

Pyromellitic Dianhydride-Modified β -Cyclodextrin Microspheres for Pb(II) and Cd(II) Adsorption

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ABSTRACT: In this work, the pyromellitic dianhydride (PMDA)-grafted β -cyclodextrin (β -CD) microspheres have been prepared for the removal of lead and cadmium metal ions in aqueous solution by a batch-equilibration technique. The effects of the pH of the solution, contact time, and initial metal concentration were studied. The adsorption capacities for the two metal ions increase significantly as a large number of carboxyl groups are present on the microspheres surface. The equilibrium process is better described by the Langmuir isotherm than the Freundlich isotherm. The maximum adsorption capacities are 135.69

and 92.85 mg g⁻¹ for Pb(II) and Cd(II), respectively. Kinetic studies show good correlation coefficients for a pseudo-second-order kinetic model, confirming that the sorption rate is controlled by chemical adsorption. The regeneration of the adsorbent can be carried out by treating the loaded microspheres with 0.2 (mol L⁻¹) HCl obtaining high desorption rate for the two metal ions. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3418–3425, 2007

Key words: β -cyclodextrin; pyromellitic dianhydride; modification; microspheres; adsorption

INTRODUCTION

Heavy metal ions, one of the most hazardous classes of pollutants in water sources because of their non-biodegradability, have caused widespread environmental endangerment and serious health problems. Extraction of metals that are toxic from water has become an important challenge in environmental chemistry.¹ Numerous approaches have been proposed such as precipitation, electrochemical, and complexation methods.² A large number of materials have been synthesized to remove metal ions from wastewater. Cyclodextrins can be used in this field.

Cyclodextrins are cyclic oligosaccharides composed of six, seven, or eight glucopyranose units (α -, β -, and γ -CD, respectively) linked together by α -1,4-bonds. They have highly useful functions because of their hydrophilic exterior and hydrophobic cavity. β -Cyclodextrin (β -CD) and its derivatives have been used for the removal of polluting species from wastewater.^{3,4} They are often immobilized on a surface of polymeric matrices or insoluble supports⁵⁻⁷ as the decontaminating agents. Belyakov et al.⁸ and Belyakova and coworkers^{8,9} have immobilized β -CD

or its derivatives on the surface of hydroxylated or aminopropylsilica silica, respectively, to adsorb toxic metal ions Cu(II), Cd(II), and Pb(II). Kozłowski et al. used β -CD polymers as macrocyclic ion carrier to separate metal ions from dilute aqueous solutions by transport across polymer-inclusion membranes.¹⁰ These methods either cost much time for adsorption and modification or has low adsorptivity for metal ions.

In this study, microspheres of β -CD using toluene 2,4-diisocyanate (TDI) as the crosslinker in dimethylsulfoxide (DMSO) according to literature¹¹ with some modifications had been synthesized. Pyromellitic dianhydride (PMDA) was then grafted onto the surface of the polymer introducing a large number of carboxyl groups to remove heavy metals ions Pb(II) and Cd(II) from water. Cyclodextrin need not immobilize on any carrier and the microspheres not only have high mechanical strength and good chemical stability, but also are environmentally friendly. The adsorbent can be readily used without subsequent grinding and sieving, simplifying the treating procedure and decreasing the yield loss. The uniform and spherical particles are easy to be handled and the reproducibility of the experimental data is better in comparison with irregularly shaped ones. To the best of our knowledge, it is the first time this method is used in the field of the metal ions' adsorption.

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EXPERIMENTAL

Materials

β -CD and PMDA were purchased from Sinopharm Group Chemical Reagent (Shanghai, China) and dried in a vacuum dryer before use; DMSO and *N,N*-dimethylformamide (DMF) were predried with molecular sieves 4A in a dark bottle.¹² Poly(dimethylsiloxane) (PDMS) was purchased from Changzhou Chang Yin Organosilicon Materials Factory (Changzhou, China). TDI was from Shanghai Chemical Reagent (Shanghai, China). Aqueous solution of Pb(II) and Cd(II) nitrates was prepared from analytical-grade reagents (Shanghai Jinshan Chemical Plant, China) by dissolving them in deionized water.

Preparation of β -CD microspheres

The β -CD microspheres were prepared according to the procedures described elsewhere¹¹ with some modifications. β -CD (0.5 g) was dissolved in dry DMSO (5.0 mL) and put into a 250-mL three-necked flask, and then the dispersing medium PDMS (100 mL) was added and stirred with mechanical stirrer at high speed for 50 min at 95°C. Subsequently, crosslinker TDI (0.6 mL) was added to the DMSO/PDMS emulsion and mechanically stirred for 2.5 h under the same condition, and the emulsion with precipitation of microspheres was diluted with acetone and hexane after the flask was cooled. The product microspheres were collected by filtration and washed with water and ethanol to remove unreacted reagents and PDMS completely, and then dried in a vacuum dryer at 40°C for 24 h before use.

Modification of microspheres

In a 100-mL three-necked flask, 1.0 g β -CD microspheres were mixed with 30-mL DMF and 2.5 g PMDA was then added while stirring with a magnetic stirrer for 4 h at 50°C. Subsequently, the modified microspheres were washed with DMF and deionized water several times. Finally, the microspheres were treated with 0.1 (mol L⁻¹) NaOH and washed with water until the solution was neutral and then dried in vacuum dryer and stored at ambient temperature until use.

Characterization studies

Morphology observation

The surface morphology of the dried microspheres was examined using scanning electron microscope (SEM). A fragment of the dried microspheres was mounted on a SEM sample mount and was sputter-coated with gold. The sample was then mounted in

a SEM (X-650, Hitachi, Japan). The surface of the sample was scanned at the desired magnification. BET surface area was determined with nitrogen adsorption at 196.3 K on an Autosorb-1 Instrument (Quantachrome, USA).

FTIR spectroscopy

The dried microspheres were thoroughly mixed with KBr and pressed into a pellet and the IR spectra were measured using a Fourier Transform IR spectrometer (Nicolet NEXUS-470).

X-ray photoelectron spectroscopy analysis

The elemental conditions of the microspheres surface before and after modification were investigated by an X-ray photoelectron spectroscopy (XPS) (VG Multilab 2000) using monochromatized Mg X-ray resource. The pressure in the analysis chamber was maintained at less than 10⁻⁸ Torr during each measurement. High resolution scans for the elements were performed with the pass energy of 25 eV. All binding energies were referenced to the neutral C(1s) peak at 284.6 eV to compensate for the surface-charging effects.

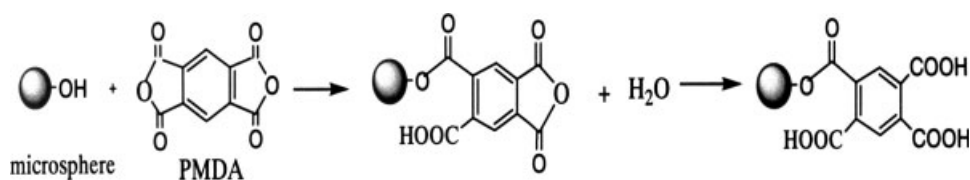
Batch-adsorption studies

Adsorption of Pb(II) and Cd(II) from aqueous solution was investigated in batch experiments. Effects of the metal ions' concentrations, the pH of the medium, contact time on the adsorption rate, and capacity were studied, and the adsorption-kinetic studies were also evaluated.

The experimental procedure was as follows: 50-mg modified microspheres samples were put into conical flasks, then, 50-mL aqueous solution of lead and cadmium were added in single component system, and vibrated at a constant speed of 150 rpm in a shaking water bath. When the adsorption reached equilibrium after 60 min, the conical flasks were taken out and centrifuged to separate the modified microspheres and the solution. The concentrations of the free metal ions in the centrifugation were analyzed using flame atomic absorption spectrometer (AAS) (AA6300, Shimadzu, Japan). The amount of adsorption was calculated based on the difference of heavy metal concentration in aqueous solution and the weight of the modified microspheres by the following equation:

$$q_e = \frac{(c_0 - c_e)V}{W} \quad (1)$$

where q_e is the amount of metal ions adsorbed onto the unit amount of the sorbents (mg g⁻¹), c_0 is the



Scheme 1 Schematic procedure of the modification onto β -CD microspheres surface.

initial heavy metal concentration (mg L^{-1}), c_e is the final or equilibrium heavy metal concentration (mg L^{-1}), V is the volume of metal solution (L), and W is the dry weight of the adsorbents (g).

The adsorption temperature was at 25°C . The initial metal concentration was 187 and 142 mg L^{-1} for lead and cadmium, respectively. For adsorption-isotherm experiments, the concentration ranges used were $31.3\text{--}312.8 \text{ mg L}^{-1}$ for lead and $23.8\text{--}237.8 \text{ mg L}^{-1}$ for cadmium.

Desorption studies

Desorption studies were performed by transferring $0.2 \text{ (mol L}^{-1}\text{) HCl}$ to the metal-loaded microspheres. The modified β -CD microspheres loaded with metal ions were placed in 20-mL desorption medium and stirred at 150 rpm until equilibrium was reached. The solutions were then separated by centrifugation and the concentration was determined by AAS, and desorption ratio was calculated by the following equation:

$$\text{Desorption ratio} = \frac{\text{Amount of metal ions desorbed to the elution medium}}{\text{Amount of metal ions adsorbed on the microspheres}} \times 100 \quad (2)$$

RESULTS AND DISCUSSION

Preparation and properties of modified β -CD microspheres

There are many OH groups on the surface of the polymerized β -CD microspheres. Although the part of the more reactive primary OH was occupied because of the polymerization, the residual OH that unreacted with the TDI could also graft PMDA, which is hypothetically described by Scheme 1 (supposing the amount of PMDA is excessive).

Figure 1 shows the SEM micrographs of the microspheres before and after the surface modification. From the figure, it is seen that there is a small increase in the diameter of the modified microsphere. The BET surface area data confirm this phenomenon with surface areas of 23.3 and $7.15 \text{ m}^2 \text{ g}^{-1}$ for the microspheres and modified microspheres, respectively, showing that larger diameter corresponds to smaller BET surface area, and vice versa.

To confirm the type of functional groups on the microspheres before and after modification, FTIR spectra are determined and shown in Figure 2. The peaks at 3388 , 2921 , 1661 , 1530 , 1407 , 1220 , and 1025 cm^{-1} are observed in the β -CD pristine microspheres spectrum shown in Figure 2(a). The broad and strong band ranging from 3200 to 3600 cm^{-1} may be attributed to the stretching vibration of OH groups

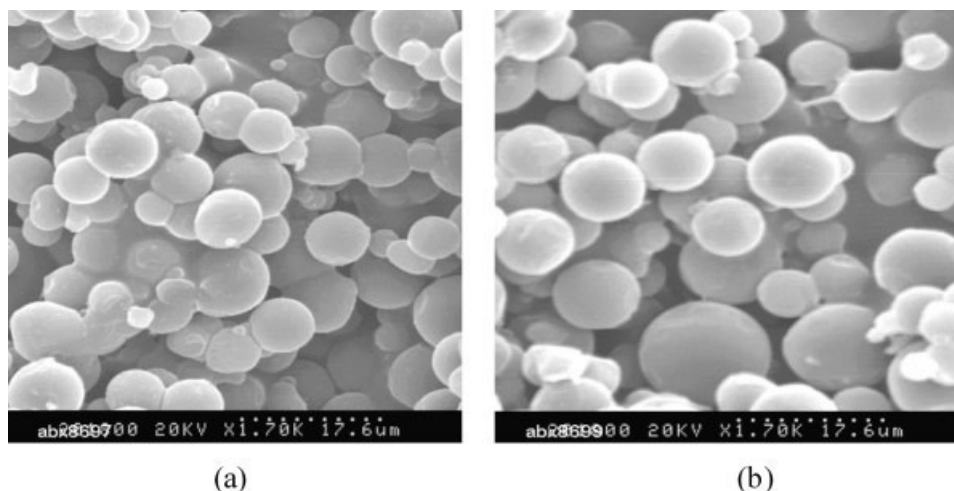


Figure 1 SEM micrograph of microspheres before and after modification: (a) microspheres and (b) modified microspheres $\times 1700$.

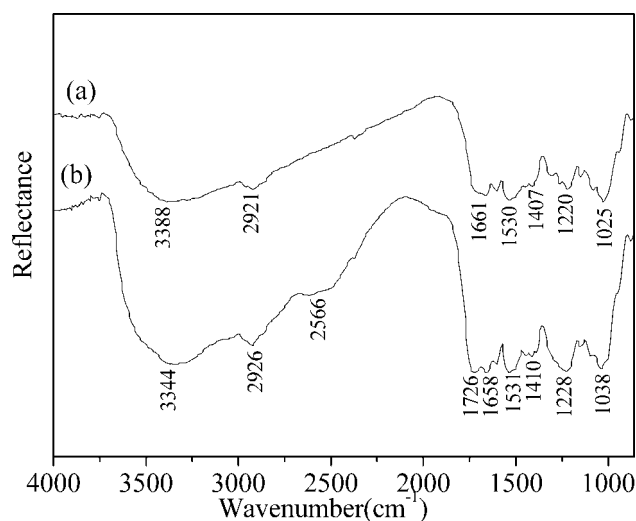


Figure 2 FTIR spectra of (a) microspheres and (b) modified microspheres.

in the polymer, the band at 2921 cm^{-1} is due to CH stretching vibration of CH, and CH_2 groups, which are consistent with the peak at 1407 cm^{-1} assigned to a CH-bending vibration. The bands at 1661 and 1530 cm^{-1} are assigned to C=O and NH stretchings,¹³ respectively, in the carbamate formed from the crosslinking reaction. The bands of C—O stretching are at 1220 and 1025 cm^{-1} .^{14,15} When comparing with the microspheres, the spectrum presented some changes after the microspheres are modified with PMDA, as shown in Figure 2(b), a new peak at 1726 cm^{-1} is observed distinctly, which can be assigned to the C=O stretching of COOH,¹⁶ and the OH adsorption band shifts from 3388 to 3344 cm^{-1} with the increasing intensity and wider range ($2500\text{--}3600\text{ cm}^{-1}$) because of strong hydrogen bonding, indicating the increase of OH groups.

Further evidences in supporting the modification onto the microspheres have been obtained from XPS analysis. Figure 3 shows the C(1s) XPS spectra of the

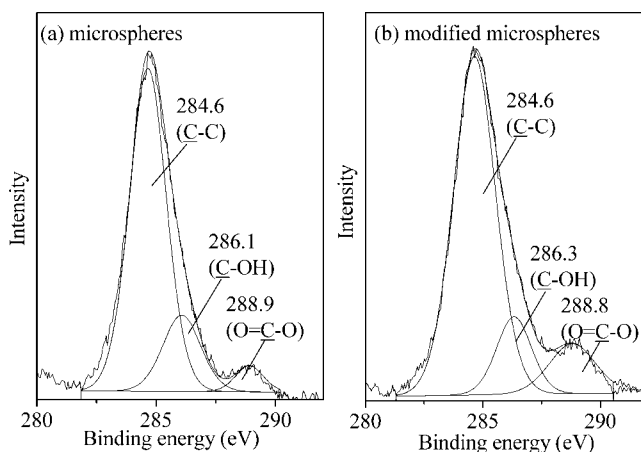


Figure 3 XPS C(1s) core-level spectra.

microspheres before and after modification. As shown in Figure 3(a), three peaks (284.6, 286.1, 288.9 eV) can be fitted to the C(1s) spectra of the microspheres, which are assigned to the carbon in C—C, C—OH, and O=C—O, respectively. This result indicates that there are a higher concentration of hydroxyl groups and lower concentration of carboxylate groups on the surface of the microspheres. After the microsphere surface was grafted with PMDA, the C(1s) changed [Fig. 3(b)] significantly in the area ratio of the three moieties for carbon 1s in the microspheres. As shown in Figure 4, the area ratio for the peak at 288.8 eV attributed to carboxyl group increases significantly from 6.0 to 16.0% after modification, thus indicating the existence of PMDA. Meanwhile, the area ratio for C—OH at 286.0 eV decreases from 24.0 to 19.0%, which may be due to the coverage of anhydride on these sites.

From the FTIR and XPS analyses, it is confirmed that PMDA has been successfully grafted onto the microspheres.

Effect of pH

The pH of the solution is one of the most important variables governing metal sorption.¹⁷ The effects of the pH of the sample solutions on the adsorption were evaluated by adjusting the pH by HCl or NaOH. Figure 5 shows that the metal ions removals increase with increasing solution initial pH, and the capabilities of the adsorbent almost reach plateau value at $\text{pH} \sim 5.0$, which is similar to what have been reported.^{18–20}

The reason is that at low pH the proton concentration is high and the studied metal ions are present in solution as free cation, so that protons can compete with the lead and cadmium cations for surface active sites. This fact is corroborated by the desorp-

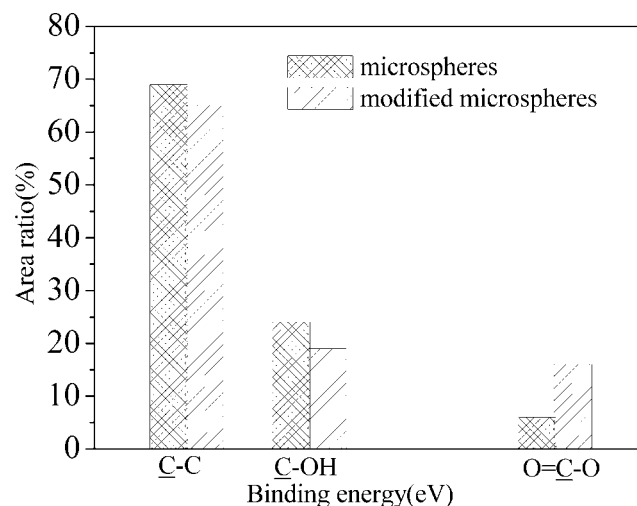


Figure 4 Area ratio of C(1s) spectra of the microspheres before and after modification.

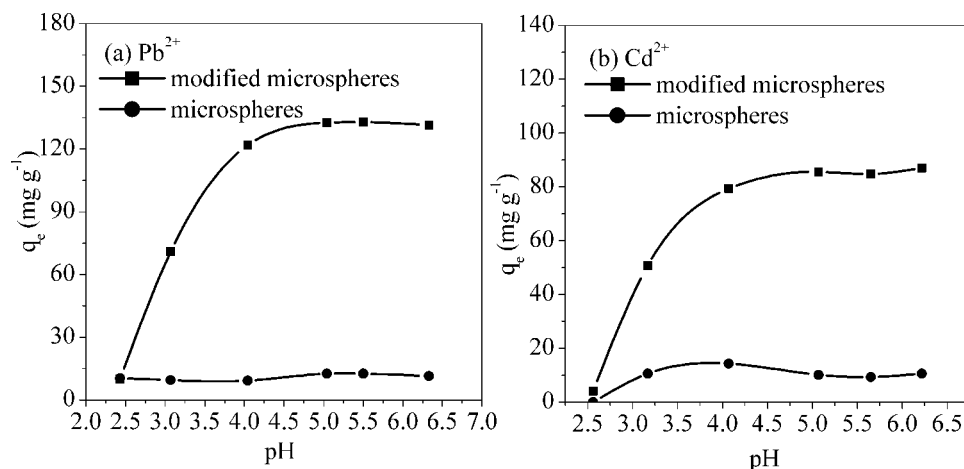


Figure 5 Effect of pH on lead and cadmium adsorption: 50 mg microspheres in 50-mL metal solution; Initial metal solution concentration 187 and 142 mg L⁻¹ for lead and cadmium, respectively; adsorption time: 1 h; temperature: 25°C.

tion results, which put the sorbents in 0.2 mol L⁻¹ HCl solution for regeneration.²¹ With an increase in pH, the concentration of the proton becomes lower and the competition of proton reduced. Metal ions replace hydrogen ions from microspheres surface and the extent of adsorption increases with the increase in pH in the acidic range, and a maximum value is reached in the range of 4.5–6.2, and so the plateau is obtained. The pH of the original metal solution is 5.0 and 6.2 for lead and cadmium, respectively, which is within the range of the plateau values, and so we used the original metal solution to perform next experiments avoiding adjusting the pH, simplifying the experimental operation and minimizing the experimental error.

In addition, from Figure 5, large differences are observed for the metal ions adsorption on the microspheres before and after modification. The uptakes of lead and cadmium ions increase from 12.6 to 132.6 at pH 5.0, and from 10.5 to 87.3 at pH 6.2, respectively. It is observed that the adsorption capacities for the metal ions increase significantly after the microspheres have been modified with PMDA.

Table I shows the comparison between the two metal ions removals by PMDA-modified β -CD

microspheres and others found in the literature. It is seen that the modified microspheres have higher adsorption capacities for both metal ions than others and present superiority.

Adsorption-kinetics studies

Pseudosecond-order equations

The effects of contact time on the adsorption are shown in Figure 6(a,c). The results show that lead and cadmium adsorption are very fast. After 6 min, adsorption of lead and cadmium was practically completed. The adsorption equilibrium reached within 15 min. This short adsorption-equilibrium time is most probably due to high affinity rate between the metal ions and the adsorbent. So, we choose 60 min as the adsorption time in the experiments.

To examine the controlling mechanism of the adsorption process, such as mass transfer and chemical reaction, kinetic models are used to test the experimental data. Figure 6(b,d) shows the adsorption kinetics of lead and cadmium ions using the microspheres before and after modified. Pseudosecond-order equation was applied based on adsorption-

TABLE I
Comparison of the Lead and Cadmium Removals Between PMDA-Modified β -CD Microspheres and Others Found in Literature

Adsorbents	Pb			Cd			References
	pH	<i>T</i> (°C)	<i>q</i> (mg g ⁻¹)	pH	<i>T</i> (°C)	<i>q</i> (mg g ⁻¹)	
PMDA- β -CD	5.0	25	132.6	6.2	25	87.3	This work
Cellulose/chitin	4.0	Room temperature	68.4	5.0	Room temperature	35.9	22
Cellulose- β -CD	7.0	25	62.2	7.0	25	35.2	23
PEI-PMMA	5.0	20	26.1	5.0	20	30.2	24
P(HEMA-co-MAH)	5.0	20	112.9	5.0	20	38.0	25

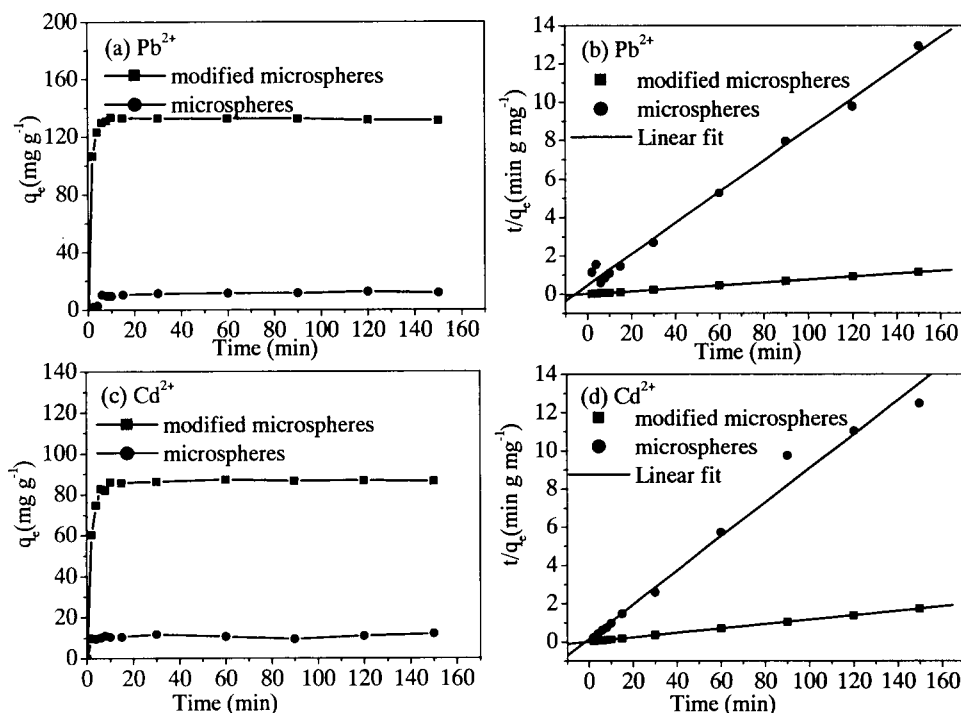


Figure 6 Adsorption kinetics of lead and cadmium ions on the microspheres before and after modification: (a) Pb(II) adsorption-kinetics data; (b) modeled results for Pb(II) adsorption using the pseudo-second-order equation; (c) Cd(II) adsorption-kinetics data; (d) modeled results for Cd(II) adsorption using the pseudo-second-order equation. Microspheres (50 mg) in 50-mL metal solution; initial metal solution concentration 187 mg L⁻¹ with pH 5.0 and 142 mg L⁻¹ with pH 6.2 for lead and cadmium, respectively; temperature: 25°C.

equilibrium capacity, which may be expressed in the form²⁶:

$$dq_t/dt = k_2(q_e - q_t)^2 \quad (3)$$

where k_2 (g mg⁻¹ min⁻¹) is the rate constant of pseudo-second-order adsorption. Integrating eq. (3) and applying the boundary conditions leads to

$$(1/(q_e - q_t)) = (1/q_e) + k_2t \quad (4)$$

Or equivalently for a linear form

$$(t/q_t) = (1/k_2q_e^2) + (1/q_e)t \quad (5)$$

A plot of t/q_t vs. t should give straight line. The rate constant (k_2) and the equilibrium concentration (q_e) can be calculated from the intercept and the slope.

Results using the pseudo-second order equation for the lead and cadmium adsorption kinetics are shown in Figure 6(b,d). For the modified microspheres, the good fit ($R^2 = 0.9999$) obtained for both the metal ions indicates that the adsorption conforms to the pseudo-second-order-reaction mechanism, confirming that the adsorption rate is controlled by chemical sorption. Because the PMDA was grafted onto the microspheres surface, it seems that cation exchange, which occurred on carboxyl groups, would dominate the adsorption process. The corresponding parameters and correlation coefficients for the plot are given in Table II, with q_e values at 131.75 and 86.8 mg g⁻¹ for lead and cadmium, respectively, for the modified microspheres. Whereas, the corresponding microspheres values are at 12.36 and 11.2 mg g⁻¹. It can be seen from Table II that the adsorption behavior of the two metal ions

TABLE II
Kinetic Parameters of the Pseudo-Second-Order Equation for Pb²⁺ and Cd²⁺ Adsorption

Metal ions	Absorbent	q_e (mg g ⁻¹)	k_2 (g mg ⁻¹ min ⁻¹)	R^2
Pb (II)	Modified microspheres	131.75	6.192×10^8	0.9999
	Microspheres	12.36	3.29×10^2	0.9919
Cd (II)	Modified microspheres	86.68	1.829×10^6	0.9999
	Microspheres	11.2	7.95×10^2	0.9864

by the modified microspheres shows far larger rate constant (k_2) and higher correlation coefficients (R^2) than the pristine microspheres embodying the superiority of the modification.

Adsorption isotherms

Langmuir and Freundlich isotherms have been successfully used to model many sorption processes. The Langmuir isotherm model assumes monolayer adsorption on a surface with a finite number of identical sites that are energetically equivalent and there is no interaction between the adsorbed molecules. The Freundlich expression is an empirical equation for adsorption on heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface and multilayer sorption can occur. The Langmuir and Freundlich isotherms may be expressed respectively as²⁷

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} b c_e} \quad (6)$$

$$\log q_e = \frac{1}{n} \log c_e + \log K_F \quad (7)$$

where q_{\max} is the maximum adsorption at monolayer coverage (mg g^{-1}) and b is the Langmuir adsorption-equilibrium constant (L mg^{-1}), reflecting the energy of adsorption. K_F and $1/n$ are the Freundlich characteristic constants, related to the adsorption capacity and adsorption intensity, respectively.

Figure 7 shows the adsorption isotherms of lead and cadmium ions on the modified microspheres. The adsorption capacities increase for both the metal ions with increasing metal ions concentrations at low

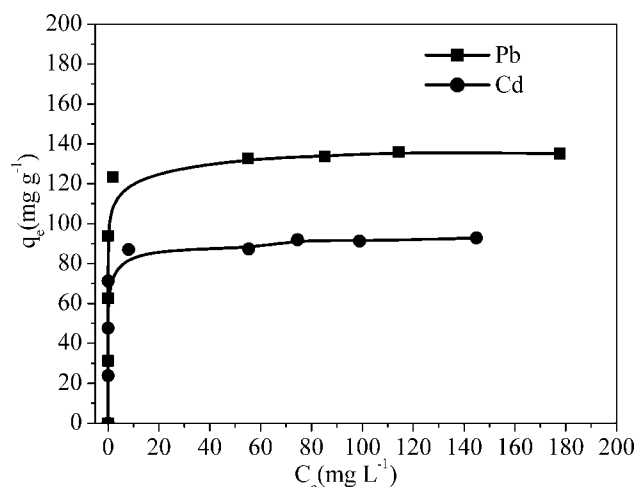


Figure 7 Adsorption isotherms of Pb(II) and Cd(II) on modified microspheres. Microspheres (50 mg) in 50-mL metal solution; pH 5.0 and 6.2 for lead and cadmium, respectively; adsorption time: 1 h; temperature: 25°C.

TABLE III
Constants of Eqs. (6) and (7) for Various Concentrations

Metal ions	Langmuir model			Freundlich model		
	q_m (mg g^{-1})	b (L mg^{-1})	R^2	K_F	$1/n$	R^2
Pb (II)	135.69	1.679	0.9999	121.5	0.0219	0.9844
Cd (II)	92.85	0.9633	0.9999	82.7	0.0212	0.6347

concentration approaching a constant value corresponding to each metal ion at high concentration. The maximum loading capacities are evaluated from these values. As shown in Figure 7, the metal ions uptakes q_e by the modified microspheres are 132.6 and 87.3 mg g^{-1} for Pb(II) and Cd(II), respectively, in the plateau region at initial concentration of 187 mg L^{-1} for Pb(II) and 142 mg L^{-1} for Cd(II). The experimental data modeled according to Langmuir and Freundlich isotherms and the evaluated constants are given in Table III. It is found that the Langmuir isotherm [eq. (6)] equation gives better fit than the Freundlich isotherm equation for both lead and cadmium ions adsorption (correlation coefficient, $R^2 > 0.999$), the adsorption capacities for lead and cadmium can be evaluated by plotting C_e/q_e vs. C_e , the intercept of the graph yields $1/q_m$. The q_m values are 135.69 and 92.85 mg g^{-1} for lead and cadmium, respectively, which are very close to the data we got from the experiments. These results indicate that these heavy metal ions are adsorbed on modified microspheres as a monolayer.

Desorption studies

The regeneration of the adsorbent is likely to be a key factor in improving process economics. Desorption of the adsorbed metal ions from the modified microspheres was also studied in batch experiments. Using HCl (0.2 mol L^{-1}) as the desorption medium and desorption time as 1 h, desorption ratio was calculated using eq. (2). From the desorption experiments, it is clear that desorption ratios are very high and the average desorption percentage is obtained for Pb (96.7%) and Cd (98.2%) from triplicate measurements without losing the modified microspheres adsorption capacities significantly in three cycles.

CONCLUSIONS

From this work, it is seen that PMDA-modified β -CD microspheres can be an excellent adsorbent for heavy metal ions. The adsorption capacities of the modified β -CD microspheres for Pb(II) and Cd(II) were enhanced significantly in comparison with the pristine ones. The presence of PMDA onto the

microspheres surface was verified using FTIR and XPS. The morphology of the microspheres was observed by SEM and BET surface area determination. The kinetics of adsorption for both metal ions follows the pseudo-second order equation demonstrating that the ion-exchange is the dominant mechanism for the two metal ions adsorption. The experimental data are well fitted to the Langmuir isotherm model. And the regeneration experiments with 0.2 (mol L⁻¹) HCl show that modified microspheres can be reused in several sorption/desorption cycles. This study indicates that the graft onto the surface of β -CD microspheres is very effective for the removals of the two heavy metal ions Pb(II) and Cd(II).

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