

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Efficient removal of cadmium using facile functionalized of mesoporous silica via a biomimetic coating

Yan Chen, Junkai Gao*, Xiaofei Wen, Wenfeng Wu

School of Maritime and Civil Engineering, Zhejiang Ocean University, Zhoushan 316022, China

ABSTRACT

A mesoporous material (DMOS), prepared by a facile surface modification strategy based on grafting polydopamine onto meso-structured silica (MOS), was developed as a sorbent to sequester Cd^{2+} . The method used to modify MOS was simple, facile and cost-effective. The DMOS was characterized by SEM, TEM, XRD, BET and FT-IR, showing that the material had clear multilayer structures, large surface area of $431 \text{ m}^2/\text{g}$ and large pore size of 12.7 nm . The influences of pH, contact time, solid-to-liquid ratio, ionic strength and adsorption–desorption cycles on the sorption process were investigated. It was demonstrated that the adsorption capacity of Cd^{2+} by DMOS was dramatically improved by functionalization with the maximum adsorption capacity of 107 mg/g at pH 6.0 and that the sorption equilibrium time was 90 minutes. Additionally, the influence of the solid-to-liquid ratio and ionic strength on the sorption was very weak, and the Cd^{2+} adsorption capacity of regenerated DMOS still remained 86.5% after ten adsorption-desorption cycles. All the results illustrated that the DMOS exhibited excellent performance for the removal of Cd^{2+} .

KEYWORDS

Dopamine; Biomimetic coating; Mesoporous material; Adsorption; Cadmium

1 Introduction

Toxic heavy metals can cause water and soil contamination, which jeopardize human health and damage bio-organisms. In particular, Cd^{2+} is considered as one of the most hazardous metals present in waste water discharge from many industries.

* Corresponding author. Tel./fax: +86 580 2554491. E-mail address: gaojk@zjou.edu.cn.

Numerous technologies of removing heavy metals from aqueous solutions, including chemical precipitation,^{1,2} adsorption,³⁻⁶ ion exchange^{7,8} and membrane processes,^{9,10} have been developed. Among these methods, adsorption is a preferential choice because of its high efficiency, easy operation and reversibility. A number of absorbents including metal oxides,^{11,12} silica nanotubes,¹³ mesoporous carbons,¹⁴ carbon nanotubes,¹⁵ sepiolites,¹⁶ palygorskite¹⁷ and montmorillonite¹⁸ have been used for the capture of heavy metals from aqueous solutions. Among those materials, mesoporous silicas were regarded as promising absorbents owing to their large pore size, high surface areas, uniform pore structures, and excellent mechanical stability.¹⁹ However, the mesoporous silicas still suffered from the drawback of low sorption capacity in many cases. To promote their sorption ability, surface modification with functional groups was performed.^{4, 20-22} Jeong *et al.*²⁰ developed an effective sorbent for the removal of Cu(II) from aqueous solution with tetrakis(4-carboxyphenyl)porphyrin functionalized mesoporous silica SBA-15 (TCPP-SBA-15). Huang *et al.*²¹ synthesized a Cr(III) sorbent with tannin-immobilized mesoporous silica bead (BT-SiO₂) that could be a highly effective sorbent during purification of Cr(III) from aqueous solutions. Aguado *et al.*⁴ prepared SBA-15 materials functionalized with amino for efficient extraction of heavy metals in wastewater. Da'na *et al.*²² grafted 3-aminopropyltrimethoxy-silane onto SBA-15 to develop Cu²⁺ ions sorbent, and under suitable conditions, the sorbent exhibited high adsorption capacity.

However, typical strategies for immobilizing heavy metal ligands onto mesoporous silicas relied on refluxing in organic solvents for several hours.^{20, 23-26} Such treatment was aggressive and tedious, and hazardous reagents were needed sometimes. Motivated by the adhesive proteins secreted by mussels, Lee *et al.*²⁷ reported a mild approach utilizing dopamine as a modification reagent to form a polydopamine coating on almost all types of material surfaces. As a class of catecholamines, polydopamine had an extremely excellent ability to bind metals.²⁸⁻²⁹ In this case, strategies that combine surface modification by dopamine with removal of heavy metals from aqueous solutions are of great interest.³⁰⁻³² Yu *et al.*³⁰ synthesized Cu(II)

sorbent with bio-inspired polydopamine coated zeolites, and its adsorption capacity was obviously improved compared with the natural zeolites. Nematollahzadeh *et al.*³¹ grafted polydopamine onto maghemite nanoparticles to develop effective, fast and dosage-saving sorbent for the separation of Cr(VI) from aqueous solution. To promote the sorption capacity and achieve faster sorption kinetics, we developed a novel dopamine-functionalized SBA-15 (DMS) with high surface areas as a sorbent to extract U(VI) from aqueous solution.³² However, to avoid the blockage of mesoporous channels result from the bulkiness of polydopamine, high ligand loading amount could hardly be obtained, thus limiting applications. To overcome this drawbacks, mesoporous silica with larger pore size was needed.

In this work, a mesoporous material (DMOS), prepared by a facile surface modification strategy based on grafting polydopamine onto meso-structured silica (MOS), was developed as a sorbent to sequestration Cd^{2+} . This is the first time that dopamine was used as surface functionalization reagent to modify MOS. The MOS has mesopores of 10 nm diameter,³³ which has the potential of increasing the amount of polydopamine loaded on its surface and meanwhile avoiding the blockage of mesopores. DMOS was firstly used to remove Cd^{2+} from aqueous solution, and the influences of pH, contact time, ionic strength, solid-to-liquid ratio and adsorption–desorption cycles on the sorption process were investigated. The results demonstrated that the DMOS exhibited excellent performance for the removal of Cd^{2+} , and it had great potential for practical applications.

2 Experimental

2.1 Materials

Poly (ethylene glycol)-b-poly (propylene glycol)-b-poly (ethylene glycol) (P123) and dopamine·HCl were purchased from Sigma-Aldrich. Cadmium nitrate, 1,3,5-trimethylbenzene (TMB) and tetraethoxysilane (TEOS) were purchased from Meryer, China. All of these materials were used as received. A standard stock solution (1.052 g/L) of Cd^{2+} was prepared by dissolving $\text{Cd}(\text{NO}_3)_2$ in deionized water. The standard stock solution was diluted by deionized water to prepare desired Cd^{2+} solutions (10~300 mg/L). All of the other reagents were of analytical reagent grade

and used as received without further purification.

2.2 Preparation of dopamine-functionalized MOS (DMOS)

The MOS was synthesized as described by Jun *et al.*³³ Dopamine-functionalized MOS was synthesized using the post-grafting method. Specifically, 1 g of MOS was suspended in 200 mL of 1.25 g/L dopamine solution freshly prepared in Tris-HCl buffer (pH 8.5), and the mixture was stirred for 2 h. Then, the suspension was centrifuged, washed with deionized water, and dried at 40 °C in vacuum for 24 h. The as-prepared material was denoted as DMOS.

2.3 Batch adsorption experiments

In the batch adsorption experiments, an exact amount of DMOS was added into 50 mL cadmium nitrate solution in a conical flask, and the suspension was agitated with a mechanical shaker at 200 rpm at 298 K. The initial pH of solutions was adjusted using 0.1 M NaOH or 0.1 M HNO₃. In equilibrium study, the initial pH of the solution was adjusted to 6.0. When the sorption equilibrium was reached, all of the solution was filtered, and the Cd²⁺ concentration was measured by atomic absorption spectrophotometer (361CRT, INESA Analytical Instrument Company Limited, China). The experiments were carried out twice, and the results were given as average values. The equilibrium sorption capacity q_e (mg/g) of Cd²⁺ and sorption capacity q_t (mg/g) of Cd²⁺ at time t (min) were determined by equations (1) and (2), respectively:

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

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad (2)$$

where C_0 , C_e and C_t are the concentrations of Cd²⁺ (mg/L) at the initial time, equilibrium time and time t , respectively; V and m represent the volume of the Cd²⁺ solution (L) and the weight of DMOS (g), respectively.

2.4 Adsorption–desorption recycle experiments

In the adsorption–desorption recycle experiments, 5 mg of DMOS was added into

10 mL cadmium nitrate solution (initial concentration 100 mg/L; pH value 6.0 and temperature 298 K), and the suspension was agitated for 150 min. Then the solution was centrifuged at 8000 rpm for 30 minutes, and 5 mL supernatant was removed for Cd^{2+} concentration determination. Subsequently, 0.1 M HNO_3 solution was added, followed by 150 min shaking at 298 K to desorb the loaded Cd^{2+} ions, and the final Cd^{2+} concentration were determined. Then the sorbent was separated and washed with deionized water to reuse in the next adsorption–desorption process.

2.5 Characterization

The morphological images of the DMOS were characterized by scanning electron microscopy (SEM, S-4800, Hitachi, Japan). Transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan) images were obtained at 200 kV. Small angle X-ray diffraction (XRD, D/MAX-2500, Rigaku, Japan) pattern was taken at 40 kV and 40 mA. The surface-area of MOS and DMOS were calculated according to the Brunauer-Emmett-Teller (BET, BELSORP-max, BEL, Japan) method, and the pore size distributions were obtained by the Barrett-Joyner-Halenda (BJH) method using adsorption isotherm branches. The Fourier transform infrared (FT-IR, VECTOR22, Bruker, Germany) spectra was realized by the KBr pellet method.

3 Results and discussion

3.1 Characterization of DMOS

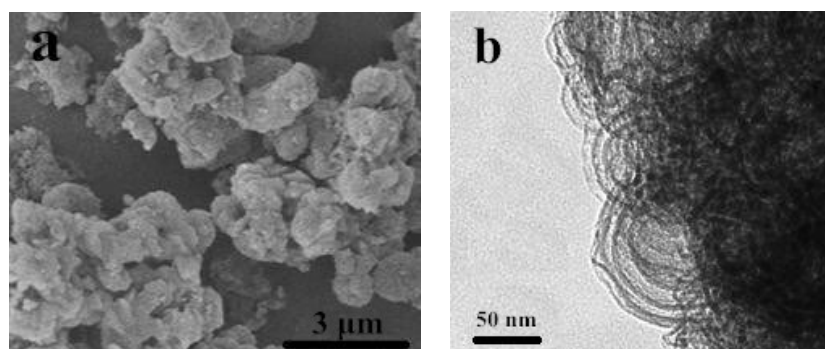


Fig. 1. Characterization of DMOS: (a) SEM image; (b) TEM photograph.

The characterization results of DMOS are shown in Fig. 1. The SEM image (Fig. 1 (a)) showed that DMOS was made up of hundreds of nanometer sized onions particles aggregated into secondary micrometer sized particles, in accordance with the previous reports.^{33,34} The TEM photograph (Fig. 1 (b)) indicated that the DMOS had clear

multilayer structures, and the mesopore size between the layers was about 13 nm.

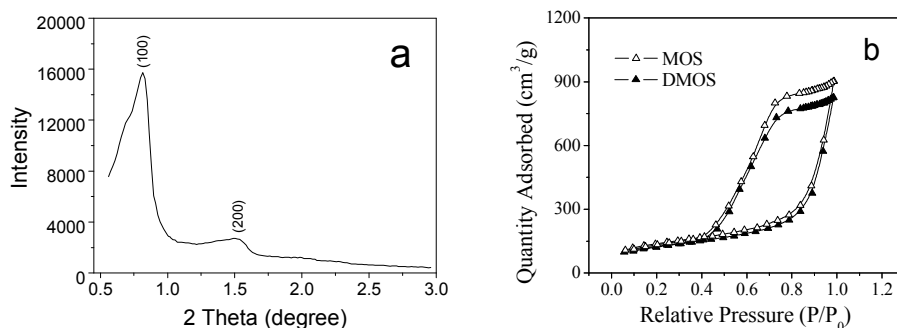


Fig. 2. (a) XRD pattern; (b) N₂ adsorption/desorption isotherms.

Small angle X-ray scattering data (Fig. 2 (a)) revealed that the DMOS possessed onion-like mesostructure.³³ Two peaks at $2\theta=0.82$ and 1.51 were attributed to the characteristic (100) and (200) diffractions of the multilayer vesicular structure.³⁵ The N₂ adsorption/desorption isotherms of both MOS and DMOS are shown in Fig. 2 (b), and they were found to be the typical type IV,³⁶ which were consistent with the mesoporous material. The BET specific surface area of MOS was $476 \text{ m}^2/\text{g}$, and the BJH adsorption cumulative volume and pore size were calculated to be $1.29 \text{ cm}^3/\text{g}$ and 14.3 nm , respectively. The large pore size and pore volume benefited the accommodation of dopamine. After modification by dopamine, the BET specific surface area of DMOS was $431 \text{ m}^2/\text{g}$, and the pore volume and pore size were $1.19 \text{ cm}^3/\text{g}$ and 12.7 nm , respectively. Such pore sizes were large enough for the Cd^{2+} entering the internal structure of DMOS to promote the sorption capacity. Compared with unfunctionalized MOS, the specific surface area, cumulative volume and pore size of DMOS decreased observably, indicating the success of the modification.

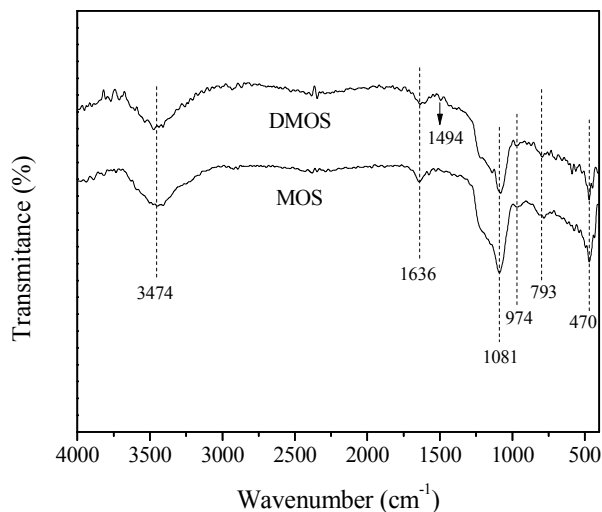


Fig. 3. FT-IR spectra of the MOS and DMOS.

The FT-IR spectra of MOS and DMOS are shown in Fig. 3. The peaks at 1081 cm^{-1} , 793 cm^{-1} and 470 cm^{-1} can be assigned to asymmetric stretching, symmetric stretching and bending vibration of Si-O-Si bonds from all of the samples, indicating that the structure of MOS was well preserved in DMOS.³⁷ The adsorption band at 974 cm^{-1} could be ascribed to symmetric stretching vibration of Si-OH groups.³⁸ The adsorption peaks at 3474 cm^{-1} and 1636 cm^{-1} were due to stretching and bending vibration of -OH, which suggested the presence of hydroxyl and H₂O in the MOS and DMOS.³⁹ Compared to the FT-IR spectrum of MOS, the peak at 1494 cm^{-1} of DMOS could be ascribed to the stretching of the benzene ring from dopamine.⁴⁰ This result confirmed that dopamine was successfully immobilized on the surface of MOS.

The above results validated that the dopamine functionalized MOS was successfully prepared. To the best of our knowledge, the exact interaction mechanism of dopamine with silica is not fully understood so far. In the previous study, we proposed that the interaction mechanism of dopamine with mesoporous silica was because of the H bonds formed by the catechols in polydopamine and the two distinct types of silanols on the surface of silica, as shown in Fig. 4.³²

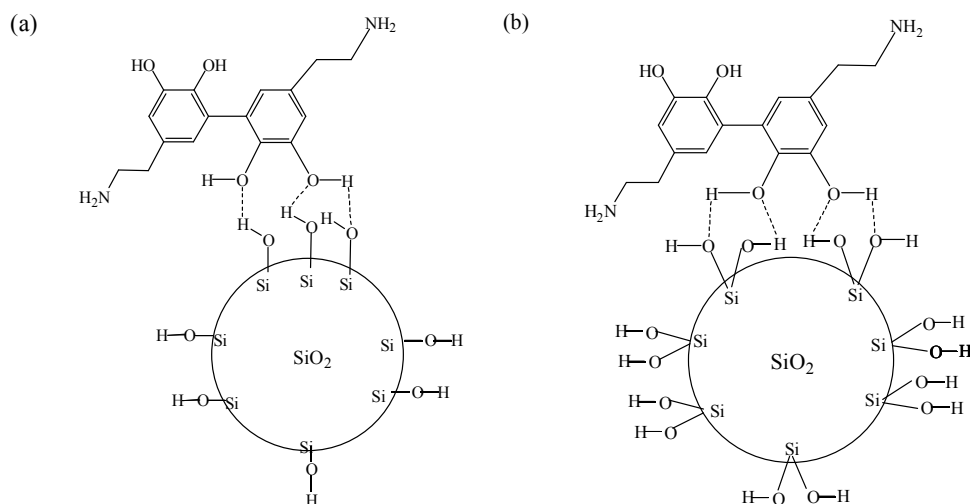


Fig. 4. The interaction mechanism of (a) isolated silanols and (b) geminal silanols on the surface of silica with catechol in polydopamine.³²

3.2 Sorption kinetics

Contact time is one of the most important parameters for metal ions adsorption, and it can be used to investigate the adsorption kinetics. The adsorbed amount of Cd^{2+} on DMOS versus time was studied at an initial Cd^{2+} concentration of 100 mg/L and a DMOS concentration of 0.4 g/L while the contact time varied from 5 to 420 min, and the results are shown in Fig. 5. It was observed that the adsorption equilibrium was reached within 90 min, and the sorption consisted of two stages. The Cd^{2+} uptake increased sharply in the first stage of 0-60 min, then rose slowly, and gradually reached equilibrium in the next step of 60-90 min. In the initial adsorption stage, the faster adsorption rate could be attributed to the larger number of binding sites on the surface of DMOS and the larger Cd^{2+} concentration gradient in the solution. In the second stage, the sorption mainly depended on the cadmium ions penetrating into the inside pores of DMOS, which needed more energy, therefore, the amount of Cd^{2+} adsorbed increased slowly.³² The experimental results showed that the sorption equilibrium could be reached within 90 min, and a contact time of 150 min was selected in subsequent experiments to ensure completeness of sorption.

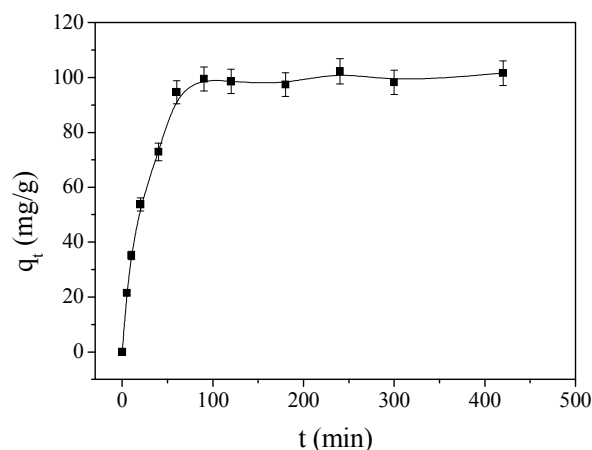


Fig. 5. The effect of contact time on the sorption of Cd^{2+} on DMOS; pH=6.0, T=298 K,

$$[\text{Cd}^{2+}]_{\text{initial}}=100 \text{ mg/L}, m_{\text{sorbent}}/V_{\text{solution}}=0.4 \text{ g/L}.$$

The adsorption rate of Cd^{2+} on DMOS were analyzed using the pseudofirst order and pseudosecond order kinetics models as shown in Eqs. (3) and (4):⁴¹

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where k_1 and k_2 are the rate constants of the pseudofirst order adsorption (min^{-1}) and pseudosecond order adsorption ($\text{g}/(\text{mg min})$), respectively.

The kinetic model parameters values of k_1 , k_2 and q_e were calculated from the slopes and intercepts of the straight lines (Fig. 6), and the results are presented in Table 1. Compared with the determination coefficient (R^2) of the pseudofirst order kinetic equation, the value of the R^2 of pseudosecond order kinetic equation was higher, and the value of q_e obtained from the pseudosecond order kinetic model was close to that determined experimentally (105 and 99 mg/g). Therefore, the adsorption process of Cd^{2+} on DMOS could be described by the pseudosecond order kinetic model.

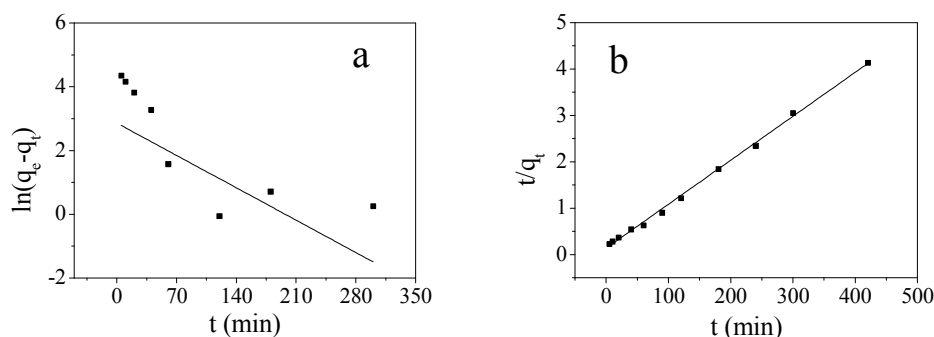


Fig. 6. The pseudofirst order (a) and pseudosecond order (b) kinetics for the Cd^{2+} sorption by DMOS.

Table 1 Kinetic parameters of Cd^{2+} adsorbed in DMOS.

Pseudofirst order			Pseudosecond order		
k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 (g/(mg min))	q_e (mg/g)	R^2
0.015	17.5	0.146	0.001	105	0.997

3.3 The effect of initial pH

The effect of the solution pH on the sorption of metal ions can be associated with its remarkable effect on the surface charge of the sorbent, the metal ionization and speciation in solution.⁴² Adsorption of Cd^{2+} by DMOS was studied at different initial pH values in the range of 2.0 to 6.0 at 298 K, DMOS concentration of 0.4 g/L for 150 min, and an initial cadmium concentration of 100 mg/L. Fig. 7 shows that the adsorption of Cd^{2+} on DMOS was pH-dependent. It could be seen that the amount of Cd^{2+} adsorbed was increased when the pH value of the solution increased from 2.0 to 6.0. At lower pH, the surface of DMOS was positively charged due to the protonation of the surface functional groups on DMOS, and the sorption capacity of cadmium were low because of the electrostatic repulsion.⁴² The low sorption capacity at lower solution pH values was also caused by the competition of hydrogen ions with Cd^{2+} for active binding sites.²³ With increasing the pH values of the solutions, the surface charge of DMOS was more negative, which was more favoured for the sorption of Cd^{2+} , and the sorption capacity obviously increased. When the pH of the solution was higher than 6.0, hydrolysis of cadmium ion occurred and resulted in the precipitation

of metal hydroxide, therefore it was difficult to distinguish between the precipitation and adsorption of cadmium ion removed from solutions.⁴³

Compared with the unmodified MOS, the adsorption capacity of Cd^{2+} by DMOS was dramatically improved by functionalization with dopamine. The meliorated performance of DMOS was mainly attributed to the excellent Cd^{2+} ion chelation ability of the functional groups on the surface of DMOS. Furthermore, the method used to modify MOS was simple, facile and cost-effective. Therefore, the DMOS has great potential for widespread practical applications.

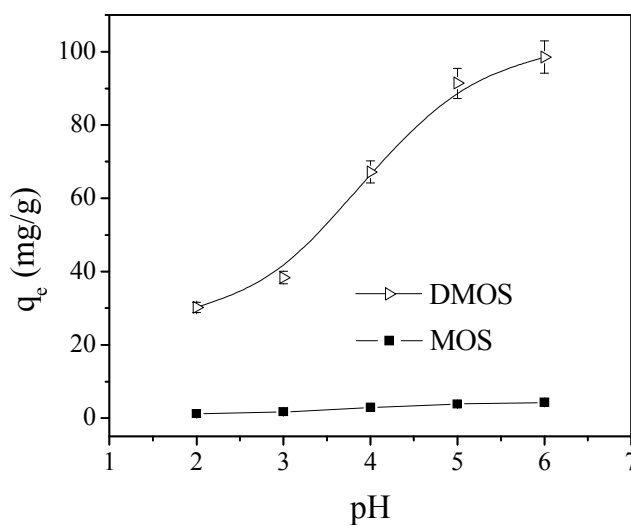


Fig. 7. The effect of initial pH on the sorption of Cd^{2+} on MOS and DMOS; $T=298\text{ K}$,

$$[\text{Cd}^{2+}]_{\text{initial}}=100\text{ mg/L}, m_{\text{sorbent}}/V_{\text{solution}}=0.4\text{ g/L}.$$

3.4 The sorption isotherm

To inspect the sorption capacity of DMOS for Cd^{2+} and the detailed adsorption characteristics, aqueous solutions with DMOS dosage of 0.6 g/L and varying initial Cd^{2+} concentrations from 10 to 300 mg/L, were used to determine the adsorption isotherm. The adsorption isotherm of Cd^{2+} on DMOS is shown in Fig. 8. With the increasing equilibrium cadmium ion concentration, the amount of Cd^{2+} adsorbed increased, and the maximum adsorption capacity of DMOS was 107 mg/g. The sorption capacity of Cd^{2+} by DMOS was also compared with other adsorbents, as shown in Table 2. Though the sorption capacity of DMOS was not the largest one, the

method used to functionalize MOS in this work was simple, facile and cost-effective. Therefore, the DMOS had greater potential for practical applications. Moreover, the performance of DMOS was competitive, and this was mainly attributed to that the functional groups on the surface of DMOS had excellent ability of chelation with Cd^{2+} ions and the large surface areas of DMOS.

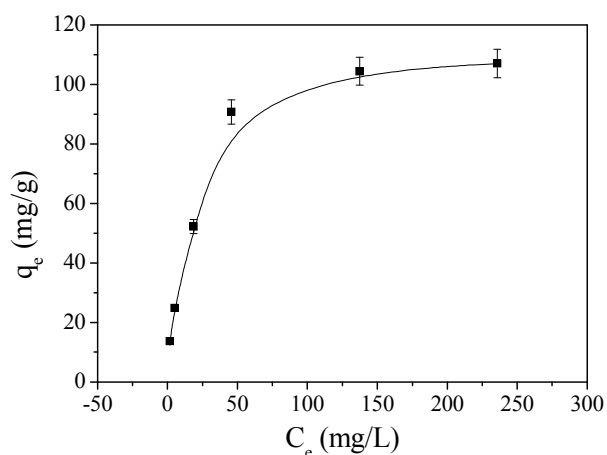


Fig. 8. The sorption isotherms of Cd^{2+} on DMOS; pH=6.0, T=298 K, $m_{\text{sorbent}}/V_{\text{solution}}=0.6$ g/L.

Table 2 Comparison of DMOS with other adsorbents.

Adsorbent	Sorption capacity (mg/g)	Contact time (h)	References
DMOS	107	2	This work
XYPAL-SH	30	6	Liang et al. ¹⁷
MDA-magMCM-48	114	1.5	Anbia et al. ⁴⁴
HMS-NH ₂	28	24	Machida et al. ²⁴
Amine-functionalised SBA-15	41	2	McManamon et al. ⁶
Lignin	137	48	Mohan et al. ⁴⁵
MSEP-NT	35	24	Liang et al. ¹⁶
pMF	4	2	Li et al. ⁴⁶
BCSH	35	24	Bogusz et al. ⁴⁷
MDA-SBA-15	98	2	Shahbazi et al. ²³
MnO ₂ /o-MWCNTs	41.6	2.5	Luo et al. ⁴⁸
Bamboo Charcoal	12	6	Wang et al. ⁴⁹

NH ₂ -MCM-41	18	2	Heidari et al. ⁵⁰
Sulfonic-functionalized PDMS	100	24	Silva et al. ⁵¹

The adsorption data of Cd²⁺ on DMOS was analyzed with Langmuir and Freundlich models, and their linear equations are shown in Eqs. (5) and (6).³⁰

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (5)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

where q_m is the maximum adsorption capacity (mg/g). K_L is the Langmuir constant (mg/dm³). K_F is the Freundlich constant (dm³/mg), and n is the adsorption intensity.

The fitting curves of Langmuir and Freundlich models are shown in Fig. 9, and the fitting parameters of the two models were listed in Table 3.

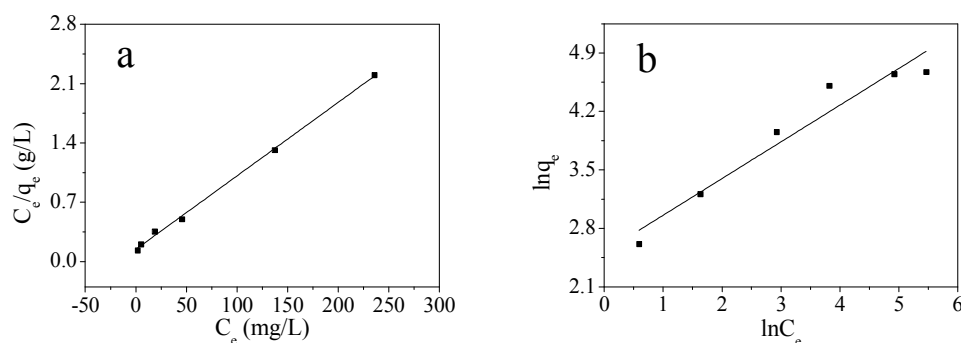


Fig. 9. Linearized (a) Langmuir model plot (Eq. (7)) and (b) Freundlich model plot (Eq. (8)) for the Cd²⁺ sorption by DMOS.

Table 3 Adsorption isotherm parameters of Cd²⁺ adsorbed on DMOS.

Model parameters	Langmuir			Freundlich		
	K_L	q_m (mg/g)	R^2	K_F	n	R^2
Value	0.061	115	0.997	12.4	2.28	0.928

The determination coefficient (R^2) value in Table 3 indicated that the sorption data of Cd²⁺ on DMOS fitted the Langmuir model ($R^2=0.997$) better than the Freundlich

equation ($R^2=0.928$). The calculated Langmuir adsorption capacity was 115 mg/g, which was close to the actual experimental adsorption capacity of 107 mg/g, confirming that the sorption data could be properly described by the Langmuir model. The Langmuir equation indicated that the adsorption of Cd^{2+} might occur at homogeneous binding sites of DMOS and formed a monolayer coverage of adsorbate.³⁰

The phenolic groups possessed chelation ability with a variety of metals,²⁸ therefore, one of the mechanisms of polydopamine on the surface of DMOS interaction with cadmium ions might be attribute to the bidentate chelating bonding in which two oxygen atoms bound to a cadmium, as illustrated in Fig. 10. Furthermore, Cd^{2+} is a borderline metal with ambivalent property that has the affinity with amino-functional groups,²³⁻²⁴ hence the amino ligands in the polydopamine could bind to cadmium ions as shown in Fig. 10.

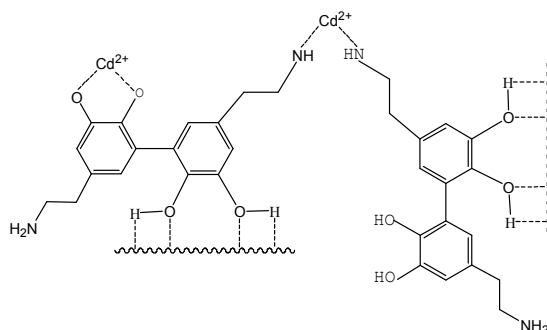


Fig. 10. The proposed interaction mechanism of polydopamine with Cd^{2+} .

3.5 The effect of the solid-to-liquid ratio

The solid-to-liquid ratio is another important parameter which represents the adsorptivity of the sorbent. The effect of solid-to-liquid ratio was investigated by varying the volume of solution from 25 to 500 mL. The total amounts of Cd^{2+} ions and DMOS in the solution were 2.5 mg and 10 mg, respectively, which were kept constant. As shown in Fig. 11, while the solid-to-liquid ratio decreased from 0.4 to 0.02 g/L, the adsorption amount of Cd^{2+} on DMOS declined from 96.7 to 82.0 mg/g. It was clear that the decrease of sorption capacity of DMOS was not significant even when the solid-to-liquid ratio changed greatly. The results indicated that the DMOS could still had excellent adsorption capacity even under the condition that the

concentration of cadmium ions was very low.

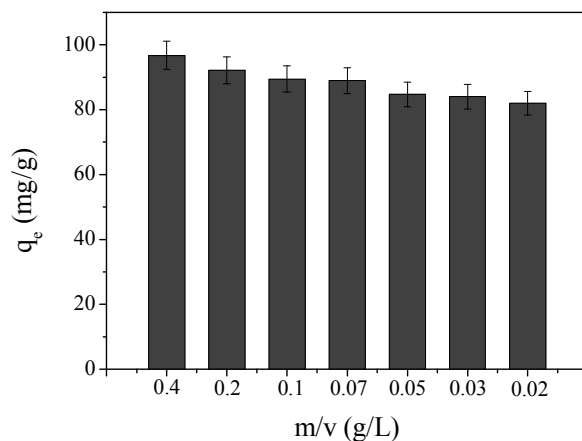


Fig. 11. The effect of the solid-to-liquid ratio on the Cd²⁺ sorption by DMOS. Total amount of Cd²⁺ was 2.5 mg in all solutions; m_{sorbent}=10mg, pH=6.0, T=298 K.

3.6 The effect of ionic strength

The effect of ionic strength on the Cd²⁺ adsorption by DMOS was investigated by changing the Na⁺ (NaNO₃) or K⁺ (KNO₃) concentrations of solution. The initial Cd²⁺ concentration and DMOS dose were 100 mg/L and 0.4 g/L, respectively, and the K⁺ and Na⁺ concentrations varied from 0.01 to 0.4 mol/L. The results are shown in Fig. 12. It could be seen that with increasing Na⁺ or K⁺ concentrations, the sorption amount of Cd²⁺ decreased from 101 to 87.8 mg/g or 101 to 88.5 mg/g, respectively. Therefore, the coexisting Na⁺ or K⁺ ions had no obvious influence on the adsorption of Cd²⁺ on DMOS. The possible explanation for this result could be that the phenolic groups on the surface of DMOS possessed more excellent chelation capacity with polyvalent metal ions than monovalent ones. Moreover, the competition between Na⁺ (K⁺) ions and Cd²⁺ ions for the active sites on DMOS and the decrease of activity of cadmium ions induced by increased ionic strength might also be responsible for the decline of Cd²⁺ sorption capacity.⁵²

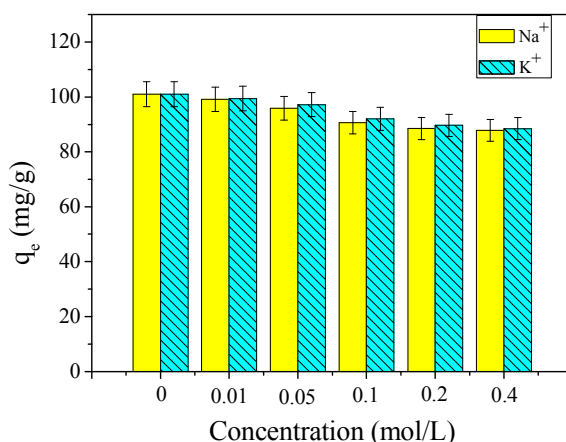


Fig. 12. The effect of K^+ and Na^+ concentrations on the sorption of Cd^{2+} on DMOS; pH=6.0,

$$T=298 \text{ K}, [Cd^{2+}]_{\text{initial}}=100 \text{ mg/L}, m_{\text{sorbent}}/V_{\text{solution}}=0.4 \text{ g/L}.$$

3.7 Desorption and reusability

For practical applications, the regeneration and reuse of sorbent is necessary. As illustrated in Fig. 7, the adsorption amount of Cd^{2+} was low at low pH, which indicated that the cadmium ions could be desorbed by acidic solution. The 0.1 M HNO_3 solution was used as the desorption agent to regenerate the spent sorbent. The results are shown in Fig. 13. The decrease of adsorption capacity of DMOS might be caused by the irreversible occupation of part adsorption sites or the loss of the sorbent.¹² However, the Cd^{2+} adsorption capacity of regenerated DMOS still remained 86.5% after ten adsorption-desorption cycles. Therefore, the DMOS offers the possibility to be used as reusable and recyclable sorbents for the removal of Cd^{2+} ions.

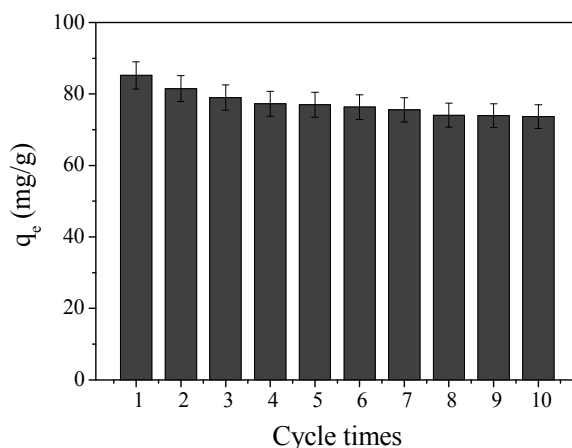


Fig. 13. Adsorption capacity of Cd²⁺ by DMOS in adsorption-desorption cycles; pH=6.0, T=298

K, [Cd²⁺]_{initial}=100 mg/L, m_{sorbent}/V_{solution}=0.5 g/L.

4 Conclusions

In summary, a simple, facile and cost-effective method was used to synthesize dopamine-functionalized mesoporous silica (DMOS), and the adsorption capacity of Cd²⁺ by DMOS was dramatically enhanced in comparison with MOS. The sorption equilibrium time was 90 minutes and the influence of the solid-to-liquid ratio and ionic strength on the sorption was very weak. Importantly, the DMOS could be easily regenerated by 0.1 M HNO₃ solution, and it still remained high adsorption capacity after ten adsorption-desorption cycles. Taken together, the DMOS exhibited great potential as an excellent adsorbent for practical applications in Cd²⁺ removal from waste water. Moreover, because the polydopamine had favorable ability to coordinate with a variety of metals,²⁸⁻²⁹ the DMOS could be used to adsorb other heavy metal ions in the environmental remediation.

Acknowledgement

The authors are grateful for financial support by the Scientific Research Foundation of Zhejiang Ocean University.

References

- [1] M.M. Matlock, B.S. Howerton and D.A. Atwood, *Water Res.*, 2002, 36, 4757-4764.
- [2] M.J. González-Muñoz, M.A. Rodríguez, S. Luque and J.R. Álvarez, *Desalination*, 2006, 200,

742-744.

- [3] Y. Zhao, Q. Gao, T. Tang, Y. Xu and D. Wu, *Mater. Lett.*, 2011, 65, 1045-1047.
- [4] J. Aguado, J.M. Arsuaga, A. Arencibia, M. Lindo and V. Gascon, *J. Hazard. Mater.*, 2009, 163, 213-221.
- [5] L. Hajiaghbabaei, A. Badieli, M.R. Ganjali, S. Heydari, Y. Khaniani and G.M. Ziarani, *Desalination*, 2011, 266, 182-187.
- [6] C. McManamon, A.M. Burke, J.D. Holmes and M.A. Morris, *J. Colloid. Interf. Sci.*, 2012, 369, 330-337.
- [7] C.S. Barton, D.I. Stewart, K. Morris and D.E. Bryant, *J. Hazard. Mater.*, 2004, 116, 191-204.
- [8] T.M. Zewail and N.S. Yousef, *Alex.Eng.J.*, 2015, 54, 83-90.
- [9] W.-P. Zhu, J. Gao, S.-P. Sun, S. Zhang and T.-S. Chung, *J. Membr. Sci.*, 2015, 487, 117-126.
- [10] J. Gao, S.P. Sun, W.P. Zhu and T.S. Chung, *Water Res.*, 2014, 63, 252-261.
- [11] H. Zhang, M. Xu, H. Wang, D. Lei, D. Qu and Y. Zhai, *Colloids Surf., A.*, 2013, 435, 78-84.
- [12] S. Zhang, Y. Zhang, G. Bi, J. Liu, Z. Wang, Q. Xu, H. Xu and X. Li, *J. Hazard. Mater.*, 2014, 270, 27-34.
- [13] P. Wang, M. Du, H. Zhu, S. Bao, T. Yang and M. Zou, *J. Hazard. Mater.*, 2015, 286, 533-544.
- [14] M. Barczak, K. Michalak-Zwierz, K. Gdula, K. Tyszczyk-Rotko, R. Dobrowolski and A. Dąbrowski, *Micropor. Mesopor. Mat.*, 2015, 211, 162-173.
- [15] X. Zhang, Q. Huang, M. Liu, J. Tian, G. Zeng, Z. Li, K. Wang, Q. Zhang, Q. Wan, F. Deng and Y. Wei, *Appl. Surf. Sci.*, 2015, 343, 19-27.
- [16] X. Liang, Y. Xu, G. Sun, L. Wang, Y. Sun, Y. Sun and X. Qin, *Chem. Eng. J.*, 2011, 174, 436-444.
- [17] X. Liang, Y. Xu, X. Tan, L. Wang, Y. Sun, D. Lin, Y. Sun, X. Qin and Q. Wang, *Colloids Surf., A.*, 2013, 426, 98-105.
- [18] M. Addy, B. Losey, R. Mohseni, E. Zlotnikov and A. Vasiliev, *Appl. Clay Sci.*, 2012, 59-60, 115-120.
- [19] E. Da'na, N. De Silva and A. Sayari, *Chem. Eng. J.*, 2011, 166, 454-459.
- [20] E.Y. Jeong, M.B. Ansari, Y.H. Mo and S.E. Park, *J. Hazard. Mater.*, 2011, 185, 1311-1317.
- [21] X. Huang, X. Liao and B. Shi, *J. Hazard. Mater.*, 2010, 173, 33-39.
- [22] E. Da'na and A. Sayari, *Chem. Eng. J.*, 2011, 166, 445-453.
- [23] A. Shahbazi, H. Younesi and A. Badieli, *Chem. Eng. J.*, 2011, 168, 505-518.
- [24] M. Machida, B. Fotoohi, Y. Amamo, T. Ohba, H. Kanoh and L. Mercier, *J. Hazard. Mater.*, 2012, 221-222, 220-227.
- [25] J. Chung, J. Chun, J. Lee, S.H. Lee, Y.J. Lee and S.W. Hong, *J. Hazard. Mater.*, 2012, 239-240, 183-191.
- [26] Y. Xie, J. Wang, M. Wang and X. Ge, *J. Hazard. Mater.*, 2015, 297, 66-73.
- [27] H. Lee, S.M. Dellatore, W.M. Miller and P.B. Messersmith, *Science*, 2007, 318, 426-430.
- [28] J. Guo, Y. Ping, H. Ejima, K. Alt, M. Meissner, J.J. Richardson, Y. Yan, K. Peter, D. von Elverfeldt, C.E. Hagemeyer and F. Caruso, *Angew. Chem.*, 2014, 53, 5546-5551.
- [29] Q. Ye, F. Zhou and W. Liu, *Chem. Soc. Rev.*, 2011, 40, 4244-4258.
- [30] Y. Yu, J.G. Shapter, R. Popelka-Filcoff, J.W. Bennett and A.V. Ellis, *J. Hazard. Mater.*, 2014, 273, 174-182.
- [31] A. Nematollahzadeh, S. Seraj and B. Mirzayi, *Chem. Eng. J.*, 2015, 277, 21-29.
- [32] J.K. Gao, L.A. Hou, G.H. Zhang and P. Gu, *J. Hazard. Mater.*, 2015, 286, 325-333.
- [33] S.-H. Jun, J. Lee, B.C. Kim, J.E. Lee, J. Joo, H. Park, J.H. Lee, S.-M. Lee, D. Lee, S. Kim, Y.-M.

- Koo, C.H. Shin, S.W. Kim, T. Hyeon and J. Kim, *Chem. Mater.*, 2012, 24, 924-929.
- [34] J. Gao, Q. Wang, Y. Jiang, J. Gao, Z. Liu, L. Zhou and Y. Zhang, *Ind. Eng. Chem. Res.*, 2015, 54, 83-90.
- [35] C. Yu, J. Fan, B. Tian, G. D. Stucky and D. Zhao, *J. Phys. Chem. B*, 2003, 107, 13368-13375.
- [36] V. Hernández-Morales, R. Nava, Y.J. Acosta-Silva, S.A. Macías-Sánchez, J.J. Pérez-Bueno and B. Pawelec, *Micropor. Mesopor. Mat.*, 2012, 160, 133-142.
- [37] P.-Y. Hoo and A.Z. Abdullah, *Chem. Eng. J.*, 2014, 250, 274-287.
- [38] V. Brahmkhatri and A. Patel, *Appl. Catal. A: Gen.*, 2011, 403, 161-172.
- [39] Y. Jiang, Y. Wang, H. Wang, L. Zhou, J. Gao, Y. Zhang, X. Zhang, X. Wang and J. Li, *New J. Chem.*, 2015, 39, 978-984.
- [40] Y. Zheng, L. Zhang, J. Shi, Y. Liang, X. Wang and Z. Jiang, *Micropor. Mesopor. Mat.*, 2012, 152, 122-127.
- [41] Q. Yuan, N. Li, Y. Chi, W. Geng, W. Yan, Y. Zhao, X. Li and B. Dong, *J. Hazard. Mater.*, 2013, 254-255, 157-165.
- [42] M. Anbia and A.H. Davijani, *Chem. Eng. J.*, 2013, 223, 899-907.
- [43] H. Gao, Y. Sun, J. Zhou, R. Xu and H. Duan, *ACS Appl. Mater. Inter.*, 2013, 5, 425-432.
- [44] M. Anbia, K. Kargoshab, S. Khoshbooeic, *Chem. Eng. Res. Des.*, 2015, 93, 779-788.
- [45] D. Mohana, C. U. Pittman Jr., P. H. Steeleb, *J. Colloid Interf. Sci.*, 2006, 297, 489-504.
- [46] C. Li, H. Duan, X. Wang, X. Meng and D. Qin, *Chem. Eng. J.*, 2015, 262, 250-259.
- [47] A. Bogusz, P. Oleszczuk and R. Dobrowolski, *Bioresour. Technol.*, 2015, 196, 540-549.
- [48] C. Luo, R. Wei, D. Guo, S. Zhang and S. Yan, *Chem. Eng. J.*, 2013, 225, 406-415.
- [49] F. Y. Wang, H. Wang and J. W. Ma, *J. Hazard. Mater.*, 2010, 177, 300-306.
- [50] A. Heidaria, H. Younesia and Z. Mehrabanb, *Chem. Eng. J.*, 2009, 153, 70-79.
- [51] F. A.B. Silva, F. L. Pissetti, *J. Colloid Interf. Sci.*, 2014, 416, 95-100.
- [52] X. Wang, G. Zhu and F. Guo, *Ann. Nucl. Energy.*, 2013, 56, 151-157.

A mesoporous material (DMOS), prepared by grafting polydopamine onto meso-structured silica (MOS), was developed as a sorbent to sequestrate Cd^{2+} .

