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Enhanced Cadmium(II) Adsorption by Poly(glycidyl methacrylate) Microspheres Modified with Two Layers of Di(2-ethylhexyl)dithiophosphoric Acid

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Enhanced Cadmium(II) Adsorption by Poly(glycidyl methacrylate) Microspheres Modified with Two Layers of Di(2-ethylhexyl)dithiophosphoric Acid

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Running title: Selective Cd(II) Removal by D2EHDTPA-Modified PGMA

ABSTRACT

Poly(glycidyl methacrylate) (PGMA) microspheres were modified with two layers of di(2-ethylhexyl)dithiophosphoric acid (D2EHDTPA) through a sequential ring-opening reaction and hydrophobic impregnation, and the resulting adsorbent (PGMA-D2EHDTPA) was applied to the selective removal of Cd(II) from aqueous solutions. The adsorbent was characterized by scanning electron microscopy (SEM), Fourier-transform infrared (FT-IR) spectroscopy and N_2 adsorption measurements, and the D2EHDTPA loading reached 1.029 mmol/g. Batch experiments examined the effects of pH, initial concentration, contact time and adsorbent dose on Cd(II) adsorption in the presence of Zn(II). PGMA-D2EHDTPA adsorbed Cd(II) efficiently over pH 3.0–7.0, with a maximum uptake of 59.33 mg/g (0.528 mmol/g) at pH 7.0, corresponding to a D2EHDTPA/Cd(II) molar ratio of about 2:1. The Cd/Zn separation factor exceeded 80 over the whole pH range and reached 330, indicating a strong preference for Cd(II) over Zn(II). The loaded adsorbent was regenerated with 6 mol/L HCl and retained 90% of its initial capacity after six cycles. FT-IR analysis showed that Cd(II) and Zn(II) bind through cation exchange of the S–H group and coordination with the P=S group, D2EHDTPA having a stronger affinity for Cd(II). Compared with solvent extraction, this adsorbent markedly reduces organic extractant consumption and operates under milder conditions, showing promise for selective cadmium recovery from contaminated water.

Keywords Cd(II) · Poly(glycidyl methacrylate) · Di(2-ethylhexyl)dithiophosphoric acid · Selective adsorption · Cd/Zn separation

1 Introduction

Heavy metal pollution in water bodies has emerged as a critical environmental concern due to its detrimental

effects on ecosystems and human health [1]. Cadmium (Cd), widely utilized in industries such as Ni-Cd batteries, metal plating, pigments, and plastics, is particularly concerning owing to its non-biodegradability and high carcinogenicity [2]. Exposure to cadmium can severely damage vital organs including the kidneys, liver, and lungs, and adversely affect the cardiovascular, immune, and reproductive systems [3, 4]. With increasingly stringent environmental regulations, there is a pressing need for efficient and selective techniques to recover cadmium from wastewater prior to discharge.

Numerous methods, including electrochemical treatment [5], solvent extraction [6], chemical precipitation [7], membrane process [8], ion exchange [9], and adsorption [10], have been employed for heavy metal removal. Among these, adsorption stands out as a promising technique due to its operational simplicity, minimal sludge production, and potential for adsorbent regeneration [11].

Various adsorbents including carbon-based adsorbents [2], minerals [12], agricultural wastes [13], polymeric adsorbents [14], and composite materials [15] have been explored for Cd(II) removal. However, achieving high selectivity for Cd(II) over other coexisting metal ions, particularly Zn(II), remains a challenge [16–20].

Di(2-ethylhexyl)dithiophosphoric acid (D2EHDTPA) plays an important role in hydrometallurgical processes because it forms various heavy metal complexes characterized by very high values of the extraction constants [21]. Previous works demonstrated its high selectivity for Cd(II) [21, 22].

In this work, we innovatively modified poly(glycidyl methacrylate) (PGMA) microspheres with two layers of D2EHDTPA to enhance their selectivity and capacity for Cd(II) adsorption. The obtained adsorbent, PGMA-D2EHDTPA, was applied for the selective removal of Cd(II). The effects of pH, initial metal ions concentration, and contact time on the adsorption capacity of PGMA-D2EHDTPA were investigated in batch experiments. The adsorption mechanism and the Cd/Zn selectivity were also studied.

2 Experimental

2.1 Materials

Glycidyl methacrylate (GMA), trimethylolpropane trimethacrylate (TRIM) and polyvinylpyrrolidone (PVP, K-30, Mw = 40,000) were purchased from Sigma-Aldrich Corp. Ltd. (St. Louis, MO, USA). Isooctanol, phosphorus pentasulfide (P2S5) and n-hexane were of analytical grade and obtained from Xilong Chemical Industry Co. Ltd. (Shantou, China). Cadmium sulfate octahydrate ($CdSO_4 \cdot 8H_2O$, ≥ 99.0%), zinc sulfate ($ZnSO_4$, ≥ 99.0%), toluene, triethylamine (TEA) and 2,2′-azobisisobutyronitrile (AIBN) were supplied by Sinopharm Chemical Reagent Co. Ltd. (Beijing, China). D2EHDTPA was synthesized in our laboratory from isooctanol and P2S5 as described in Sect. 2.2. All other reagents, including ethanol, hydrochloric acid and sodium hydroxide, were of analytical grade and used as

received. Deionized water was used throughout the experiments.

2.2 Preparation of PGMA-D2EHDTPA microspheres

The synthesis route of PGMA-D2EHDTPA microspheres is depicted in Fig. 1. Initially, PGMA microspheres were synthesized via suspension polymerization of GMA and TRIM using toluene as a porogen [23]. Subsequently, D2EHDTPA was grafted onto the microspheres through a ring-opening reaction between the epoxy groups of GMA and the sulfhydryl groups of D2EHDTPA [24], followed by impregnation of a second layer of D2EHDTPA via hydrophobic interactions [25].

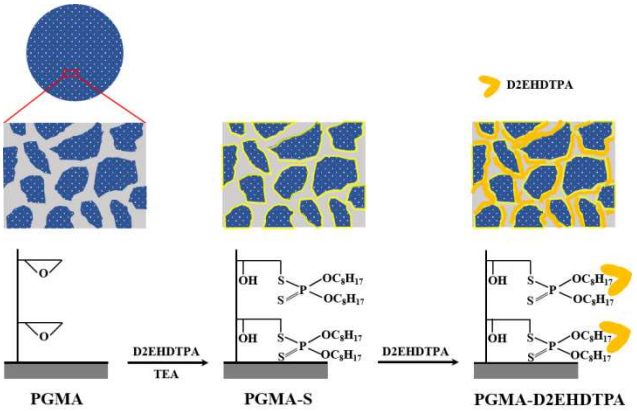


Fig. 1 Synthesis route of PGMA-D2EHDTPA microspheres

D2EHDTPA was synthesized and purified according to the procedures described in previous literature [24]. The chemical equation follows as:

$$4ROH + P_2S_5 = 2(RO)_2PSSH + H_2S \quad (1)$$

where ROH represents isooctanol, and $(RO)_2PSSH$ represents D2EHDTPA.

2.3 Characterization of PGMA-D2EHDTPA microspheres

The FT-IR spectra of the samples were recorded using a FT-IR spectrophotometer (Bruker T27, Germany). Morphological analysis was performed using scanning electron microscopy (SEM, JEOL JSM-6700F, Japan). The pore size distribution of PGMA microspheres was determined by the BET adsorption method (Quantachrome Autosorb-1-C-TCD, USA).

The capacity of physically immobilized D2EHDTPA in PGMA-D2EHDTPA microspheres was measured using a volumetric method as follows [26]: 100 mg of PGMA-D2EHDTPA microspheres were dispersed in ethanol and incubated at room temperature for 1 h in an air bath shaker at 150 r/min. Subsequently, the microspheres were separated from the ethanol and the ethanol was then transferred into a 50-mL volumetric flask. The separated microspheres were washed three times with ethanol and the ethanol was also transferred into the volumetric flask. Additional ethanol was added to the flask to reach the mark. The concentration of D2EHDTPA in the volumetric flask was titrated with a

standard ethanol solution of NaOH. This titration was repeated at least three times and the data were averaged. The capacity of D2EHDTPA (mmol/g) was calculated using the following equation:

$$Capacity\ of\ D2EHDTPA = 50C_{NaOH}V_{NaOH}/0.1V_{D2EHDTPA} \quad (2)$$

2.4 Batch adsorption experiments

The adsorption performance of PGMA-D2EHDTPA microspheres for Cd(II) and/or Zn(II) was evaluated in batch mode. The equilibrium adsorption capacity was calculated based on the initial and equilibrium concentrations of metal ions, determined using an inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin Elmer Optima 7000DV, USA). The equilibrium adsorption capacity (q_e, mg/g) was calculated using the following equation:

$$q_e = V(C_0 - C_e)/m \quad (3)$$

where C_0(mg/L) and C_e(mg/L) are the initial and equilibrium Cd(II) concentrations in the aqueous solution; V(mL) is the volume of the solution and m(mg) is the adsorbent dose.

3 Results and discussion

3.1 Characterization of the adsorbents

The SEM images of PGMA, PGMA-S and PGMA-D2EHDTPA microspheres are shown in Fig. 2. As illustrated in Fig. 2(A), the microspheres exhibit a standard spherical form and a range of sizes. Additional details about the surface of PGMA, PGMA-S and PGMA-D2EHDTPA microspheres are provided in Fig. 2(B), Fig. 2(C) and Fig. 2(D), respectively. It can be observed that D2EHDTPA treatment results in a smoother surface.

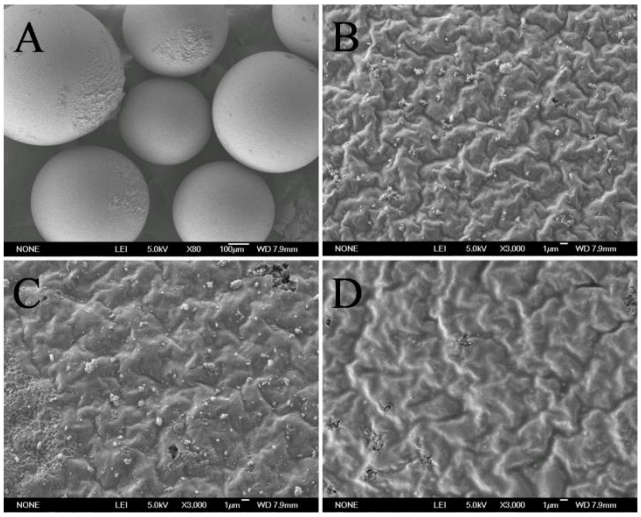


Fig. 2 SEM images of the microspheres: (A) and (B) PGMA, (C) PGMA-S, (D) PGMA-D2EHDTPA

Photographs of PGMA, PGMA-S, and PGMA-D2EHDTPA microspheres in water are shown in Fig. 3. PGMA,

PGMA-S, and PGMA-D2EHDTPA microspheres were hydrophilic, hydrophobic and hydrophilic, respectively. The impregnated extractants in the PGMA-D2EHDTPA microspheres orient their hydrophilic functional groups towards the aqueous solutions [27].

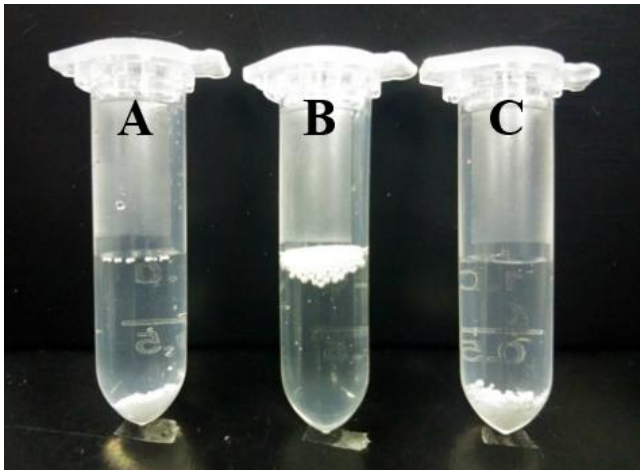


Fig. 3 Photos of the microspheres: (A) PGMA, (B) PGMA-S, (C) PGMA-D2EHDTPA in water

Nitrogen adsorption was used to determine the pore size distribution of PGMA microspheres. The pore size distribution of PGMA microspheres is relatively wide, ranging from 3 to 55 nm, as shown in Fig. 4

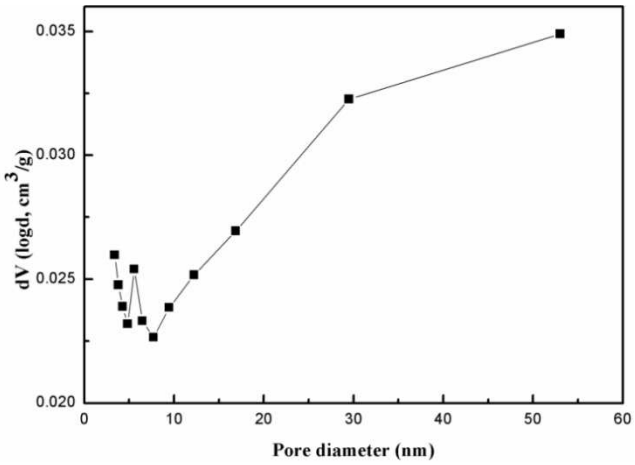


Fig. 4 The pore size distribution of PGMA microspheres

The FT-IR spectrum of D2EHDTPA is shown in Fig. 5. The strong band at 672 cm^{-1} represents P=S vibrations [21]. The bands in the range of 2600 to 2400 cm^{-1} are attributed to the stretching vibrations of (P)-S-H bonds in monomeric D2EHDTPA [21]. Dialkyldithiophosphates are primarily extracted as monomeric compounds, but some of them are associated in the organic phase [21].

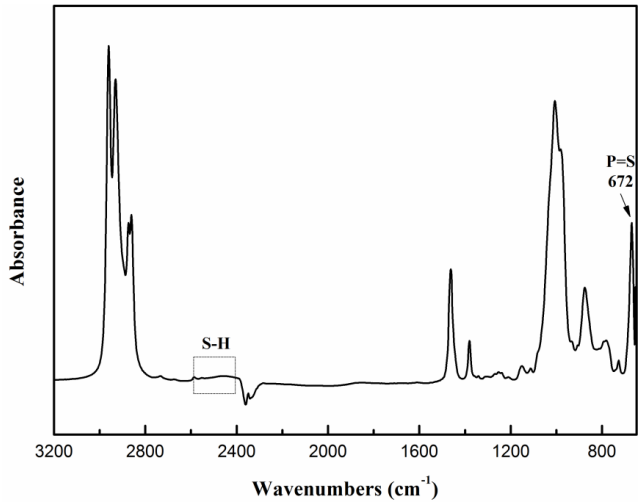


Fig. 5 FT-IR spectrum of synthesized D2EHDTPA

The FT-IR spectra of PGMA, PGMA-S, and PGMA-D2EHDTPA microspheres are shown in Fig. 6. In the spectrum of PGMA microspheres, the absorption bands at 848 cm−1 and 908 cm−1 can be attributed to the epoxy groups of PGMA microspheres [28]. In the spectrum of PGMA-S microspheres, the absorption band at 672 cm−1 corresponding to P=S vibrations appears [21], and the adsorption bands at 848 cm^{-1} and 908 cm^{-1} are no longer present. The FT-IR spectra confirm the successful ring-opening reaction between the epoxy groups of GMA and the sulfhydryl groups of D2EHDTPA. The bands in the range of 2600-2400 cm^{-1} and at 672 cm^{-1} in the spectrum of PGMA-D2EHDTPA microspheres indicate the successful impregnation of D2EHDTPA through physical interactions [21].

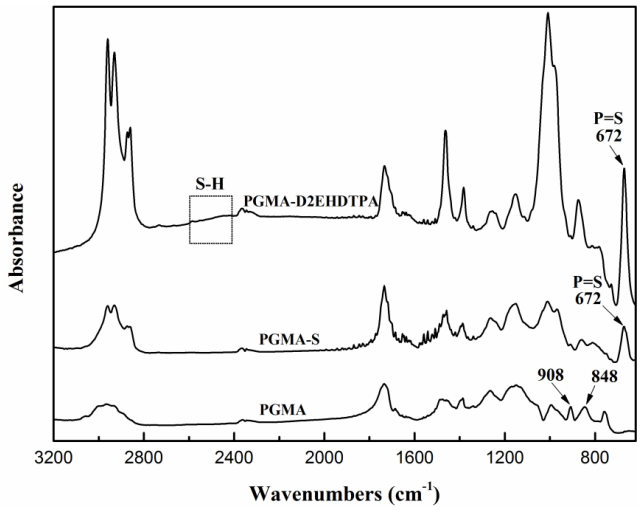


Fig. 6 FT-IR spectra of PGMA, PGMA-S and PGMA-D2EHDTPA microspheres

The capacity of D2EHDTPA in PGMA-D2EHDTPA microspheres measured with the volumetric method was 1.029 mmol/g.

3.2 Effect of pH on Cd(II) adsorption

PGMA-D2EHDTPA demonstrated effective Cd(II) adsorption across a wide pH range (3.0 – 7.0), with optimal performance observed at pH 7.0 (Fig. 7). These findings are consistent with previous reports showing that Cd(II) is completely extracted by D2EHDTPA from media with pH values ranging from 3.0 to 7.0 [21]. Therefore, pH 7.0 was selected as the optimum condition for the subsequent experiments.

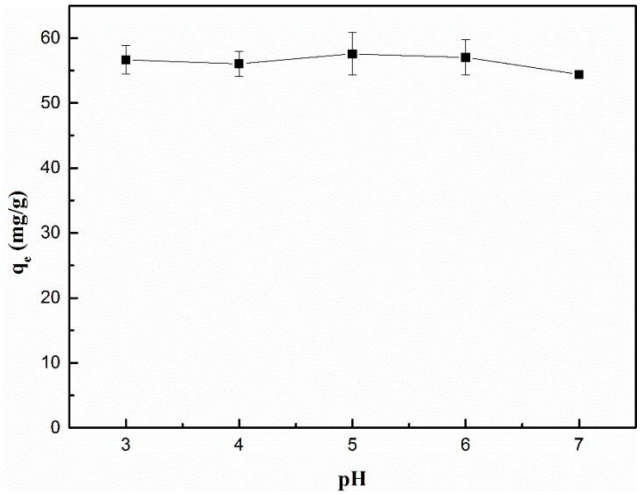


Fig. 7 Effect of pH on the equilibrium Cd(II) adsorption capacity on PGMA-D2EHDTPA (adsorbent dose, 0.01 g; V = 10 mL; C0=100 mg/L; T = 25 °C; t=10 h)

Notably, the adsorbent exhibited high selectivity for Cd(II) over Zn(II) throughout the pH range studied (Fig. 8).

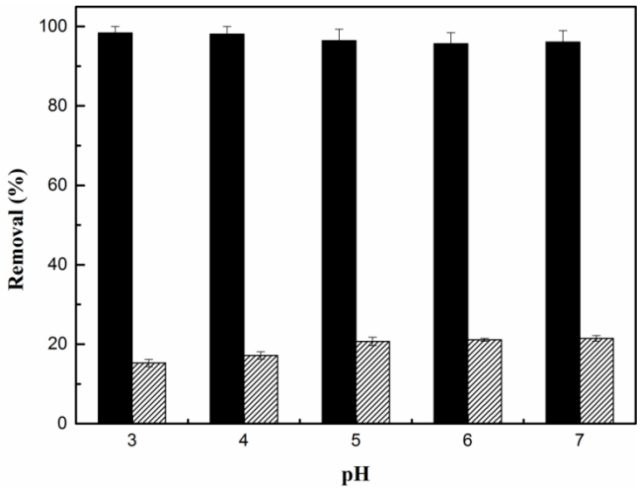


Fig. 8 Effect of pH on the selectivity for Cd(II) towards Zn(II) on PGMA-D2EHDTPA (the black bar: the removal efficiency of Cd(II); the grey bar: the removal efficiency of Zn(II); adsorbent dose, 0.01 g; V = 10 mL; C0=0.44 mmol/L Cd(II) and 0.44 mmol/L Zn(II)); T = 25 °C; t=10 h)

The Cd/Zn selectivity of PGMA-D2EHDTPA was investigated. The thermodynamic equilibrium constants for Cd(II) and Zn(II) are denoted as $K_{p,Cd}$ and $K_{p,Zn}$, respectively, which can be calculated by equation (4). The Cd/Zn

selectivity factor $\alpha_{Cd/Zn}$ is obtained using equation (5) to evaluate the separation ability of PGMA-D2EHDTPA [29]:

$$K_p = q_e/C_e = V(C_0 - C_e)/(mC_e) \quad (4)$$

$$\alpha_{Cd/Zn} = K_{p,Cd}/K_{p,Zn} \quad (5)$$

The molar concentrations of Cd(II) and Zn(II) were the same, namely 0.44 mmol/L for Cd(II) and 0.44 mmol/L for Zn(II). The value of $\alpha_{Cd/Zn}$ in the pH range of 3.0 to 7.0 is greater than 80, even up to 330 as illustrated in Fig. 9, indicating good selectivity for Cd(II) over Zn(II). Lu et al. [22] used a 0.1 mol/L D2EHDTPA-toluene extraction system for Cd/Zn separation with 1-4 mol/L H_2SO_4 in the aqueous phase, and the volume ratio of oil to water was 1:2. Compared to the extraction system reported by Lu et al. [22], the PGMA-D2EHDTPA used less organic solvent and the operation conditions were milder.

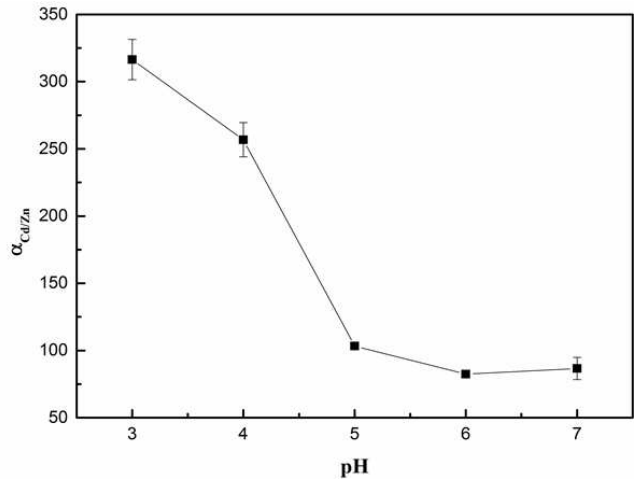


Fig. 9 The Cd/Zn selectivity factor of PGMA-D2EHDTPA (adsorbent dose, 0.01 g; V = 10 mL; C0=0.44 mmol/L Cd(II) and 0.44 mmol/L Zn(II); T = 25 °C; t=10 h)

Compared with the references, it is found that PGMA-D2EHDTPA has high Cd/Zn selectivity, as concluded in Table 1.

Table 1 Comparison of Cd/Zn separation factors of Cd(II) adsorbents

Adsorbents	pH	$\alpha_{Cd/Zn}$	References
Cd(II)-IIP	6.0	66.937	[30]
Cd^{2+}-imprinted polymer	6.77	1.38	[31]
mPHEMAC-Cd^{2+}	7.4	160.7	[32]
PF-Cd(II)-SPANDS	6.0	7.4	[33]
Cd(II)-IIPs	6.0	35.3	[34]
Mag-MIP	7.4	117.5	[35]
Saponified apple waste	7	26.6	[36]

Adsorbents	pH	$\alpha_{Cd/Zn}$	References
Tourmaline	2–7	1.05–2.37	[37]
PEI-CS_2/alginate	4	3.45	[19]
PGMA-D2EHDTPA	3–7	80–330	This work

IIP ion-imprinted polymer; MIP molecularly imprinted polymer

3.3 Effect of initial Cd(II) concentration on adsorption

The adsorption capacity of PGMA-D2EHDTPA increased with the initial Cd(II) concentration, reaching a maximum of 59.33 mg/g (0.528 mmol/g) (Fig. 10). The molar ratio of D2EHDTPA to adsorbed Cd(II) was approximately 2:1, suggesting a specific interaction mechanism (Eq. 6) [38]:

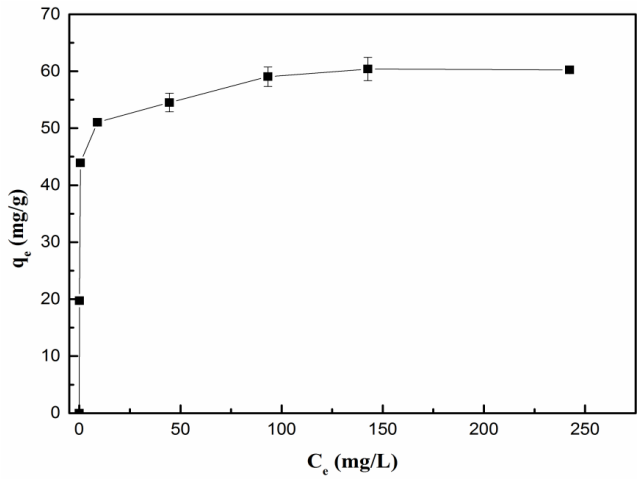


Fig. 10 Effect of initial concentrations on Cd(II) adsorption on PGMA-D2EHDTPA (adsorbent dose, 0.01 g; V = 10 mL; pH = 7.0; T = 25 °C; t=10 h)

$$M^{2+} + 2HA = MA_2 + 2H^+ \quad (6)$$

Similar results were obtained for the uptake of Zn(II) by PGMA-D2EHDTPA. The molar ratio of the D2EHDTPA capacity to the saturated Zn(II) was approximately 2:1. The reaction between D2EHDTPA and Zn(II) ions may also proceed as Eq. (6) [38].

To describe the equilibrium behaviour quantitatively, the isotherm data of Cd(II) in Fig. 10 were fitted with the Langmuir (Eq. 7), Freundlich (Eq. 8) and Temkin (Eq. 9) models:

$$q_e = \frac{q_m K C_e}{1 + K C_e} \quad (7)$$

$$q_e = K_f C_e^{\frac{1}{n}} \quad (8)$$

$$q_e = \frac{RT}{b_T} \ln(a_T C_e) \quad (9)$$

The fitted parameters are summarized in Table 2. The Langmuir model gives the best correlation (R^2 = 0.999), and the maximum monolayer capacity of 58.48 mg/g agrees well with the experimental value of 59.33 mg/g, indicating that Cd(II) is bound as a monolayer on the dithiophosphate-functionalized surface; the Langmuir constant of 0.474 L/mg reflects the strong affinity of the chelating groups for Cd(II). The Freundlich exponent n = 9.55 (1/n = 0.105) is far above unity, which again characterizes a favourable uptake, whereas its lower correlation coefficient (R^2 = 0.929) shows that the empirical Freundlich equation describes the isotherm less faithfully. The Temkin model also reproduces the data reasonably well (R^2 = 0.975); because this model assumes that the heat of adsorption decreases linearly with coverage, its good fit suggests that the binding sites are not energetically uniform, in line with the coexistence of the covalently grafted inner layer and the impregnated outer layer of D2EHDTPA.

Table 2 Simulating parameters for different isotherm models

Langmuir constant			Freundlich constant			Temkin constant		
q_m	K	R^2	K_f	n	R^2	a_T	b_T	R^2
58.48	0.474	0.999	36.536	9.55	0.929	29.549	0.636	0.975

q_m (mg/g), maximum monolayer adsorption capacity; K (L/mg), Langmuir equilibrium constant; K_f, Freundlich constant; n, Freundlich heterogeneity factor; a_T (L/mg), Temkin equilibrium binding constant; b_T (kJ/mol), Temkin constant related to the heat of adsorption; R^2, correlation coefficient.

3.4 Effect of contact time on Cd(II) adsorption

The adsorption kinetics revealed that equilibrium was achieved within 10 hours for Cd(II) and 3 hours for Zn(II) in single-component systems (Fig. 11). In double-component systems, Zn(II) adsorption initially increased but then decreased, indicating preferential adsorption of Cd(II) at equilibrium. It can be inferred that the diffusion rate of Zn(II) ions through the liquid/liquid interface (aqueous solution within the pores of the resin/extractant) in PGMA-D2EHDTPA microspheres was faster than that of Cd(II) ions. However, PGMA-D2EHDTPA microspheres showed preferential adsorption towards Cd(II) at equilibrium. To better understand this phenomenon, some ionic properties are collected and presented in Table 3 [39, 40]. Cd(II) has a larger ionic radius than Zn(II), and both Cd(II) and Zn(II) have ionic radii and hydrated ion radii smaller than the pore size of PGMA microspheres, which is approximately 3.389 nm. Generally, cations with larger ionic radii exhibit slower migration rates.

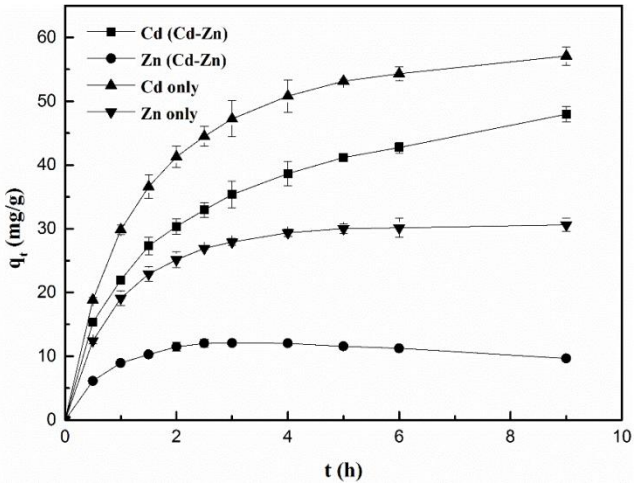


Fig. 11 Effect of contact time on Cd(II) and/or Zn(II) adsorption on PGMA-D2EHDTPA (adsorbent dose, 0.1 g; V = 100 mL; C0=50 mg/L Cd and/or 28.9 mg/L Zn; T = 25 °C; pH = 7.0)

Table 3 Ionic properties of Cd(II) and Zn(II)

Ion	Ionic radius (pm)	Pauling electronegativity	Hydrated ion radius(nm)
Cd(II)	95	1.69	0.426
Zn(II)	74	1.65	0.430

3.5 Effect of adsorbent dose on Cd(II) adsorption

The effect of adsorbent dose on the selective removal of Cd(II) was studied. Different doses of PGMA-D2EHDTPA microspheres were used to adsorb Cd(II) from solutions containing Zn(II). The volume of the solution was 10 mL, the concentration of Cd(II) and Zn(II) were both 1 mmol/L (112 mg/L Cd and 65 mg/L Zn). The adsorbent dose varied from 0 to 50 mg. The removal (%) of Cd(II) and Zn(II) with different adsorbent doses is illustrated in Fig. 12. When the dose was small, PGMA-D2EHDTPA exhibited preferential adsorption towards Cd(II), making it feasible to achieve nearly 100% removal of Cd(II) with little removal of Zn(II) by using an appropriate adsorbent dose.

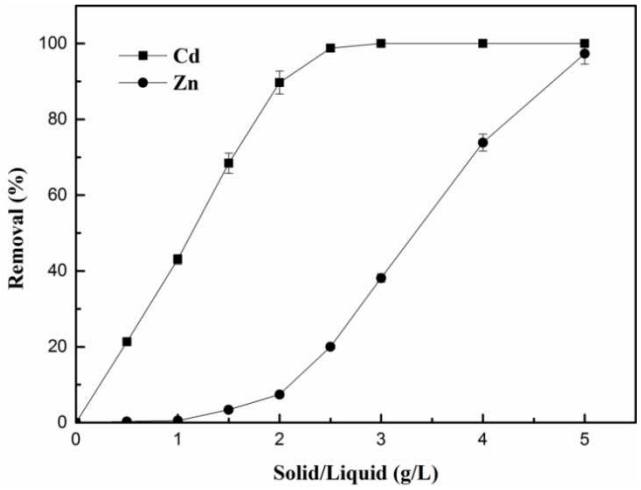


Fig. 12 Effect of adsorbent dose on Cd(II) and Zn(II) removal (V = 10 mL; C0=112 mg/L Cd and 65 mg/L Zn; T = 25 °C; pH = 7.0; t=10 h)

3.6 Adsorption mechanism

D2EHDTPA was impregnated onto PGMA-D2EHDTPA microspheres through strong hydrophobic interactions. To elucidate the mechanism of Cd(II) and Zn(II) adsorption on PGMA-D2EHDTPA, the interactions between Cd(II), Zn(II) and D2EHDTPA were investigated. FT-IR spectroscopy was employed to study the interactions between Cd(II), Zn(II) and D2EHDTPA.

FT-IR spectra of D2EHDTPA, D2EHDTPA-Cd, and D2EHDTPA-Zn were recorded, respectively (Fig. 13). In the spectrum of D2EHDTPA, the strong band at 672 cm^{-1} represents P=S vibrations [21]. The bands in the range of 2600 to 2400 cm^{-1} are attributed to (P)-S-H stretching vibrations of monomeric D2EHDTPA [21]. In the spectrum of D2EHDTPA-Cd, the bands in the 2600 to 2400 cm^{-1} disappear, indicating that the hydrogen ion of the S-H was replaced by a Cd(II) ion, namely, there was a cation-exchange mechanism [21]. Instead of the strong band at 672 cm^{-1} due to asymmetric vibrations of P=S in D2EHDTPA, new bands with a strong one at 643 cm^{-1} and a medium one at 664 cm^{-1} appear in the spectrum of D2EHDTPA-Cd. The change in position and shape of P=S band proves the occurrence of an interaction between the sulphur atom of the P=S group and metal ions [21]. Similar phenomena were observed for D2EHDTPA-Zn, indicating that Zn ions interacted with S-H and P=S groups of D2EHDTPA [21]. However, the change in position and shape of P=S band for D2EHDTPA-Zn was smaller than that for D2EHDTPA-Cd. It could be concluded that D2EHDTPA has stronger affinity with Cd(II) than that with Zn(II).

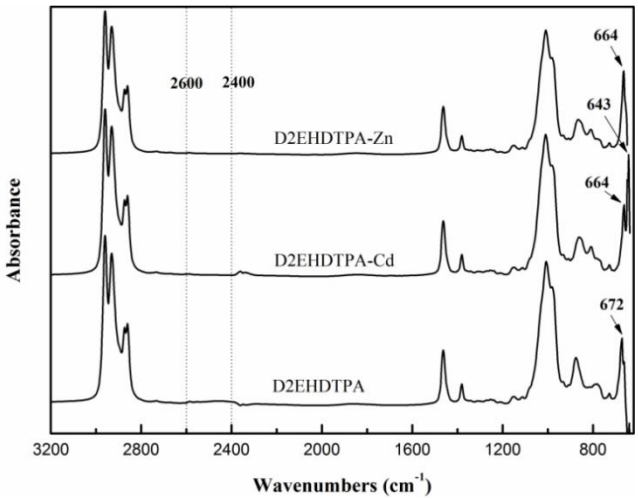
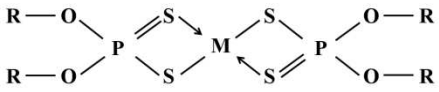


Fig. 13 FT-IR spectra of D2EHDTPA, D2EHDTPA-Cd and D2EHDTPA-Zn

Based on the results presented in Sects. 3.2 and 3.3, the structures of the D2EHDTPA-Cd complex and the D2EHDTPA-Zn complex can be described as follows [22]:



Where M represents Cd(II) or Zn(II) ions.

3.7 Regeneration studies

PGMA-D2EHDTPA microspheres maintained 90% of their initial adsorption capacity after six adsorption-desorption cycles using 6 mol/L HCl as the eluent (Fig. 14), indicating excellent regenerability and stability.

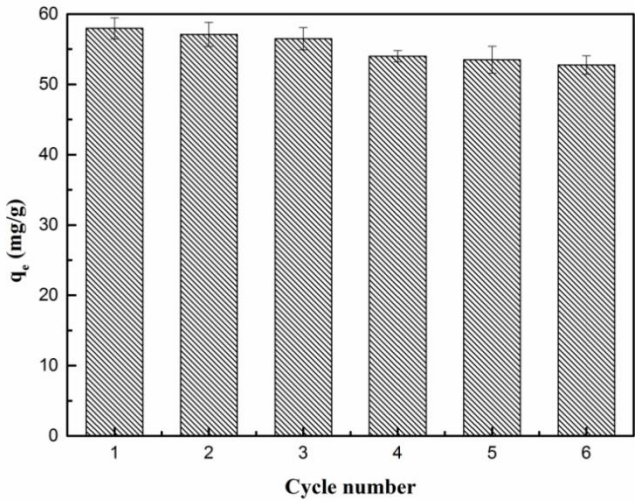


Fig. 14 Regeneration studies of PGMA-D2EHDTPA for Cd removal (adsorbent dose, 0.01 g; V = 10 mL; C0=100 mg/L; T = 25 °C; t=10 h; stripping solution, 10 mL 6 mol/L HCl)

4 Conclusions

In this study, we successfully synthesized PGMA-D2EHDTPA microspheres with two layers of D2EHDTPA for the selective adsorption of Cd(II) from wastewater. The adsorbent exhibited high selectivity and capacity for Cd(II) over a wide pH range, with minimal leaching of D2EHDTPA during adsorption and desorption processes. The adsorption mechanisms involved both cation-exchange and coordination interactions. PGMA-D2EHDTPA offers a promising, environmentally friendly alternative to traditional solvent extraction methods for heavy metal remediation.

STATEMENTS AND DECLARATIONS

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Data availability The data that support the findings of this study are available from the corresponding author upon reasonable request.

Author contributions Tingting Dong: methodology, investigation, data curation, writing—original draft. Huiyong Wu: investigation, formal analysis. Yingying Lv: investigation. Qiang Zeng: investigation. Wenjuan Li: conceptualization, supervision, writing—review and editing. Liangrong Yang: conceptualization, supervision, funding acquisition.

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