A small molecular fluorescent sensor functionalized silica microsphere for detection and removal of mercury, cadmium, and lead ions in aqueous solutions

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Abstract

In this paper, we report a sensitive fluorescent sensor (**FSCHP**) for detection and removal of toxic metal ions (Cd^{2+} , Hg^{2+} and Pb^{2+}) in aqueous samples. **FSCHP** is a 2,2-dipicolylamine (DPA) modified naphthalimide fluorophore followed by immobilization to the surface of silica microsphere and support high affinity for Cd^{2+} , Hg^{2+} and Pb^{2+} . Metal adsorption by **FSCHP** was featured by an enhancement in its fluorescence intensity. The limit of detection of 36 nM for Cd^{2+} , 48 nM for Hg^{2+} , and 39 nM for Pb^{2+} , was measured respectively. Moreover, **FSCHP** can also be used as adsorbent for the separation of toxic metal ions in the contaminated aqueous solution with high adsorptivity, and can be regenerated by acid treatment. The metal ion removal capacity of **FSCHP** was retained after five removal/regeneration cycles.

Keywords:

Fluorescent sensor; Heavy metal ions; Detection; Removal; Reusable

1. Introduction

Cadmium, mercury, and lead are naturally occurring toxic heavy metals in air, water and soil [1, 2], they are not biodegradable, and accumulate in the environment. These toxic metals enter human body through contaminated food or water, and cause damages to the cardiovascular system, the nervous system, the immune system and organs including kidney, lungs, liver, etc. [3-7] Therefore, the heavy metal pollution has attracted intensive attention since last century [3]. The Food and Agriculture Organization (FAO), Environmental Protection Agency (EPA) and World Health Organization (WHO) have regulated the concentration limits of these metals in food and drinking water [2, 4].

Sensitive detection of heavy metals plays a key role in the control of heavy metal pollution, atomic absorption spectrometry [5] and inductively coupled plasma mass spectrometry [6] are the most common methods used to detect toxic metals (Cadmium, Lead and Mercury). On the other hand, removal of toxic metals from contaminated water is necessary to remedy the heavy metal pollutions. Nowadays, some techniques have been developed to separate toxic metals from various samples, such as, redox co-precipitation, chemical deposition, ion displacement, membrane filtering, absorption technique and solid-phase extraction [7-14].

Fluorometry is a convenient method for simply, accurately and rapidly tracking metal ions in biological and environmental samples [2, 15-17]. In recent years, small molecule fluorescent probes for heavy metal ions have flourished in detection of metal ions. However, they are incapable of removing of heavy metal ions upon

recognition due to their diffusive nature. Therefore, immobilization of a small molecule probe to a solid surface to prepare heterogeneous fluorescent sensors has been an ongoing interest of the field [18-25]. Previously, we reported a bifunctional fluorescent sensor for sensing and separating Hg^{2+} [26], it can detect trace mercury ions in aqueous sample, and can be used as an adsorbent to remove mercuric ions from contaminated aqueous sample. Herein, we report our recent progress in improvement of the detection sensitivity, adsorptivity and regeneration capability of new bifunctional fluorescent sensor.

With good affinity to Zn^{2+} , 2,2-dipicolylamine (DPA) unit and its derivatives have been the most widely used receptors for zinc ions since 1996 [27]. DPA and its derivatives can also chelate with various heavy metal ions and have been harnessed by some fluorescent sensors to detect Cd^{2+} , Pb^{2+} or Cu^{2+} [28-34]. We envisage that DPA derivatives might be a versatile receptor for heavy metal ions, which can be used to develop a fluorescent sensor for detect and remove these ions. In this work, we have prepared a novel heterogeneous reusable assembly (**FSCHP**) for detection/removal of toxic metal ions, i.e. mercury, cadmium, and lead ions, by conjugate ion, N,N'-bis(pyridin-2-ylmethyl)ethane-1,2-diamine modified naphthalimide fluorophore onto the surface of silica microsphere.

Scheme 1. Plausible mechanism of bifunctional fluorescent sensor **FSCHP** for the detection and removal of toxic metal ions.

2.Experimental

2.1. Materials and instruments

Dimethylformamide were purified by reduced pressure distillation; other solvents were purchased from TCI Co or J&K Co. Tetraethoxysilane (TEOS); aminopropyltriethoxysilane was purchased from TCI Co. ^1H NMR spectra; ^{13}C NMR spectra were recorded in CDCl_3 at $25\text{ }^\circ\text{C}$ on a Bruker AV-400 spectrometer. All pH titration were carried out by using a pH-Meter PB-10. Elemental analysis was analyzed with a Germany Elementar Vario EL III. Concentrations of metal ions were determined by a Varian 710ES Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

SEM images of the microsphere were taken by Hitachi S-520 scanning electron microscopy to assess the size and shape of the microsphere samples. Dynamic light scattering (DLS) was measured by an ALV/CGS-5022F from ALV Ltd. (German).

2.2. Preparation

The synthetic route of bifunctional fluorescent sensor **FSCHP** is depicted in Scheme 2.

Scheme 2. Preparation of bifunctional fluorescent sensor **FSCHP**.

2.2.1. Synthesis of compound 1

Compound **2** (100 mg, 0.179 mmol) and aminopropyltriethoxysilane (38 mg, 0.172 mmol) were dissolved in 5 mL of anhydrous DMF and heated to 60 °C for 1 h under nitrogen atmosphere. Then the solvent was removed by rotary evaporation and the residue was directly purified by flash column chromatography (silica gel, CH₂Cl₂/CH₃OH = 30/1, v/v) to provide **1** (50 mg, 38.3 %) as the yellow powder. m.p. > 300 °C. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 8.60 (d, *J* = 7.2 Hz, 1H), 8.56 (d,

$J = 4.8$ Hz, 2H), 8.25 (d, $J = 8.4$ Hz, 1H), 8.17 (d, $J = 8.8$ Hz, 1H), 7.61~7.71 (m, 3H), 7.45 (d, $J = 8.0$ Hz, 2H), 7.16 (t, $J = 6.0$ Hz, 2H), 7.05 (d, $J = 8.4$ Hz, 2H), 6.73 (d, $J = 8.4$ Hz, 2H), 6.77 (d, $J = 8.4$ Hz, 2H), 5.77 (br, 1H, -NH-), 3.92 (br, 1H, -NH-), 3.91 (s, 4H), 3.87 (q, $J = 7.2$ Hz, 6H), 3.83~3.88 (m, 2H), 3.20 (t, $J = 5.6$ Hz, 2H), 2.90 (t, $J = 5.6$ Hz, 2H), 1.91~1.98 (m, 2H), 1.26 (t, $J = 7.2$ Hz, 9H), 0.82 (t, $J = 8.0$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 166.31, 164.73, 159.13, 149.72, 149.11, 148.42, 136.62, 134.79, 131.38, 130.29, 129.13, 126.24, 124.93, 124.53, 123.56, 123.26, 122.24, 120.43, 113.06, 110.32, 104.25, 60.34, 58.65, 53.43, 52.83, 45.75, 41.71, 22.10, 18.33, 7.92. IR (KBr, cm^{-1}): 3375, 2925, 1656, 1582, 1363, 1260, 1112, 910. HRMS (EI): calculated for 732.3455, found 732.3450. Compound **2** was prepared according to the reported procedure [35].

2.2.2. Synthesis of silica microsphere

The silica microsphere was prepared via a modified Stöber–Van Blaaderen method [36, 37]. TEOS (1 mL, 2.7 mmol) in aqueous solution (10 mL) was added to ammonia solution (50 mL, 1%) slowly for 5 h in a 35 $^\circ\text{C}$ thermostated vessel. After stirring for 8 h, the reaction mixture was centrifuged to remove the remaining reagents. The particles were washed with 75% alcohol and ultrapure water. IR (KBr, cm^{-1}): 3650, 3415, 1050, 760.

2.2.3. Preparation of the fluorescent sensor (*FSCHP*)

Compound **1** (37 mg, 0.05 mmol) and as-synthesized silica microsphere (activated in vacuum drier at 130 $^\circ\text{C}$ for 24 h) were added to a solution of toluene (20 mL) and DMF (5 mL). The mixture was stirred and refluxed for 24 h under argon atmosphere.

After that, the microsphere was washed and centrifugated for at least five times, until the UV/Vis spectrum of the supernate showed the absence of absorption in 300 nm~800 nm. The fluorescent sensor **FSCHP** was then obtained, and elemental analysis revealed C and N of 35 mg and 6.0 mg per 1 g of **FSCHP**, respectively. IR (KBr, cm^{-1}): 3415, 2950, 1645, 1560, 1363, 1100, 750.

2.3. Fluorescence detection of Cd^{2+} , Pb^{2+} and Hg^{2+} by **FSCHP**

$\text{Hg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$, $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ were of analytical grade, and the stock solutions of different metal ions were prepared with ultrapure water.

The concentration of **1** was calculated to be 3.6×10^{-5} M for a suspension of 5 mg of the **FSCHP** in 10 mL of water solution. After **FSCHP** (5 mg) was suspended in aqueous solution (10 mL), the emission spectra of the suspension with different concentrations of Cd^{2+} , Pb^{2+} and Hg^{2+} were obtained upon excitation at 450 nm. All the measurements were repeated three times and the general average was obtained.

2.4. Adsorption of Cd^{2+} , Pb^{2+} and Hg^{2+}

Adsorption capacity of **FSCHP** was investigated by following steps: a 5 mg of **FSCHP** was mixed in 10 mL of aqueous solution with different concentrations of Cd^{2+} , Hg^{2+} and Pb^{2+} in centrifuge tubes. After the mixture was dispersed by mechanically shaking for several seconds at room temperature, the tubes were centrifuged for 5 min in centrifuge and 1 mL of supernatant was pipetted to measure the concentration of metal ions. The adsorption capacity of **FSCHP** was then calculated.

The equilibrium adsorption capacity (Q_e , mg/g) and the adsorptivity (the percentage

of metal ions removed from the solution) can be calculated by the following equations:

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

$$\text{adsorptivity} = \frac{(C_0 - C_e)}{C_0} \times 100\%$$

Where C_0 (mg L^{-1}) and C_e (mg L^{-1}) are the initial and equilibrium concentrations of toxic heavy metal ions, respectively. V (L) is the solution volume and m (g) is the mass of the adsorbent.

3. Results and discussion

3.1. Characterization of microspheres

FSCHP was prepared by immobilization of the silanized small molecular probe as a precursor onto the surface of silica microspheres. The form of the **FSCHP** microspheres was examined by Scanning Electron Micrographs (SEM). **FSCHP** particles were spherical in shape (Fig. 1) with an average diameter of *ca.* 0.8 μm (Fig. S1, analyzed by dynamic light scattering).

Fig. 1. Scanning electron micrograph of **FSCHP**.

3.2. Fluorescence properties of **FSCHP**

The fluorescence stability against acidity is an important property of a sensor [38]. As shown in Fig. 2, the fluorescence of **FSCHP** was minimal in basic environment presumably due to PET mechanism. A fluorescence enhancement was observed when the solution pH go below *ca.* 3. At this point, the electron donating nitrogen atoms are all protonated and the PET processes are inhibited. It shows that the property of **FSCHP** will not be affected in a wide range of pH (pH 3~10).

Fig. 2. Changes of fluorescence intensity of **FSCHP** under different pH (adjusted by 1 M HCl or 1 M NaOH) in water solution. Conditions: [**FSCHP**] = 0.5 mg mL⁻¹, λ_{ex} = 450 nm, λ_{em} = 550 nm, 25°C, water.

The signal responses of **FSCHP** toward Cd²⁺, Pb²⁺ and Hg²⁺ were shown in Fig. 3.

With the addition of metal ions (Cd^{2+} , Pb^{2+} or Hg^{2+}), the fluorescence intensity increased linearly in low concentrations of metal ions. The **FSCHP** exhibited 4.6-fold fluorescence enhancement upon Cd^{2+} . Upon addition of Cd^{2+} (0~10 μM), the fluorescence intensity of **FSCHP** almost increased linearly (Fig. 3b). The limit of detection [26, 39], was found to be 3.6×10^{-8} M. **FSCHP** have similar property to Pb^{2+} and Hg^{2+} (Fig. S3, S4), and the limit of detection is 4.8×10^{-8} M for Hg^{2+} , and 3.9×10^{-8} M for Pb^{2+} , respectively. The Job's plot showed that the coordination form of **1** with Cd^{2+} or Hg^{2+} ion was 1:1, and the association constant of **FSCHP**- M^{2+} is 2.27×10^7 M^{-1} (for Cd^{2+}) or 4.36×10^7 M^{-1} (for Hg^{2+}) [40, 41].

Fig. 3. a) Fluorescence spectra of **FSCHP** upon addition of Cd(II), Inset: Change of intensity plots of **FSCHP** vs different concentration of Cd(II). b) Fluorescence response of **FSCHP** as a function of Cd(II) (0-10 μ M). Condition: [**FSCHP**] = 0.5 mg mL⁻¹, λ_{ex} = 450 nm, 25 °C, pH = 7.0 (adjusted by 0.1 M Tris-HCl buffer solution).

3.3. Adsorption kinetics

As one of the main properties of newly prepared absorbing material towards the metal ions, the interaction time very important to exhibit the efficiency of absorbing materials [42]. Therefore, we investigated the profile of the adsorption capacity of **FSCHP** in the different adsorption time. **FSCHP** (2.5 mg) was added to water solution (5 mL) containing different concentrations of metal ions (1×10^{-6} , 1×10^{-5} , 1×10^{-4} M) of Cd²⁺, Pb²⁺ or Hg²⁺, respectively, and the mixed solution was oscillated for different times (0.5~3 min). Then the mixture was centrifuged and the supernate was pipetted off for determination of remaining concentration of metal ions. The concentrations of metal ions (Cd²⁺, Pb²⁺ and Hg²⁺) were measured by ICP-AES. As shown in Fig. 4, **FSCHP** could adsorb Cd²⁺ very quickly (less than 30 sec), and there is negligible variation of the **FSCHP** toward Cd²⁺ in different adsorption time (0.5~3 min). And similar results were found for Hg²⁺ and Pb²⁺ (Fig. S5), respectively. The non-functionalized silica microspheres have no adsorption ability to Cd²⁺, Hg²⁺ and Pb²⁺ as control. The results demonstrated that **FSCHP** has high affinity and short response time toward toxic metals ions, which can be used for rapid separation of toxic metals ions from aqueous system.

Fig. 4. Effect of adsorption time on Cd(II) adsorption onto **FSCHP** microspheres (initial metal ion concentration: 1×10^{-6} , 1×10^{-5} , 1×10^{-4} M, $[\text{FSCHP}] = 0.5 \text{ mg mL}^{-1}$, pH = 7.0 (adjusted by 0.1 M Tris-HCl solution).

3.4. Fluorescence response for different initial concentrations of metal ions and adsorption isotherm

The relationship between the fluorescence responses toward metal ions and the adsorptivity of **FSCHP** is shown in Fig. 5 and Fig. S6. As shown in Fig. 5, as the concentration of cadmium ions increased in the solution, the fluorescence intensity at 550 nm enhanced by 4.6-fold. Meanwhile, and the adsorption capacity of **FSCHP** was estimated to be ca. 7.5 mg/g for Cd^{2+} . Note that we can monitor the equilibrium adsorption capacity of **FSCHP** from the fluorescence fluctuation. Similar results are shown in Fig. S6 for Hg^{2+} and Pb^{2+} ions, respectively. Besides, the saturated adsorption capacity (Q_{max}) of Cd^{2+} and Hg^{2+} were found to be related to the content of compound **1** (from elemental analysis) in **FSCHP**. That is, the adsorption capacity of

FSCHP is related to the content of **1** onto the surface of **FSCHP** microsphere. The saturated adsorption capacity ($Q_{\max}$) of **FSCHP** of Cd^{2+} , Hg^{2+} and Pb^{2+} is shown in Table 1. The data of $Q_{\max}$ were found at the initial M^{2+} concentration of 0.1 mM.

Fig. 5. Adsorption isotherms and fluorescence response of **FSCHP** microspheres for Cd(II) ions with different concentrations in water at room temperature. [**FSCHP**] = 0.5 mg mL^{-1} , $\text{pH} = 7.0$ (adjusted by 0.1 M Tris-HCl solution). I_0 is the initial fluorescence intensity of this system.

Table 1.

The saturated adsorption capacity of **FSCHP**.

	Cd^{2+}	Pb^{2+}	Hg^{2+}
$Q_{\max} (\text{mg/g})$	7.5	11.0	14

The change of concentrations of Cd^{2+} , Hg^{2+} and Pb^{2+} ions before and after adsorption with **FSCHP** was further investigated. As shown in Fig. 6, with the

increased concentration of Cd^{2+} , the adsorptivity of **FSCHP** declined significantly, but the equilibrium adsorption capacity enhanced very quickly. When the cadmium ions concentration reduced to 10 μM , the adsorptivity of **FSCHP** for Cd^{2+} reaches to 96%. When the concentration of Cd^{2+} ions reached to 30 μM , the equilibrium adsorption capacity raised to 5.8 mg g^{-1} . However, the adsorptivity of **FSCHP** for cadmium is only 86%. Similar results were found for Hg^{2+} and Pb^{2+} ions when **FSCHP** was used as the adsorbent (Fig. S7). Since the concentration of Cd^{2+} , Hg^{2+} and Pb^{2+} ions in real water samples is very low, a higher adsorptivity can be achieved by use of a small amount of **FSCHP** (0.5 g L^{-1}) when the concentration of toxic metal ions is less than 30 μM . And when the concentration of metal ions less than 10 μM , **FSCHP** can achieve very high adsorptivity ($>95\%$).

Fig. 6. Adsorption isotherms (the amount of Cd(II) adsorbed by **FSCHP** (0.5 mg mL^{-1}))

for different concentrations of Cd(II)) and adsorptivity of **FSCHP** (0.5 mg mL⁻¹) for different concentrations of Cd(II)) of **FSCHP** in water at room temperature. pH = 7.0 (adjust by 0.1 M Tris-HCl solution).

The adsorption behavior of **FSCHP** for Cd²⁺, Hg²⁺ and Pb²⁺ was analyzed by Langmuir model, where $Q_{\max}$ is the saturation adsorption capacity of the material's surface and b is a constant related to the intensity of adsorption[43]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\max} b} + \frac{C_e}{Q_{\max}}$$

Fitting of C_e/Q_e against C_e showed a straight line in Fig. 7 and Fig. S8. The adsorption isotherm behavior of Cd²⁺, Pb²⁺ or Hg²⁺ onto **FSCHP** fits the Langmuir equation well: The model fit parameter (R^2) was 0.9998 for Cd²⁺, 0.9997 for Hg²⁺ and 0.997 for Pb²⁺, respectively. The calculated parameters $Q_{\max}$ are consistent with the real saturation adsorption capacity, as is shown in Table 1.

Fig. 7. Langmuir plot for the sorption of Cd(II) using **FSCHP**.

3.5. Effect of solution pH

The impact of the solution pH on the adsorption capacity of the **FSCHP** microspheres for Cd^{2+} , Pb^{2+} and Hg^{2+} is shown in Fig. 8. **FSCHP** has a good adsorption capacity for Cd^{2+} , Pb^{2+} and Hg^{2+} ions in the range of pH 5~8. As the solubility products pK_{SP} of $\text{Pb}(\text{OH})_2$ are 14.84, considering the prevention of the precipitation of metal hydroxides, we measure the **FSCHP**'s adsorption capacity for Pb^{2+} ions at $\text{pH} < 5.5$ [44, 45]. When the solution's pH is below 4.5, the adsorption capacity of **FSCHP** for Cd^{2+} , Pb^{2+} and Hg^{2+} ions reduces rapidly with the decrease of pH. Hence we can desorb the Cd^{2+} , Pb^{2+} and Hg^{2+} from **FSCHP** microspheres by adjusting the pH of the water solution.

Fig. 8. Effect of solution pH on the adsorption capacity of the **FSCHP** microspheres for Cd(II), Pb(II) and Hg(II), pH was adjusted by 1 M HCl solution or 1 M NaOH solution.

3.6 Recyclability of **FSCHP**

An important requirement for the solid bifunctional sensor for detection and removal of metal ions is its reusability. As shown in Fig. 8, **FSCHP** has a very low adsorption capacity for cadmium, mercury and lead ions when $\text{pH} < 2.0$, so we envision that the **FSCHP** complexed with Cd^{2+} , Pb^{2+} and Hg^{2+} can be easily desorbed and **FSCHP** can be regenerated in acidic condition ($\text{pH} < 2.0$). To investigate its reusability, 10 mg of **FSCHP** microsphere was used to complex Cd^{2+} , Pb^{2+} or Hg^{2+} in a repeated adsorption-desorption fashion. In this test, the stripping agent was 0.1 M HCl for Cd^{2+} , Pb^{2+} and Hg^{2+} . The whole test process included three steps: (1) wash the **FSCHP** microsphere with stripping agent (5 mL for three times), (2) adjust the pH value of the mixture system (by using 1 M NaOH solution. For Cd^{2+} , $\text{pH} = 7.0$; for

Hg^{2+} , pH = 7.0; for Pb^{2+} , pH = 5.5), and (3) fluorescent detection of metal ions. As shown in Fig. 9 and Fig. S9, **FSCHP** was found to reused after adsorbed Cd^{2+} , Pb^{2+} and Hg^{2+} , the complex/stripping cycles can be at least five times, and the decrease of the **FSCHP**'s fluorescence intensity may because of the effect of the mechanical process injury the fluorescence property of **FSCHP**, and **FSCHP** must have little lost in the whole regeneration experiments [26, 46]. In general, **FSCHP** showed outstanding reusability and stability towards Cd^{2+} , Hg^{2+} and Pb^{2+} within at least five regeneration cycles.

Fig. 9. Fluorescence response of **FSCHP** (0.5 mg mL^{-1}) in the $1 \times 10^{-4} \text{ M}$ of Cd(II) over five complex/stripping cycles. I corresponds to the emission intensity of **FSCHP** with cations (red bars), and I_0 corresponds to the emission intensity of **FSCHP** without cations (blue bars), $\lambda_{\text{ex}} = 450 \text{ nm}$, 25°C .

3.7. Application of **FSCHP** in water and simulated biological samples

To investigate the feasibility of **FSCHP** for the detection and removal of toxic metal ions in real samples, **FSCHP** was applied to determine the concentration of Cd^{2+} , Hg^{2+} and Pb^{2+} in water samples (tap water and waste water of lab) and simulated biological sample (dilutions of fetal calf serum). As shown in Table 2, the results showed that **FSCHP** not only is a good fluorescent sensor with actually and experimentally determined concentrations of Cd^{2+} , Hg^{2+} and Pb^{2+} , but also is an efficient adsorbent in water and simulated biological samples for Cd^{2+} , Hg^{2+} and Pb^{2+} , indicating great potential of **FSCHP** in the detection and removal of toxic metal ions in environmental and biological samples.

Table 2.

Determination of Cd^{2+} , Hg^{2+} and Pb^{2+} in water sample and simulated biological background samples.

Samples	Metal ions	Added, mg L^{-1}	Detected mg L^{-1}	Recovery (%)	Adsorbed mg L^{-1}	Adsorptivity (%)
Tap water	Cd^{2+}	0	0		0	
		0.5	0.50 ± 0.02	100	0.48 ± 0.02	96
		2.0	1.98 ± 0.04	99	1.97 ± 0.05	98.5
	Hg^{2+}	0	0		0	
		0.5	0.48 ± 0.03	96	0.49 ± 0.02	97.5
		2.0	1.97 ± 0.05	98.5	1.96 ± 0.04	98.0
	Pb^{2+}	0	0		0	

		0.5	0.52 ± 0.03	104	0.49 ± 0.02	95.0
		2.0	1.99 ± 0.06	96.5	1.91 ± 0.06	95.5
Waste water	Cd^{2+}	0	0.13 ± 0.02		0.12 ± 0.01	
		0.5	0.62 ± 0.01	98.4	0.61 ± 0.02	96.8
		2.0	2.07 ± 0.03	97.2	2.10 ± 0.06	99.0
	Hg^{2+}	0	0.22 ± 0.02		0.24 ± 0.02	
		0.5	0.71 ± 0.02	98.6	0.70 ± 0.03	95.9
		2.0	2.21 ± 0.05	99.5	2.20 ± 0.05	98.2
	Pb^{2+}	0	0.10 ± 0.02		0.09 ± 0.01	
		0.5	0.63 ± 0.02	105	0.58 ± 0.03	96.7
		2.0	2.00 ± 0.05	95	1.96 ± 0.06	93.8
1:10 diluted fetal calf serum	Cd^{2+}	0.5	0.48 ± 0.03	96	0.46 ± 0.02	92.0
		2.0	1.98 ± 0.07	99	1.97 ± 0.05	98.5
	Hg^{2+}	0.5	0.53 ± 0.04	106	0.45 ± 0.02	90.0
		2.0	1.94 ± 0.06	97	1.92 ± 0.05	96.0
	Pb^{2+}	0.5	0.46 ± 0.02	92	0.46 ± 0.03	92.0
		2.0	1.96 ± 0.05	98	1.93 ± 0.06	96.5

4. Conclusions

In conclusion, by using 2,2-dipicolylamine (DPA) derivative as the binding receptor, we have synthesized a new bifunctional fluorescent microsphere sensor **FSCHP**.

FSCHP is the first sensor which could be used for both detection and removal of three toxic metal ions (Cd^{2+} , Hg^{2+} and Pb^{2+}). The detection limit of **FSCHP** for Cd^{2+} , Hg^{2+} and Pb^{2+} were 36 nM for Cd^{2+} , 48 nM for Hg^{2+} , and 39 nM for Pb^{2+} , respectively. **FSCHP**'s fluorescence intensity can indicate the equilibrium adsorption capacity of **FSCHP** in real-time. **FSCHP** can keep good adsorptivity for Cd^{2+} , Pb^{2+} and Hg^{2+} until the **FSCHP**'s equilibrium adsorption capacity (Q_e) is close to the saturated adsorption capacity ($Q_{\max}$), which is 7.5 mg g^{-1} for Cd^{2+} , 14 mg g^{-1} for Hg^{2+} , and 11.7 mg g^{-1} for Pb^{2+} , respectively. Moreover, **FSCHP** can be regenerated by acid treatment and reused for at least five cycles. In real water samples and simulated biological samples, toxic metal ions can be completely adsorbed by **FSCHP** at low concentration of Cd^{2+} , Hg^{2+} and Pb^{2+} . Thus **FSCHP** can be used to detect and remove toxic Cd^{2+} , Hg^{2+} and Pb^{2+} pollutants from contaminated environmental and biological samples.

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