Adsorptive Removal of Pb(II) Ions from Aqueous Samples with Amino-Functionalization of Metal–Organic Frameworks MIL-101(Cr)

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ABSTRACT: Metal organic frameworks (MOFs) have been regarded as robust adsorbents for the adsorptive removal of organic pollutants because of their unique characteristics. However, the application of MOFs in the removal of metals from water is still rare. In this paper, amino-functionalization of Cr-based MOFs MIL-101 are modified through coordination bonding of unsaturated Cr metal centers with the --NH_2 group in ethylenediamine (ED), and we demonstrate their excellent performance for the removal of Pb(II) ions from water. The Fourier transform infrared verifies that the ethylenediamine was grafted successfully on MIL-101. Furthermore, the results of X-ray diffraction, scanning electron microscopy, and transmission electron microscopy show that the structure of ED-MIL-101 with an appropriate amount of ED almost does not collapse and retains the original performance of MIL-101. The adsorption capacity of ED-MIL-101, which is more than five times that of MIL-101, is $81.09 \text{ mg}\cdot\text{g}^{-1}$ for Pb(II) ions from aqueous samples. The selectivity coefficients of ED-MIL-101 for Pb(II)/Cu(II), Pb(II)/Zn(II), Pb(II)/Co(II), and Pb(II)/Ni(II) are 6.92, 24.02, 15.69, and 14.53, respectively. The adsorption kinetics of Pb(II) ions shows that the process fits well with a pseudo-second-order model, and the adsorption equilibrium time is only about 30 min. Moreover, the practical application of ED-MIL-101 achieves almost 97.22% removal efficiency for Pb(II) ions. These results indicate that ED-MIL-101 has great potential in selectively removing Pb(II) ions from water environment.

1. INTRODUCTION

Metal–organic frameworks (MOFs), a new class of microporous material, are assembled through coordination between metal ions or metal cluster and organic ligands. These materials have attracted great attention not only for their large surface areas, low framework densities, accessible cages, tunnels and modifiable pores^{1–4} but also for their potential application in gas sorption,⁵ separations,⁶ catalysis,⁷ drug delivery,⁸ optics,⁹ and sensing,¹⁰ especially in separations. The usage of MOFs in gas phase separation has been extensively studied, while the research on liquid phase area is relatively few. With a rapid increase of global industrial activities, harmful compounds and metal ions, which are usually biologically toxic and carcinogenic,¹¹ are being constantly released into the water environment. For these reasons, MOFs are regarded as promising materials in the selectively adsorptive removal of hazardous materials from wastewater.

Recently, MOF-type materials have also been investigated widely for the adsorptive removal of various hazardous materials such as pharmaceuticals, organic dyes, alcohols, and aromatic compounds from the environment. Cychosz et al.¹² have reported that MIL-100, with excellent water stability, has been used in removing furosemide and sulfasalazine from wastewater. Haque et al.¹³ have utilized chemically modified MIL-101(Cr) for the adsorptive removal of methyl orange from water, the adsorption capacity of PED-MIL-101 is 194 mg/g , which is more than 16 times that of activated carbon. Julien et al.¹⁴ have researched ZIF-8 for the separation of alcohol and water, and finds that compared with zeolites and activated carbon material, ZIF-8 has higher alcohol adsorption capacity

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Figure 1. (a) Generation of coordinatively unsaturated sites from chromium trimers in MIL-101 after vacuum treatment at 423 K for 12 h; (b) Adsorption principle of amino-functionalized MIL-101 for Pb(II) ions.

and better chemical and structural tenability. Jhung et al.^{15,16} have synthesized MIL-101 by a microwave method, finding the MIL-101 has larger capacity than SBA-15, HZSM-5 zeolite, and activated carbon in the adsorption of benzene. Besides, they also have discovered that ED-MIL-101 is 1.17 times and 1.10 times higher than MIL-101 on the adsorption of naproxen and clofibric acid, respectively.

However, systematic study and further research in adsorptive removal of metal ions from wastewater by MOFs is still relatively deficient. Zhu et al.¹⁷ have reported that the Fe-BTC shows a high arsenic adsorption capacity of more than 6 times that of iron oxide nanoparticles and 36 times that of commercial iron oxide powders. Ke et al.¹⁸ have reported that the thiol-functionalized $[\text{Cu}_3(\text{BTC})_2]_n$ exhibits remarkably strong adsorption affinity and high adsorption capacity for Hg^{2+} ions. Zou et al.¹⁹ have obtained HKUST-1-MW@ $\text{H}_3\text{PW}_{12}\text{O}_{40}$, which exhibits remarkably high adsorption affinity and adsorption capacity of metal ions, but it cannot selectively remove a specific metal ion which is important in metal ion recycling. Though MOFs exhibit initially an excellent performance for the adsorptive removal of metal ions, there is a great practical significance to develop further a new highly selective and recyclable kind of MOFs for other different metal ions from wastewater.

Lead (Pb), one of the most toxic metals, with important environmental and toxicological significance, has attracted widespread attention and has been one of the research hotspots.^{20–22} Pb(II) ions mainly diffuse to the water environment through effluents from lead smelters, battery manufacturers, printing and mining industries.^{23,24} It is generally known that an excessive amount of Pb(II) ions do serious damage to the kidneys, the neuronal system, the reproductive system, and the function of brain cells.^{25,26} Selective removal of Pb(II) ions from wastewater has significant value in environment protection and human health as well as the development of a circular economy.

The weak stability in aqueous solutions is the main factor that limits the wide application of MOFs in wastewater

treatments. Some studies suggest that MIL-101 is a novel adsorbent with the advantage of large pores, high surface areas, and greatly improved chemical stability,^{27,28} and it has been applied in the adsorption for pharmaceuticals,²⁹ organic dyes,¹³ and aromatic compounds.¹⁵ Inspired by the fact that the adsorption capacity of Pb(II) ions of silica-based mesoporous materials modified by amino groups is apparently higher than that of normal silica-based materials, MIL-101 with high stability after being modified by amino groups can probably provide many adsorptive sites to interact strongly with Pb(II) ions.^{30,31} Therefore, we describe a facile strategy to fabricate the amine-grafted MIL-101 by a postsynthetic modification method. The chromium trimers in the mesoporous cages of MIL-101 possess terminal water, removable from the framework after vacuum treatment at 423 K for 12 h (Figure 1a). They can generate open metal sites or coordinatively unsaturated sites (CUSs) as Lewis acid sites in the structure, which are usable for surface modification. Thus, ethylenediamine used as the common functional group can be easily coordinated on the CUSs of the MIL-101. The amino groups modified on the pore surface of MIL-101 afford the chelating binding sites for the adsorption of Pb(II) ions which coordinate well with nitrogen atoms of amino groups (Figure 1b). The adsorption capacity, kinetics adsorption, selectivity, and the application for the removal of Pb(II) ions from environmental water samples were studied.

2. EXPERIMENTAL SECTION

2.1. Chemicals. All chemicals were of analytical grade, purchased from commercial sources and used without further purification. Terephthalic acid (TPA) was obtained from Aldrich Chemistry Co., Ltd. (Shanghai, China). Chromium nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), hydrofluoric acid, *N,N*-dimethylformamide (DMF), ethyl alcohol, methylbenzene, ethylenediamine (ED), lead nitrate, copper chloride, and zinc nitrate hexahydrate were supplied by Xilong Chemical Co., Ltd. (Shantou, China). Nickel chloride hexahydrate and cobalt chloride hexahydrate were obtained from Shanghai Chemical

Reagent Co., Ltd. (Shanghai, China) and Shanghai green chemical technology Co., Ltd. (Shanghai, China), respectively. Water was purified with a Milli-Q water system (Bedford, USA).

2.2. Preparation of the Adsorbents. **2.2.1. Preparation of MIL-101.** The MIL-101 was synthesized under solvothermal synthesis conditions by using hydrofluoric acid as a mineralization agent, and prepared according to the literature procedure^{27,32,33} with a slight modification. Briefly, 820 mg of TPA and 2.0 g of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 35 mL of ultrapure water containing 100 μL of HF (40 %) under ultrasonic stirring for 30 min. Then the solution was transferred to an autoclave and heated at 493 K for 8 h. After cooling to room temperature (298 K), the resultant solid green-colored products were collected via centrifugation. To remove the unreacted TPA, the as-synthesized MIL-101 was further purified by two-step processes with ultrapure water, DMF, and hot ethanol. The precipitate was washed by ultrapure water (100 mL) and DMF (100 mL) for three times, respectively. The washing method was ultrasonic stirring for 10 min and centrifuging for 15 min with 8000 r/min. Then a solvothermal treatment was sequentially performed using ethanol (50 mL) at 373 K for 20 h. The resulting material was recovered by filtration, and finally dried overnight at 423 K under air atmosphere.

2.2.2. Ethylenediamine Grafting on Coordinatively Unsaturated Metal Centers of MIL-101. Amino-functionalization of Cr-based MOFs MIL-101 was modified through the coordination bond of unsaturated Cr metal centers and the $-\text{NH}_2$ group in ethylenediamine (ED), because of the open metal sites or coordinatively unsaturated sites (CUSs) that generate from trimeric chromium octahedral clusters of MIL-101 after dehydration. The preparation procedure for this material was adapted from the literature procedure^{3,34} with slight modification. Typically, 1.0 g of as-synthesized MIL-101 sample was dehydrated at 423 K in a vacuum oven for 12 h to generate CUSs (Figure 1a) and then suspended in 75 mL of anhydrous toluene. After that, an appropriate amount of 14.97 $\text{mol} \cdot \text{L}^{-1}$ ethylenediamine solution (2 mmol, 136 μL for sample A; 5 mmol, 340 μL for sample B; 10 mmol, 680 μL for sample C) was introduced, and the mixture was further refluxed for 12 h (Figure 1b). The final sample was collected by filtrating and washing with a large amount of ethanol, it was then dried overnight at room temperature (298 K). In the process of preparing ED-MIL-101, considering the apparent effect of ED on MIL-101, the material is optimized through constantly adjusting the grafting amount of ED. Afterward, given the amount of 2 mmol, 5 mmol, and 10 mmol of ED, the product shows different performance on the BET surface area, morphology, and adsorption capacity, and finally it is determined that 5 mmol grafted on MIL-101 is the optimal grafting amount of ED.

2.3. Characterization. Powder X-ray diffraction (XRD) patterns of the samples were obtained by a Bruker D8-Advance diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Fourier transform infrared (FTIR) spectra were recorded on a VERTEX 70 FTIR apparatus with KBr method. The morphologies and the microstructure of the synthesized samples were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) operated on a JEOL JSM 7401 and H-7650B, respectively. The BET surface area measurement was performed with N_2 adsorption-desorption isotherms at liquid nitrogen temperature (77 K)

after the samples were dehydrated under vacuum at 383 K for 12 h using a Micromeritics TriStar II 3020. X-ray photoelectron spectroscopy (XPS) measurement was performed on a PHI Quantera Scanning X-ray Microprobe using monochromatic $\text{Al K}\alpha$ ($\lambda = 1486.7 \text{ eV}$). A ContrAA 700 (Analytik Jena, Germany) high resolution continuum source atomic absorption spectrometer was used for the determination of Pb(II) , Cu(II) , Zn(II) , Co(II) , and Ni(II) ions.

2.4. Adsorption Experiments. **2.4.1. Batch Adsorption Experiments.** Batch adsorption experiments were conducted by using necessary adsorbents in a 100 mL stoppered conical flask containing 20 mL of test solution to obtain equilibrium data. Herein, 20 mg of adsorbents was mixed with 20 mL of Pb(II) solutions of different pH and initial concentrations. The pH of the aqueous solution was adjusted by adding 0.1 $\text{mol} \cdot \text{L}^{-1}$ HNO_3 and 0.1 $\text{mol} \cdot \text{L}^{-1}$ NaOH , and the concentration of Pb(II) ions was 50 $\text{mg} \cdot \text{L}^{-1}$. The batch experiments were carried out at 298 K for 6 h. After adsorption, the adsorbent was separated by centrifugation, and the concentration of Pb(II) ions was analyzed using a ContrAA 700 atomic absorption spectrometer. The amount of Pb(II) bound on MIL-101 and ED-MIL-101 was calculated according to the following equation.

$$Q_e = \frac{C_0 V - C_e V}{m} \quad (1)$$

where Q_e ($\text{mg} \cdot \text{g}^{-1}$) represents the adsorption capacity, C_0 ($\text{mg} \cdot \text{L}^{-1}$) is the initial concentration of Pb(II) ions, C_e ($\text{mg} \cdot \text{L}^{-1}$) is the equilibrium concentration of Pb(II) ions, m (g) is the mass of adsorbents, and V (L) is the volume of the Pb(II) ion solution.

2.4.2. Adsorption Kinetic Experiments. Adsorption kinetic experiments were carried out by adding 200 mg of adsorbents into 200 mL of a 500 $\text{mg} \cdot \text{L}^{-1}$ Pb(II) ion solution at room temperature (298 K), with constant stirring. Samples were taken out at certain intervals, and the adsorbents were separated by centrifugation. The concentrations of Pb(II) ions were measured by ContrAA 700 atomic absorption spectrometer.

2.4.3. Adsorption Selectivity Experiments. The selectivity of the ED-MIL-101 toward Pb(II) ions was valued by competitive adsorption in the presence of various competitive metal ions. A mixture of Pb(II) , Cu(II) , Zn(II) , Co(II) , and Ni(II) was added into deionized water to obtain an initial concentration of 30 $\text{mg} \cdot \text{L}^{-1}$ each for Pb(II) , Cu(II) , Zn(II) , Co(II) , and Ni(II) ions. After a competitive adsorption equilibrium reached for 6 h, the concentrations of Pb(II) , Cu(II) , Zn(II) , Co(II) , and Ni(II) ions in the remaining samples were detected by using a ContrAA 700 atomic absorption spectrometer. The following equations were used to evaluate the selectivity of ED-MIL-101.

Static distribution coefficient

$$K_D = \frac{Q_e}{C_e} \quad (2)$$

Selectivity coefficient

$$\alpha = \frac{K_{D1}}{K_{D2}} \quad (3)$$

where Q_e ($\text{mg} \cdot \text{g}^{-1}$) represents the adsorption capacity and C_e ($\text{mg} \cdot \text{L}^{-1}$) is the equilibrium concentration, K_{D1} and K_{D2} represent the distribution coefficients of Pb(II) ions and D2

(D2 represents Cu(II), Zn(II), Co(II) and Ni(II) ions), α is the selectivity coefficient.

3. RESULTS AND DISCUSSION

3.1. Characterization. 3.1.1. X-ray Powder Diffraction.

The synthesis of the ED-MIL-101 through the coordination of ethylenediamine to the unsaturated metal centers of the dehydrated MIL-101 framework was performed in anhydrous toluene under magnetic stirring. The XRD patterns of MIL-101, Pb/MIL-101, ED-MIL-101(2 mmol), ED-MIL-101(5 mmol), Pb/ED-MIL-101(5 mmol), and ED-MIL-101(10 mmol) are shown in Figure 2. The crystal structure of the

Figure 2. XRD patterns of as-synthesized and surface functional MIL-101: (a) MIL-101; (b) Pb/MIL-101; (c) ED-MIL-101(2 mmol); (d) ED-MIL-101(5 mmol); (e) Pb/ED-MIL-101(5 mmol); and (f) ED-MIL-101(10 mmol).

synthesized materials has been confirmed to be MIL-101 because the characteristic peaks of MIL-101 were obtained at 2.95°, 3.40°, 5.5°, 8.55°, and 9.15°, and the XRD patterns of the synthesized MIL-101 (see Figure 2a) matches with the reported.^{3,27,34} After the grafting of ED, the characteristic peaks of MIL-101 remained in the XRD patterns of ED-MIL-101(2 mmol) and ED-MIL-101(5 mmol), but we observed minor changes in the XRD peak intensities (see Figure 2a,c,d). Moreover, compared with the MIL-101 and ED-MIL-101(5 mmol), the Pb/MIL-101 and Pb/ED-MIL-101(5 mmol) are almost exactly the same (see Figure 2a,b,d,e). These results indicate that the crystal structures of MIL-101 and ED-MIL-101 remain conspicuously intact after adsorption of Pb(II) ions. For ED-MIL-101(10 mmol), the modification of MIL-101 with excessive ED resulted in the characteristic peaks of MIL-101 not appearing in the XRD pattern (see Figure 2d). This may be due to the destruction of the crystalline order of the framework or the decomposition of crystalline MIL-101.

3.1.2. FTIR Analysis. Figure 3 shows the results of FTIR spectra of MIL-101, ED-MIL-101(2 mmol), ED-MIL-101(5 mmol), and ED-MIL-101(10 mmol). For ED-MIL-101, peaks at 1581 and 1051 cm^{-1} can be assigned to the N–H plane stretching and C–N bond stretching, respectively.^{35,36} Moreover, the peak at 882 cm^{-1} can correspond to the $-\text{NH}_2$ stretching frequency.³⁷ In addition, the broad band from 3434 cm^{-1} to 3231 cm^{-1} is located at $-\text{NH}$ stretching.³ These above results indicate that ED has been grafted on MIL-101.

3.1.3. SEM and TEM Analysis. To investigate the surface morphology and the microstructure of the functionalized samples, the amine-functionalized samples were characterized by scanning electron microscopy (see Figure 4) and transmission electron microscopy (see Figure 5). From Figure 4a,

Figure 3. FTIR patterns of as-synthesized and surface functional MIL-101: (a) MIL-101; (b) ED-MIL-101(2 mmol); (c) ED-MIL-101(5 mmol); and (d) ED-MIL-101(10 mmol).

Figure 5a, and Figure 5b, it can be seen that the MIL-101 possesses typical octahedral structure. After modification with ED, the surfaces of the amine-modified samples ED-MIL-101(2 mmol) and ED-MIL-101(5 mmol) tend to be rougher (see Figure 4b,c and Figure 5c,d). Combined with analysis of XRD and FTIR, these results show that ED has been grafted on the surface of MIL-101. As shown in Figure 4d, because of modification of MIL-101 with excessive ED, the crystal structure of MIL-101 has been destroyed. The result is in conformity with the consequences of FTIR and XRD analysis.

3.1.4. XPS Analysis. The XPS has been used to investigate the element categories of the samples. Figure 6a shows the results of the XPS spectrum of Pb/MIL-101 and Pb/ED-MIL-101(5 mmol). The Pb/MIL-101 and Pb/ED-MIL-101(5 mmol) composites are mainly composed of Cr, O, C, and Pb elements. Cr, O, and C elements are ascribed to the MIL-101.²⁷ In addition, the N element is discovered in Pb/ED-MIL-101(5 mmol), indicating that ED has been successfully grafted on MIL-101. The relative peak intensity of Pb(II) adsorbed on ED-MIL-101(5 mmol) is much higher than MIL-101, which confirms that the ED-MIL-101 adsorption capacity is superior to that of MIL-101 in the removal of Pb(II) ions. As shown in Figure 6b, the Cr 2p energy peaks at 586.96 eV and 577.47 eV for Pb/MIL-101, 586.90 eV and 577.29 eV for Pb/ED-MIL-101(5 mmol), respectively, are similar to the results in the literature.³⁸ The energy peaks at 531.85 eV and 531.61 eV correspond to the O 1s for Pb/MIL-101 and Pb/ED-MIL-101(5 mmol), respectively³⁹ (see Figure 6c). C 1s, at 288.60 eV and 284.76 eV for Pb/MIL-101, 288.71 eV and 284.79 eV for Pb/ED-MIL-101(5 mmol), respectively, are located at the organic components within MIL-101⁴⁰ (see Figure 6d). Figure 6e shows the results of XPS spectra of Pb 4f for Pb/MIL-101 and Pb/ED-MIL-101(5 mmol). The higher energy peaks at 143.95 eV for Pb/MIL-101 and 143.69 eV for Pb/ED-MIL-101(5 mmol) can correspond to Pb 4f_{5/2}, and the lower energy peaks at 138.90 eV for Pb/MIL-101 and 138.84 eV for Pb/ED-MIL-101(5 mmol) are located at Pb 4f_{7/2}.⁴¹ According to the literature,⁴² in Figure 6f, the lower energy peak locates at 399.90 eV (N1) corresponding to the $-\text{NH}_2$, N2 (400.69 eV) due to the chelation of $-\text{NH}_2$ group for Pb(II) ions, which helps to explain why ED-MIL-101(5 mmol) has more excellent adsorption capacity than MIL-101.

Figure 4. SEM images of as-synthesized and surface functional MIL-101: (a) MIL-101, (b) ED-MIL-101(2 mmol); (c) ED-MIL-101(5 mmol); and (d) ED-MIL-101(10 mmol).

Figure 5. TEM images of as-synthesized and surface functional MIL-101: (a and b) MIL-101; (c and d) ED-MIL-101(5 mmol).

3.1.5. N_2 Adsorption–Desorption Isotherms. The BET surface area measurement was performed with N_2 adsorption–desorption isotherms at 77 K. The N_2 adsorption–desorption isotherms of the MIL-101 and ED-MIL-101 samples reveal a typical microporous material (see Figure 7). Compared with the pristine MIL-101, the ED-MIL-101 samples have a rapid decrease in both surface areas and pore volumes (see Table 1).

The BET surface areas of ED-MIL-101(2 mmol) and ED-MIL-101(5 mmol) decreased obviously from $2290 \text{ m}^2 \cdot \text{g}^{-1}$ to $1270 \text{ m}^2 \cdot \text{g}^{-1}$ and $347 \text{ m}^2 \cdot \text{g}^{-1}$, Langmuir surface area decreased from $3691 \text{ m}^2 \cdot \text{g}^{-1}$ to $2056 \text{ m}^2 \cdot \text{g}^{-1}$ and $566 \text{ m}^2 \cdot \text{g}^{-1}$, and pore volumes decreased from $1.4 \text{ cm}^3 \cdot \text{g}^{-1}$ to $0.74 \text{ cm}^3 \cdot \text{g}^{-1}$ and $0.28 \text{ cm}^3 \cdot \text{g}^{-1}$, respectively. The decrease in the porosity is probably due to the extra volumes of the organic moieties used for the modification, and the pores of the MIL-101 are partially blocked after amine-grafting, leaving limited accessible pore volume.

3.2. Adsorption Experiments. 3.2.1. The Influence of pH.

The adsorption curves of Pb(II) are shown in Figure 8. It can be observed that the adsorption capacity of MIL-101 and ED-MIL-101(5 mmol) for Pb(II) ions increases with the increase of solution pH from 2 to 6, and the rate of increase in adsorption capacity of ED-MIL-101(5 mmol) is much higher than that of MIL-101 for Pb(II) ions. It results from the fact that some of the free carboxyl groups on the MIL-101 can easily lose hydrogen ions and provide the chelating binding sites for Pb(II) ions. However, for the ED-MIL-101, the amino groups modified on the pore surface of MIL-101 also afford the chelating binding sites for the adsorption of Pb(II) ions, except for the original free carboxyl groups, which result in a much higher rate of increase in adsorption capacity of ED-MIL-101(5 mmol) than of MIL-101. The initial and final pH values of the solution of Pb(II) adsorption are shown in Table 2. From Table 2, it can be observed that the change of pH values using MIL-101 is higher than that using ED-MIL-101(5 mmol). The results verified further that there are more chelating binding sites in ED-MIL-101(5 mmol) than in MIL-101. When the solution $\text{pH} < 4$, a large amount of H^+ can coordinate with the ionized carboxyl of MIL-101 and the amino groups of ED-MIL-101. The adsorption capacity of MIL-101 and ED-MIL-101(5 mmol) is very low as pH values of the solution increase

Figure 6. XPS spectra for (a) Pb/MIL-101 and Pb/ED-MIL-101(5 mmol); (b) Cr 2p, (c) O 1s, (d) C 1s, and (e) Pb 4f of Pb/MIL-101 and Pb/ED-MIL-101(5 mmol); (f) N 1s of Pb/ED-MIL-101(5 mmol).

Figure 7. N₂ adsorption/desorption isotherms of the as-synthesized (a) MIL-101, (b) ED-MIL-101(2 mmol) and (c) ED-MIL-101(5 mmol).

indicating the decrease of the concentration of H⁺, which is due to a large amount of H⁺ competing with Pb(II) ions and the protonation of the amino group moieties. The adsorption of

Pb(II) ions on MIL-101 and ED-MIL-101(5 mmol) increased substantially from pH 4 to 6. The main reason is that the protonation of carboxyl groups and amino groups are relatively weakened and most of them chelate Pb(II) ions. When the solution pH > 6, the adsorption capacity of MIL-101 and ED-MIL-101(5 mmol) decreases, which may be due to the predominance of hydrolysis products of Pb(II) ions over the adsorption of MIL-101 and ED-MIL-101(5 mmol) for Pb(II) ions. Therefore, the pH of solution should be adjusted to 6 to obtain the optimal adsorption efficiency.

3.2.2. Adsorption Isotherms. Figure 9 shows the adsorption isotherms of Pb(II) ions adsorption on MIL-101, ED-MIL-101(2 mmol), and ED-MIL-101(5 mmol) at pH 6. Because the structures of ED-MIL-101(10 mmol) have been destroyed, we choose the MIL-101, ED-MIL-101(2 mmol), and ED-MIL-101(5 mmol) for Pb(II) adsorption. The standard deviation bars are derived from three times repeated experiments. It can be seen that the equilibrium adsorption capacities of ED-MIL-101(2 mmol) and ED-MIL-101(5 mmol) for Pb(II) increased rapidly in a low concentration range, then increased slowly, and finally achieved a maximum equilibrium adsorption capacity. The maximum adsorption capacities of MIL-101, ED-MIL-

Table 1. Textural Properties of MIL-101 and ED-MIL-101 Samples

samples	BET surface area (m ² ·g ⁻¹)	Langmuir surface area (m ² ·g ⁻¹)	total pore volume (cm ³ ·g ⁻¹)
MIL-101	2290	3691	1.40
ED-MIL-101(2 mmol)	1270	2056	0.74
ED-MIL-101(5 mmol)	347	566	0.28

Figure 8. Effect of pH on the adsorption capacity of MIL-101 and ED-MIL-101(5 mmol) for Pb(II) ions.

Table 2. Initial and Final pH Values of the Solution of Pb(II) Adsorption on MIL-101 and ED-MIL-101

sorbents	pH values					
blank	1.96	2.88	3.99	4.66	5.70	6.76
MIL-101	2.01	2.90	3.92	4.57	5.52	6.50
ED-MIL-101 (5 mmol)	2.10	3.95	5.51	5.88	6.21	6.57

Figure 9. Adsorption isotherms for Pb(II) adsorption on MIL-101, ED-MIL-101(2 mmol), and ED-MIL-101(5 mmol).

101(2 mmol) and ED-MIL-101(5 mmol) are 15.78 mg·g⁻¹, 25.59 mg·g⁻¹, and 81.09 mg·g⁻¹, respectively, indicating that ED-MIL-101(5 mmol) has a stronger affinity and more adsorption sites for Pb(II) ions than MIL-101 or ED-MIL-101(2 mmol).

In this paper, Langmuir and Freundlich models were used to fit the adsorption process for describing the Pb(II) ion distribution between the liquid and adsorbent phase and achieving the maximum adsorption uptake. The Langmuir and Freundlich isotherms are represented, respectively, by^{43–45}

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m} \quad (4)$$

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

where Q_m (mg·g⁻¹) represents the maximum adsorption capacity, K_L (L·mg⁻¹) is the Langmuir constant that represents the affinity between solute and adsorbent, and n and K_F (mg^{(1 - (1/n))}·L^(1/n)·g⁻¹) are Freundlich constants related to the adsorption capacity and intensity, respectively.

Table 3 displays the fitting results for the adsorption of Pb(II) ions on MIL-101, ED-MIL-101(2 mmol), and ED-MIL-101(5 mmol) (see Figure 10 and Figure 11). According to the

Figure 10. Langmuir isotherms for Pb(II) adsorption on MIL-101, ED-MIL-101(2 mmol), and ED-MIL-101(5 mmol).

values of correlation coefficients (R^2), the Langmuir model is more suitable than the Freundlich model for describing the adsorption process, indicating that the adsorption of Pb(II) ions on MIL-101, ED-MIL-101(2 mmol), and ED-MIL-101(5 mmol) is uniform. Moreover, the calculated values of Q_m are found to be 15.70 mg·g⁻¹, 29.33 mg·g⁻¹, and 87.64 mg·g⁻¹ for MIL-101, ED-MIL-101(2 mmol), and ED-MIL-101(5 mmol), respectively, which are very close to the experimental values of

Table 3. Langmuir and Freundlich Isotherm Constants of Pb(II) Adsorption on MIL-101 and ED-MIL-101

sorbents	Langmuir model			Freundlich model		
	Q_m	K_L	R^2	n	K_F	R^2
	mg·g ⁻¹	L·mg ⁻¹		mg ^{(1 - (1/n))} ·L ^(1/n) ·g ⁻¹	mg ^{(1 - (1/n))} ·L ^(1/n) ·g ⁻¹	
MIL-101	15.70	0.0543	0.992	10.11	8.253	0.774
ED-MIL-101(2 mmol)	29.33	0.0092	0.979	2.278	1.643	0.917
ED-MIL-101(5 mmol)	87.64	0.0201	0.997	2.669	8.742	0.945

Figure 11. Freundlich isotherms for Pb(II) adsorption on MIL-101, ED-MIL-101(2 mmol), and ED-MIL-101(5 mmol).

Q_m . As shown in Table 4, the adsorption capacity of ED-MIL-101(5 mmol) is significantly higher than those reported in the literature.^{21–25}

To further investigate the procedure of Pb(II) ions adsorption onto MIL-101 and ED-MIL-101, a Dubinin–Radushkevich (D-R) isotherm model is applied for analyzing the adsorption energy to decide the nature of adsorption process as physical or chemical. The Dubinin–Radushkevich equation is expressed by the following equation:^{46,47}

$$\ln Q_e = \ln Q_m - K\varepsilon^2 \quad (6)$$

where Q_e ($\text{mol}\cdot\text{g}^{-1}$) and Q_m ($\text{mol}\cdot\text{g}^{-1}$) is the equilibrium and theoretical saturation capacity, respectively, K ($\text{mol}^2\cdot\text{kJ}^{-2}$) is the activity coefficient related to mean free energy of adsorption, and ε ($\text{kJ}\cdot\text{mol}^{-1}$) is the Polanyi potential:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (7)$$

where R is universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), T (K) is Kelvin temperature and C_e ($\text{mol}\cdot\text{L}^{-1}$) is the equilibrium concentration. The D-R model is mainly used to estimate the average free energy of adsorption E ($\text{kJ}\cdot\text{mol}^{-1}$), which is expressed using the following equation:

$$E = \frac{1}{\sqrt{2K}} \quad (8)$$

The parameters for the D-R model are shown in Table 5. The correlation coefficients (R^2) of MIL-101, ED-MIL-101(2 mmol), and ED-MIL-101(5 mmol) from the D-R model are 0.798, 0.934, and 0.970, respectively, revealing that the experimental data of Pb(II) adsorption on ED-MIL-101 fit well with the D-R isotherm model. Moreover, when the value of E is below $8 \text{ kJ}\cdot\text{mol}^{-1}$, the adsorption process can be considered a physical adsorption, otherwise it belongs to the

Table 5. Dubinin–Radushkevich (D-R) Isotherm Model Constants of Pb(II) Adsorption on MIL-101 and ED-MIL-101

sorbents	Dubinin–Radushkevich (D-R) isotherm model			
	Q_m $\text{mol}\cdot\text{kg}^{-1}$	K $\text{mol}^2\cdot\text{kJ}^{-2}$	E $\text{kJ}\cdot\text{mol}^{-1}$	R^2
MIL-101	0.094	0.0011	21.457	0.798
ED-MIL-101(2 mmol)	0.362	0.0049	10.067	0.934
ED-MIL-101(5 mmol)	1.019	0.0040	11.249	0.970

chemical adsorption group.^{46,47} From Table 5, the mean free energy of adsorption (E) values according to the D-R model are higher than $8 \text{ kJ}\cdot\text{mol}^{-1}$ for adsorption of Pb(II) ions, which indicates that the effect of chemical adsorption will play a dominating role in the adsorption process of Pb(II) ions onto the ED-MIL-101.

3.2.3. Adsorption Kinetics. Figure 12 shows the time dependence of binding amounts of Pb(II) ions on MIL-101,

Figure 12. Adsorption kinetics for Pb(II) adsorption on MIL-101, ED-MIL-101(2 mmol), and ED-MIL-101(5 mmol).

ED-MIL-101(2 mmol), and ED-MIL-101(5 mmol). The standard deviation bars are derived from three times repeated experiments. As shown in Figure 12, the adsorption amounts of Pb(II) ions on MIL-101, ED-MIL-101(2 mmol), and ED-MIL-101(5 mmol) increase sharply during the first 15 min and then level off as equilibrium is achieved. For ED-MIL-101(2 mmol) and ED-MIL-101(5 mmol) toward Pb(II), the higher adsorption rate at the beginning can be attributed to the sufficient adsorption sites, strong chelation, the good affinity of the amino groups, and geometric matching between Pb(II) ions and the ED-MIL-101. In other words, the ED-MIL-101(5 mmol) possesses the optimal adsorption sites, chelation, affinity, and geometric matching among them.

For further investigation of the mechanism of the adsorption kinetics, the pseudo-first-order and pseudo-second-order rate

Table 4. Comparison of the Maximum Adsorption Capacities for Pb(II) Ions of Different Adsorbents

sorbents	maximum adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$)	equilibrium time (min)	ref
Pb(II) ion-imprinted crown ether	28.5	60	21
turkish kaolinite clay	31.75	30	22
lead-ion imprinted polymers	39.0		23
expanded perlite	13.39	60	24
treated granular activated carbon	29.44		25
ED-MIL-101(5 mmol)	81.09	30	this study

Table 6. Pseudo-First-Order Kinetics and the Pseudo-Second-Order Kinetics Isotherm Constants of Pb(II) Adsorption on MIL-101 and ED-MIL-101

sorbents	pseudo-first-order kinetics			pseudo-second-order kinetics			
	K_1	Q_e	R^2	K_2	Q_e	h_0	R^2
	min^{-1}	$\text{mg}\cdot\text{g}^{-1}$		$\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$	$\text{mg}\cdot\text{g}^{-1}$	$\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$	
MIL-101	0.0174	2.716	0.272	0.0272	13.29	4.796	0.996
ED-MIL-101(2 mmol)	0.0152	6.112	0.612	0.0162	27.98	12.71	0.999
ED-MIL-101(5 mmol)	0.0160	21.707	0.852	0.0043	70.42	21.54	0.998

equations have been applied to describe the adsorption kinetics of Pb(II) ions on MIL-101, ED-MIL-101(2 mmol), and ED-MIL-101(5 mmol). The linearized form of the pseudo-first-order and pseudo-second-order rate equations are given as follows:^{21,48}

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \quad (9)$$

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \quad (10)$$

$$h_0 = K_2 Q_e^2 \quad (11)$$

where Q_t ($\text{mg}\cdot\text{g}^{-1}$) is the amount of adsorbate at any time, Q_e ($\text{mg}\cdot\text{g}^{-1}$) is the amount of adsorbate at equilibrium, K_1 (min^{-1}) is the pseudo-first-order rate constant, K_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$) is the pseudo-second-order constant, and h_0 ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$) is the initial adsorption rate.

Table 6 has summarized the adsorption kinetic constants and regression coefficients. It is clear that pseudo-first-order models are not suitable to describe the kinetic profile because of the apparent lack of linear behavior. Conversely, the correlation coefficients (R^2) of MIL-101, ED-MIL-101(2 mmol), and ED-MIL-101(5 mmol) from the pseudo-second-order kinetic model are 0.996, 0.999, and 0.998, respectively (see Figure 13). The theoretical Q_e value estimated from the pseudo-

Figure 13. Pseudo-second-order kinetics isotherms for Pb(II) adsorption on MIL-101, ED-MIL-101(2 mmol), and ED-MIL-101(5 mmol).

second-order kinetic model is close to the experimental value. In addition, the initial adsorption rates h_0 are on the order of $\text{ED-MIL-101(5 mmol)} > \text{ED-MIL-101(2 mmol)} > \text{MIL-101}$. These results indicate that the pseudo-second-order mechanism is predominant. The adsorption capacity of adsorbent is proportional to the number of active sites on its surface, and chemisorption may be the rate-limiting step controlling the adsorption process.

3.2.4. Adsorption Selectivity. Ni(II), Co(II), Zn(II), and Cu(II) have been chosen as competitor ions due to the same charge to Pb(II) ions. The radii of Pb(II), Ni(II), Co(II), Zn(II), and Cu(II) ions are 0.119 nm, 0.069 nm, 0.075 nm, 0.074 nm, and 0.073 nm, respectively. The adsorption capacities of Pb(II), Ni(II), Co(II), Zn(II), and Cu(II) ions by MIL-101 and ED-MIL-101 are shown in Figure 14. It can be

Figure 14. Selectivity of MIL-101, ED-MIL-101(2 mmol), and ED-MIL-101(5 mmol).

observed that the ED-MIL-101 exhibits higher adsorption capacities for Pb(II), Cu(II), and Ni(II) than the other ions. This phenomenon can be explained by the complexation constants of EDTA with metal ions (18.80 for Cu(II), 18.62 for Ni(II), 18.04 for Pb(II), 16.50 for Zn(II), and 16.31 for Co(II)). Although the complexation constant of amines with Pb(II) is narrowly smaller than that of Cu(II) and Ni(II), the radius of Pb(II) is much larger than that of Cu(II) and Ni(II), and therefore the special pore structure of MIL-101 with the appropriate ED grafted groups can coordinate with Pb(II) ions more effectively, which leads to the higher adsorption capacity for Pb(II) than for the other ions. Static distribution coefficients and selectivity coefficients are summarized in Table 7. As shown in Table 7, we observe that the selectivity coefficients of ED-MIL-101(5 mmol) for Pb(II) ions with

Table 7. Selectivity Parameter for MIL-101 and ED-MIL-101

metal ions	MIL-101		ED-MIL-101 (2 mmol)		ED-MIL-101 (5 mmol)	
	K_D	α	K_D	α	K_D	α
Pb(II)	0.319		0.296		1.177	
Cu(II)	0.072	4.431	0.100	2.960	0.170	6.92
Zn(II)	0.046	6.935	0.034	8.705	0.049	24.02
Co(II)	0.065	4.908	0.036	8.222	0.075	15.69
Ni(II)	0.036	8.861	0.063	4.698	0.081	14.53

respect to Cu(II), Zn(II), Co(II), and Ni(II) are about 6.92, 24.02, 15.69, and 14.53, respectively, which is higher than that of MIL-101 and ED-MIL-101(2 mmol). It can indicate a higher adsorptive removal ability of ED-MIL-101(5 mmol) for Pb(II) ions with respect to the competing ions. These above results imply that special pore structure of MIL-101 with the appropriate ED grafted groups and specific binding sites for Pb(II) ions have been formed in ED-MIL-101, and the $-NH_2$ groups, which are coordinated with metal ions in ED-MIL-101, are not able to match well with Ni(II), Co(II), Zn(II), and Cu(II) ions resulting in a high recognition ability and high selectivity of ED-MIL-101 for Pb(II) ions.

3.2.5. Application of ED-MIL-101. To validate the applicability of ED-MIL-101 in removing Pb(II) ions from real environmental water samples, lake water (Tianyi Lake, Nanchang) and river water (Ganjiang River, Nanchang) were selected and analyzed. The lake water and river water were spiked with $10 \text{ mg} \cdot \text{L}^{-1}$ of Pb(II) ions, and 50 mL water samples were treated with 50 mg of ED-MIL-101(5 mmol) at an initial pH of 6 for 6 h. The concentration of Pb(II) ions in the Tianyi Lake and Ganjiang River after adsorption was $0.49 \text{ mg} \cdot \text{L}^{-1}$ and $0.28 \text{ mg} \cdot \text{L}^{-1}$, which meets with the standards of the Emission Standard of Pollutants for Lead and Zinc Industry (GB25466–2010), respectively. The results suggest ED-MIL-101 has a strong anti-interference ability in real environmental water samples.

3.2.6. Reusability of ED-MIL-101. In addition to high adsorption capacity, it was highly desirable that an adsorbent could be reused repeatedly. The regeneration capacity of the ED-MIL-101(5 mmol) was evaluated by EDTA-2Na. A 50 mg sample of Pb/ED-MIL-101 complex was treated with 100 mL of a 0.05 M EDTA solution for three times, under stirring for 2 h at 298 K, respectively. The ED-MIL-101(5 mmol) was reused in four successive adsorption–desorption cycles, and the results are illustrated in Figure 15. It can be seen that the adsorption

Figure 15. Reusability of ED-MIL-101(5 mmol).

capacity of MIL-101(5 mmol) was stable within the first two cycles without an obvious decrease in the adsorption capacity for Pb(II) ions. However, the adsorption capacity of MIL-101(5 mmol) showed about 14 % and 52 % loss in the third and fourth cycle, respectively. These data indicated the good regeneration capacity of the ED-MIL-101.

4. CONCLUSIONS

In summary, this study reveals for the first time a facile strategy to fabricate amine-grafted MIL-101 as a novel adsorbent for selective removal of Pb(II) ions from aqueous samples. Different amounts of ED are used as the amine functional group and successfully coordinated on unsaturated sites of MIL-101 by a postsynthetic modification technique. The structures, morphologies, and porosity of MIL-101 and ED-MIL-101 samples have been characterized, and ED-MIL-101 demonstrates a much higher adsorption capacity than MIL-101 in removing Pb(II) ions from aqueous solution. The isotherms of Pb(II) ions adsorption on MIL-101 and ED-MIL-101 can be well described by the Langmuir isotherms equation, and the adsorption kinetics of Pb(II) ions can be well-fitted with the pseudo-second-order model. The maximum adsorption capacities of MIL-101 and ED-MIL-101(5 mmol) are $15.78 \text{ mg} \cdot \text{g}^{-1}$ and $81.09 \text{ mg} \cdot \text{g}^{-1}$ for Pb(II) ions, respectively. Competitive adsorption studies exhibit that ED-MIL-101 has a high selectivity for Pb(II) ions. Moreover, the removal efficiency based on the application of ED-MIL-101 for the removal of Pb(II) ions achieves almost 97.22 %, indicating that the ED-MIL-101, as a novel type of adsorbents, is beneficial for the selective removal of the Pb(II) ions from a watery environment.

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Notes

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