mL anhydrous ethanol to form a clean solution. 40 mg UiO-66-NH_2 was added and distributed. After that, the suspension was vibrated at 180 rpm for 12 h at 303 K. Finally, the powder was recovered, washed and dried to get the composite of $\text{UiO-66-NH}_2/\text{CPA-MA}$. The synthesized procedure of $\text{UiO-66-NH}_2/\text{CPA-MA}$ was shown in Scheme S1. The nanocomposite was denoted as UA for the expression convenience.

2.2.3 Characterization

A X-ray powder diffractometer (Cu Ka, Rigaku III/B max) was used to test the samples. Fourier transform infrared (FT-IR) spectra investigation of the samples was conducted on an ALPHA-T FT-IR spectrometer

(Bruker, Germany), and the testing range was set as from 4000 to 400 cm^{-1} . The scanning electron microscopy (SEM) images of the samples were recorded by a FEI Quanta 200F SEM. The color change of the composite after Ce^{4+} loading was qualitatively detected by naked eye, and quantitatively measured by a solid-state visible spectrophotometer (AvaSpec, China).

2.2.4 Measurement and removal of Ce^{4+}

Ce^{4+} can be visually detected and simultaneously removed by the UA nanocomposite. 5 mg UA nanocomposite was placed into 10 mL solutions containing different initial concentrations of Ce^{4+} (from 10 to 300 mg/L). The suspensions were vibrated at 180 rpm for 12 h at 298 K. After that, the composite was collected by filtrations. To determine the adsorbed Ce^{4+} , the residue Ce^{4+} concentration was measured by CPA-MA according to the previous report [1, 2], and the adsorbed Ce^{4+} can be calculated by the difference between the original and the residue concentrations. Naked eyes and a solid-state visible spectrophotometer were used to qualitatively and quantitatively investigate the color change of the hybrid after Ce^{4+} loading.

2.2.5 Kinetic analysis

Kinetic analysis was studied at 298 K with the adsorbent dose of 0.5 g/L. The UA nanocomposite was added into 100 mg/L Ce^{4+} solutions. The mixtures were vibrated at 180 rpm. At different time intervals, the mixtures were sampled to determine the related Ce^{4+} concentration.

2.2.6 Effects of co-existing ions investigation

The co-existing ions effect (Mg^{2+} , Cu^{2+} and Zn^{2+}) toward Ce^{4+} sorption were studied at 298 K. The initial Ce^{4+} concentration was 100 mg/L, while the co-existing ions concentration were set as 0, 100, 150, 200, 250 and 300 mg/L, respectively. The mixtures were vibrated at 180 rpm at 298 K for 12 h. The adsorbent dose is 0.5 g/L.

3. Results And Discussion

The XRD patterns of pristine UiO-66- NH_2 and UA composite are indicated in Fig. 1(a). The pristine UiO-66- NH_2 exhibits characteristic peaks at the 7.3°, 8.3° and 25.6° which are in consistent with the early report, showing the successful synthesis of UiO-66- NH_2 and its high crystallization [4]. These characteristic peaks also appear in the XRD pattern of UA composite, showing the existence of crystal UiO-66- NH_2 in the UA nanocomposite.

FT-IR spectra of UiO-66- NH_2 and UA are indicated in Fig. 1(b). As to UiO-66- NH_2 , the peaks at 1580 and 1420 cm^{-1} are attributed to C-O bonding and C-C vibrational modes in carboxylates, respectively [5]. 1258 and 1385 cm^{-1} are ascribed to the C-N stretching of aromatic amines [6]. The adsorption bands at 764 and 659 cm^{-1} are ascribed to Zr-O as longitudinal and transverse modes [7]. The bands located 3475 and 3352 cm^{-1} are designated to the asymmetric and symmetric vibrations of N-H bond in NH_2 , respectively

[8, 9]. These characteristic bands are in consistence with early literatures, confirming the successful synthesis of UiO-66-NH₂. As to CPA-MA, the band located 1676 cm⁻¹ is ascribed to the stretching of C=O [10]. It can be found that the typical bands of UiO-66-NH₂ and CPA-MA appear in the spectrum of UA, indicating the well incorporation of UiO-66-NH₂ and CPA-MA, furthermore, peaks related to the NH₂ of UiO-66-NH₂ (3475 and 3352 cm⁻¹), and the peak related to the C=O of CPA-MA (1676 cm⁻¹) are all significantly weakened in the spectrum of UA, showing the NH₂ groups in UiO-66-NH₂ have condensed with the C=O groups in CPA-MA to form the composite of UA.

As shown in Fig. 1 (c)-(e), the SEM and TEM imagines show that the UA nanocomposites exhibits a morphology of cube with the sizes of around 60-80 nm. The chemical composition of UA was further determined by the mapping and EDX analysis (Fig. 1 (f), (g)). It can be seen that the elements of Zr, N, C, Cl, O, P and S exist and uniformly distribute in UA composite. These results confirm that UiO-66-NH₂ was successfully incorporated with CPA-MA to form the composite of UA.

To investigate the effects of adsorbent dosage toward Ce⁴⁺ capture, dosage of UA was set from 0.5 to 2 g/L, and the related adsorption capacities are indicated in Fig. S1. As one can see that the highest unit adsorption capacity appears when the dosage is 0.5 g/L, so 0.5 g/L was determined as the optimal dosage. The kinetic process of UA adsorbing Ce⁴⁺ was investigated (Fig. S2 (a)). Results showed that the adsorption course was more preferably described by the pseudo-second-order kinetic model (Fig. S2 (b), (c) and Table S1). The adsorption capacity of UA was compared with other previously reported Ce⁴⁺ adsorbents, the results are shown in Table S2, indicating it being among the top Ce⁴⁺ adsorbents.

In order to test the response of UA toward Ce⁴⁺, the adsorptions were conducted with Ce⁴⁺ concentration, and the related diffuse reflectance spectra reflecting were recorded with a visible light spectrophotometer. The results indicate that the adsorbent can change its color as capturing Ce⁴⁺ ions with different concentration. The color of crude UA is olive drab. In the testing Ce⁴⁺ concentration range, the Ce⁴⁺ load UA shows light cyan, and the chroma of UA decrease with the increase of Ce⁴⁺ concentration (insert in Fig. 2 (a)), which can be testified by the intensity decrease at $\lambda=454$ nm with the increase of Ce⁴⁺ concentration (Fig. 2 (a)). Furthermore, as plot the Ce⁴⁺ concentration vs. intensity value at 454 nm, it can be found that the intensity changing have linear relationship with the Ce⁴⁺ concentration, as shown in Fig. 2 (b). The high coefficient (R^2) values of 0.9700 exhibits the high linear dependence, indicating that Ce⁴⁺ concentration can be measured by chroma changing of UA.

The limits of detection (LOD) is 3.24 mg/L, which can be calculated by follows:

$$LOD = \frac{3M}{S} \quad (1)$$

where M refers to the standard deviation obtained in the blank, and S refers to the slope of the linear range in the calibration graph.

So as to study the anti-interference ability, the adsorption capacities of UA toward Ce^{4+} were tested with several co-existing ions (Mg^{2+} , Zn^{2+} and Cu^{2+}). In the experiments, 100 mg/L Ce^{4+} was paired with 0, 100, 150, 200, 250, or 300 mg/L the competing ion, respectively. It can be seen in Fig. 3 (a), the existence of competing ions can affect the adsorption of Ce^{4+} on the nanocomposite in different level, depending on the species. Cu^{2+} shows the least competitiveness, the nanocomposite removal rate can be retained ~87%. In the presence of Zn^{2+} , which is the most competitive, the nanocomposite removal rate can be retained ~80%. These consequences show that UA has a relatively high anti-interference capacity as adsorbing Ce^{4+} .

The crude UA is olive drab. When UA captures 10 mg/L Ce^{4+} , its color quickly changes to be pale green in seconds. When UA was added to the solution containing other metal ions such as Mg^{2+} , Zn^{2+} and Cu^{2+} , even their concentrations are 30 times higher than that of Ce^{4+} , they can not change UA' color a bit. The results are shown in Fig. 3 (b), which indicates that Ce^{4+} can be qualitatively detect even by naked-eye according to UA's color.

4. Conclusion

In summary, a novel nanocomposite of UA was successfully prepared in this study. It can not only effectively remove Ce^{4+} by adsorption, but can also qualitative and quantitatively measure Ce^{4+} . Furthermore, Ce^{4+} ions can be detected by UA with the LOD of 3.24 mg/L. UA has a high anti-interference ability. Several competing metal ions can co-exist with Ce^{4+} and will not affect its adsorption and detecting ability. The novel nanocompoiste of UA can fast remove hazardous Ce^{4+} ions, and can simultaneously visually detect Ce^{4+} . It is a highly potential multifunctional adsorbent to efficiently deal with rare earth containing water.

Declarations

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Figures

Figure 1

(a) XRD patterns of UiO-66-NH₂ and UA composite; (b) FT-IR spectrum of UiO-66-NH₂ and UA composite; SEM and TEM images of UA (c-e); Elements mapping analysis and EDX pattern of UA (f, g).

Figure 2

(a) the UV/Vis diffuse reflection spectroscopy of UA adsorbing Ce^{4+} with different concentrations. (b) the linear relationship spectrum. (The experiments were parallel performed in five times. The error bars are shown with absolute values of standard deviation (SD) lower than 3%).

Figure 3

(a) Effects of co-existing ions on Ce^{4+} adsorption on UA composite (initial Ce^{4+} concentration 100 mg/L, adsorbent dose 0.5 g/L); (b) The color of UA when it captures different metal ions.

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