

# ZIF-8 as an adsorbent of aqueous phase for Eu and Tb ions

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In the present work, the adsorption behaviours of zeolitic imidazolate framework (ZIF-8) as the adsorbent to europium (Eu) and terbium (Tb) in aqueous phase have considerably been investigated. ZIF-8 shows the excellent adsorption performance such as quickness (in several minutes), efficiency (~14% saturated amount) and lower adsorption limit (tens of parts per billion). Specially, ZIF-8 prefers to adsorb lanthanide ions of low concentration (40 ppm) under high pH value (>6). Fourier transform infrared spectroscopy and X-ray diffraction of used ZIF-8 display that the hydroxyls generated from the hydrolysis of ZIF-8 are responsible for catching the Eu or Tb by the formation of zinc (Zn)–O–Eu or Zn–O–Tb.

**1. Introduction:** Zeolitic imidazolate frameworks (ZIFs) have drawn more attentions owing to uniformed porous structure, high surface area and extraordinary thermal stability [1–4]. Meanwhile, the applications have extensively being explored in a plenty of fields such as gas-storage/gas-separation, drug delivery, chemical catalysis, chemical sensor [5–9] etc. With industries continuously being moved forward, the pollutants of the biosphere are exponentially growing in every year. The metal ions and polyoxoanions comprise of a kind of main pollutants heavily to menace human health [10, 11]. Since these inorganic species of water body are low concentration and exist in many formats, the treatment process is complicated and expensive. Recently, metal–organic framework materials exhibit the capacity to capture the metal ion or polyoxoanion in the water system by both the metal ion/cluster as the node and the functionalised ligand as the strut. UIO-68-P(O)(OEt)<sub>2</sub> and UIO-68-P(O)(OH)<sub>2</sub> can capture the uranyl in both water and seawater with high saturated amount of 217 and 188 mg/g [12]. Also, UIO-66-NH<sub>2</sub> is more capable of attracting the HPO<sub>4</sub><sup>2-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> ions than UIO-66 [13]. The open metal position refers to the event that some coordination of the metal ion is ligated by the solvent or water or hydroxyl rather than organic ligand. In aqueous phase, the metal ion with open metal position can more easily interact with polyoxoanion by the mode of hydrogen bond. This is found in MIL-53(Fe), MIL-53(Al) and MIL-100(Fe) [14–16]. Interestingly, Nu-1000 exhibits the rapid and effective adsorption to selenate and selenite depended on Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(CO<sub>2</sub>)<sub>12</sub> cluster of open metal position and 30 Å of aperture [17]. Recently, Li *et al.* [18] have reported the adsorption of ZIF-8 to H<sub>x</sub>AsO<sub>4</sub><sup>3-x</sup> species. Thereinto, two merits are worth pointing out: low adsorption limit (9.8 parts per billion (ppb)) and supposed adsorption mechanism. In their work, they think that the adsorption of ZIF-8 to H<sub>x</sub>AsO<sub>4</sub><sup>3-x</sup> species takes place by the monodentate and bidentate interactions between H<sub>x</sub>AsO<sub>4</sub><sup>3-x</sup> species and surface hydroxyls of ZIF-8. The surface hydroxyl of ZIF-8 is generated from the hydrolysis of zinc (Zn) ion because the 4-coordinated Zn is metastable state with respect to its diameter. To this point, Howarth *et al.* [19] agree to this opinion as well and cite this result in their review. In addition, Zhao *et al.* [20] report the adsorption of ZIF-8 to metal ions. They find that ZIF-8 can rapidly reach the adsorption equilibrium in several minutes and prefer to Cu<sup>2+</sup>.

The recovery of expensive and rare metals in the abandoned materials is very important. Lanthanide, called as the industrial ‘vitamin’, has applications extensively in many fields, especially

in the luminescent materials [21]. Since the luminescent lanthanides are rare, the recovery is becoming tremendously important. The lanthanides in luminescent materials are usually lower concentration; hence it is difficult directly to extract lanthanide. Otherwise, the popular extractant is expensive and consumable in the treated process. Therefore, the simple and economic route to recover the lanthanides is becoming urgent. In this work, taking advantage of ZIF-8, we have studied the adsorption of ZIF-8 to europium (Eu) and terbium (Tb) in order to provide a route to efficiently capture the lanthanides from lower concentration waste.

## 2. Experimental section

**2.1. Synthesis and characterisation:** According to the described method in [9], Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (2970 mg, 10 mmol) and 2-methylimidazole (820 mg, 1 mmol) were dissolved in 250 ml of methanol. Under room temperature, both the solutions were mixed together. Afterward, the mixture was maintained for 24 h under room temperature. ZIF-8 was centrifugally separated, washed three times by methanol and activated at 150°C in oven for 24 h.

Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku D/MAX PC2200 diffractometer for Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ), with a scan speed of 5°/min. The morphologies and size of the samples were inspected on a transmission electron microscope (TEM, JEOL-2000ex). The thermal gravimetric (TG) analyses were performed on Pyris STA 6000 instrument used with a heating rate of 10°C/min and 20 ml/min flow of N<sub>2</sub>. N<sub>2</sub> isothermal adsorption experiments were performed at 77 K with TriStar II 3020 (Micromeritics Instrument Corporation) apparatus using nitrogen as the probing gas. The samples were vacuumed for 10 h at 150°C before the data were collected. Fourier transform infrared (FTIR) spectra were recorded within the 400–4000 cm<sup>-1</sup> region on a Nicolet iS10 FTIR spectrometer using potassium bromide pellets. The Zn, Eu and Tb content were determined by IRIS Intrepid II ICP instrument (Inductively Coupled Plasma, Thermo Electron Corp.). The samples were dissolved by the H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> and diluted to a certain concentration.

**2.2. Adsorption experiments:** The 500 ml of Eu and Tb solutions (500 ppm) were prepared by dissolving 0.7335 g of Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and 0.6840 g of Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O in 500 ml deionised water. The adsorptions of ZIF-8 to Eu and Tb ions were studied using the batch methods. All experiments were completed under stirring.

The kinetics experiments were carried out by casting 60 mg of ZIF-8 into 60 ml of 100 ppm solutions of Eu or Tb. Since it was found that the adsorption was completed quickly, seven adsorption experiments were simultaneously carried out in order to reduce the deviation arisen from volumetric change. The determined intervals were 1, 2, 3, 4, 5, 10 and 30 min, respectively. About 10 ml of aliquots were sampled and centrifuged. The Eu or Tb concentrations were determined by ICP.

The saturated adsorption amounts were implemented by adding 10 mg of ZIF-8 into the different concentrations of Eu or Tb solutions varying from 10 to 100 ppm. The mixture was continuously stirred for 20 min in order to attain the saturated adsorption. Then, 10 ml of aliquots were sampled and centrifuged. The ionic concentration of the sample was determined by ICP.

The adsorption amounts of ZIF-8 to Eu and Tb ions were calculated using the following equation:

$$q = ((c_0 - c_e) \times V) / m \quad (1)$$

The  $q$  was adsorption amount (mg/mg) of ZIF-8 to Eu or Tb ions,  $V$  was the solution volume (ml) and  $m$  was the mass of the ZIF-8 (mg). Here,  $c_0$  and  $c_e$  were the initial and equilibrium Eu/Tb concentrations in the solution ( $\mu\text{g/ml}$ ), respectively.

### 3. Results and discussion

**3.1. Material characterisation:** The PXRDs of ZIF-8 show that the diffraction peaks of as-prepared ZIF-8 completely consist with the simulated one, proving the homogeneity and crystallinity of as-synthesised samples (Fig. 1). The other characterisations of ZIF-8 including TEM diagram,  $N_2$  isothermal adsorption at 77 K and TG analysis are contained in supporting information, which is comparable with the reported ones.

**3.2. Eu and Tb adsorption:** The pH usually plays a crucial role in the extraction process of lanthanide. In present industrial process, the lanthanide ions are often extracted when the pH is beyond 6. To meet the current extraction process of lanthanide, we first investigate the effects of pH on the lanthanide adsorption. The adsorption data of ZIF-8 to Eu or Tb at different pH have been collected to offer the suitable pH range. With regard to ZIF-8 stability to pH, Zn ion concentrations in solution at the different pH have meanwhile been collected (Figs. 2 and 3). Both the curves of Eu and Tb have the same tendency and the adsorption amount is very close to each other at every pH. The adsorption amounts are basically sustained below 15% with 6–8 of pH and the adsorption amounts rapidly increase when pH is more than 10. Through calculation, the Eu and Tb ions have completely been absorbed by ZIF-8 beyond 10 of pH. This is essentially impossible. We think that except for adsorption of ZIF-8 to lanthanide, there simultaneously exists the induced precipitation of lanthanide ion resulted from ZIF-8. The collected Zn ion

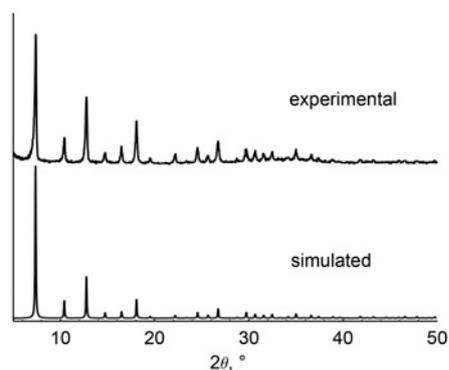


Fig. 1 Experimental and simulated PXRD patterns of ZIF-8

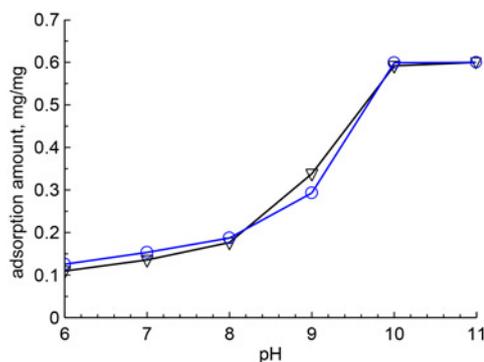


Fig. 2 Effect of pH on the adsorption of ZIF-8 against Eu/Tb: (open circle) ZIF-8 against Eu and (inverted triangle) ZIF-8 against Tb

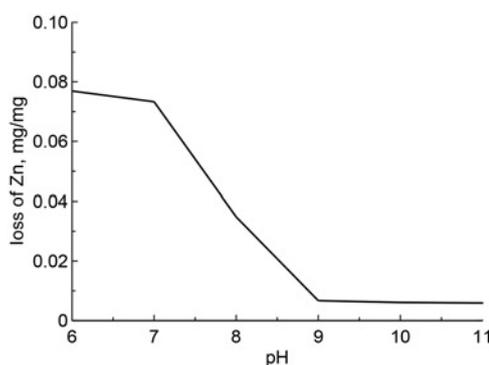


Fig. 3 Loss of Zn ion at different pH value

concentration in solution shows that the Zn ion is partially leaked till 9 of pH (Fig. 3). The Zn ion is lost about 3.48% at 8 of pH. To avoid the occurrence of induced precipitation of lanthanide ions, the adsorption experiments in this context are performed at 8 of pH though the loss of Zn at 8 of pH is bigger than that at 9 of pH.

The kinetics experiments of ZIF-8 to Eu or Tb ions are investigated by the dependence of adsorption amount versus time. The resulted curves show that all adsorptions are very fast and almost finished in 5 min (Fig. 4). By simulating the data, it concludes from the kinetics simulations that both of them would prefer pseudo-second-order kinetic equation to pseudo-first-order kinetic equation.

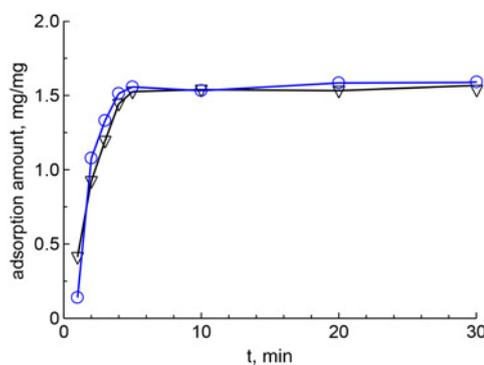
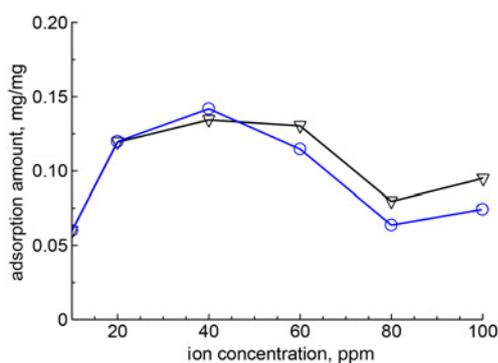


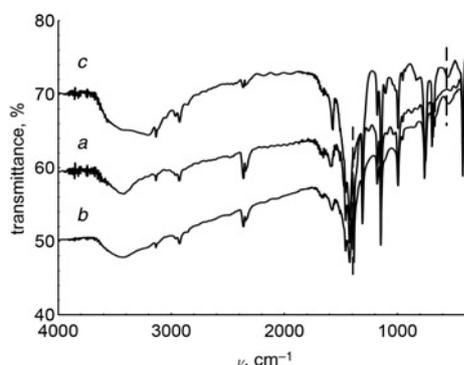
Fig. 4 Dependence of the adsorption amount versus time: (open circle) ZIF-8 against Eu, the kinetics equations: pseudo-first-order,  $y = 0.327x + 0.142$ ,  $R^2 = 0.791$ ; pseudo-second-order,  $y = -0.133x^2 + 1.12x - 0.787$ ,  $R^2 = 0.973$ ; (inverted triangle) ZIF-8 against Tb, the kinetics equations: pseudo-first-order:  $y = 0.275x + 0.276$ ,  $R^2 = 0.929$ ; and pseudo-second-order:  $y = -0.0629x^2 + 0.652x - 0.164$ ,  $R^2 = 0.997$



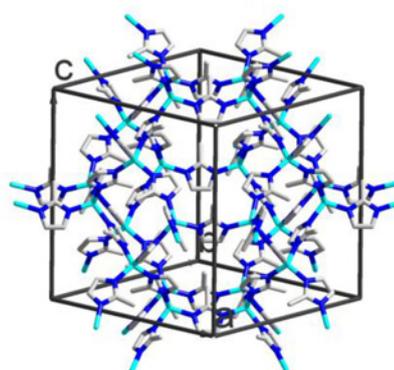
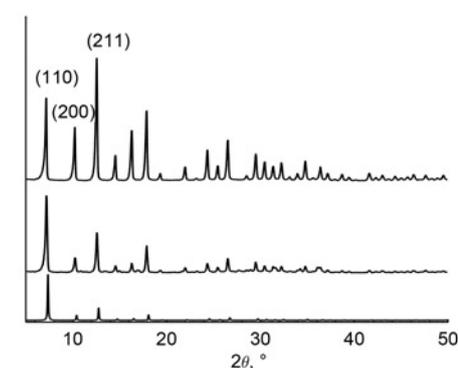
**Fig. 5** Dependence of the adsorption amount to ion concentrations. (open circle) ZIF-8 against Eu; (inverted triangle) ZIF-8 against Tb

The saturated adsorption amount is performed by modifying the concentration of lanthanide ions with fixing the volume of solution and casting amount of ZIF-8. The results exhibit that the saturated adsorption amounts of ZIF-8 against Eu and Tb are 0.1418 and 0.1343 mg/mg, respectively (Fig. 5). However, the adsorption amount decreases with increasing the ion concentration. We believe that the adsorption of ZIF-8 to Eu or Tb is partially impeded because the cluster size of polymerised lanthanide ions at higher concentration is beyond 3.4 Å of ZIF-8 aperture. Additionally, a very important parameter should be noted. The adsorption limit of ZIF-8 against Eu and Tb can reach tens of ppb under lower concentration. For example, ion concentrations of Eu and Tb in solution are about 0.0197 and 0.0361 ppm after absorbed by ZIF-8 when started ion concentration is at 10 ppm.

**3.3. Proposed adsorption mechanism of ZIF-8 against Eu and Tb:** Since 4-coordinated Zn is metastable state with respect to the ion diameter, Li *et al.* have concluded that the adsorption of ZIF-8 to  $H_xAsO_4^{3-x}$  species is achieved by the monodentate and bidentate interactions between  $H_xAsO_4^{3-x}$  species and surface hydroxyl of ZIF-8 which is generated from the partial hydrolysis of Zn ion. Howarth *et al.* agree to this opinion as well and cite this result in their review. Besides, the adsorption of ZIF-8 to metal ions has been reported by Zhao *et al.* In this Letter, ZIF-8 exhibits preferential adsorption to  $Cu^{2+}$  rather than the other ions, whereas adsorption mechanism has not been referred to. In this work, we confirm that the hydroxyl produced from the hydrolysis of Zn ion is responsible for the adsorption of metal ions by FTIR and PXRD. From FTIR (Fig. 6), the peak of ZIF-8-Eu and ZIF-8-Tb (ZIF-8-Eu and ZIF-8-Tb are defined as ZIF-8 adsorbing Eu or Tb) at  $554\text{ cm}^{-1}$  is assigned to Zn–O vibration, proving the



**Fig. 6** FTIR curves of  
a ZIF-8  
b ZIF-8-Eu  
c ZIF-8-Tb



**Fig. 7** Top: PXRD patterns of ZIF-8 adsorbing the Eu or Tb ions; down: as-synthesised ZIF-8; middle: ZIF-8-Eu; upper: ZIF-8-Tb; and bottom: the crystal structure of ZIF-8 drawn from cif file

hydrolysis of Zn ion in ZIF-8. The peak of ZIF-8-Eu and ZIF-8-Tb appearing at  $1380\text{ cm}^{-1}$  is attributed to bridged Zn–O–M vibration, which implies the existence of the Zn–O–Eu(Tb) vibration. The ZIF-8-Eu and ZIF-8-Tb are further testified by PXRD (Fig. 7). Compared with as-synthesised ZIF-8, the peak positions of ZIF-8-Eu and ZIF-8-Tb are basically unchanged, which proves the stability of ZIF-8. However, intensities of (110) facet in both ZIF-8-Eu and ZIF-8-Tb remarkably decrease. By inspecting the crystal structure of ZIF-8, (110) facet of ZIF-8 is corresponded with 2-methylimidazole rings of  $\alpha$ -cage of sodalite. After absorbing the Eu or Tb ions, the coordinated number of Zn ion in ZIF-8 framework increases to 5 or 6 owing to the formation of Zn–OH and Zn–O–M, and of course the position of 2-methylimidazole ring at (110) facet simultaneously happens to disorder.

**4. Conclusion:** In summary, ZIF-8 exhibits excellent adsorption performances to Eu and Tb at low concentration such as quickness (in several minutes), high adsorption amount (~14% saturated amount) and low adsorption limit (tens of ppb). The adsorption of ZIF-8 to Eu and Tb is attained by the interaction between Eu or Tb and the hydroxyls of ZIF-8 generated from the hydrolysis of Zn ions.

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