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Graphical Abstract

Scheme 1. Synthetic route of SRD and SSRD (A), Schematic illustration of the functionalization of a Poly(vinyl alcohol) electrospun nanofiber membrane by SRD (X=O, M^{n+}= Fe^{3+} or Cr^{3+}) or SSRD (X=S, M^{n+}= Hg^{2+}) and metal detection/adsorption applications (B)

Fig 1. SEM images of PVANF membrane (A), PVANF-O membrane (B), PVANF-SRD membrane (C), PVANF-SSRD membrane (D)

Fig 2. FI-IR spectra of PVANF membrane (a), PVANF-O membrane (b), PVANF-SRD membrane (c), PVANF-SSRD membrane (d)

Fig 3. C1s ,N1s, O1s and S1s XPS for of PVANF membrane (a), PVANF-O membrane (b), PVANF-SRD membrane (c), PVANF-SSRD membrane (d)

Fig 4. Photographs of the PVANF-SRD membrane (A) and PVANF-SSRD membrane (B) immersed into K^+, Mg^{2+}, Ca^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Ba^{2+}, Al^{3+}, Cu^{2+}, Cd^{2+}, Ag^+, Hg^{2+}, Cr^{3+}, Fe^{3+} aqueous solutions(1.0×10^{-3} M) for 5 min

Fig 5. Fluorescence intensity changes of the PVANF-SRD membrane (A) and PVANF-SSRD membrane (B) immersed into K^+, Mg^{2+}, Ca^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Ba^{2+}, Cd^{2+}, Ag^+, Al^{3+}, Cu^{2+}, Hg^{2+}, Cr^{3+}, Fe^{3+} aqueous solutions(1×10^{-3} M, respectively) for 10 min (λ_{exc} = 525 nm)

Fig. 6. Fluorescence intensity changes of the PVANF-SRD membrane after being immersed into the aqueous solution of chromium ions (A) or ferric ion (B) (1×10^{-3}M) only and aqueous coexistence solution containing K^+, Mg^{2+}, Ca^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Ba^{2+}, Cd^{2+}, Ag^+, Al^{3+}, Hg^{2+}, Cu^{2+}(1×10^{-3} M), respectively; PVANF-SSRD membrane after being immersed into the aqueous solution of mercury ion (C) (1×10^{-3}M) and aqueous coexistence solution containing K^+, Mg^{2+}, Ca^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Ba^{2+}, Cd^{2+}, Ag^+, Al^{3+}, Cu^{2+}, Fe^{3+},Cr^{3+} (1×10^{-3} M), respectively (λ_{exc} = 525 nm).

Fig.7. UV-vis absorption spectra of the PVANF-SRD membrane after being immersed into Fe^{3+} (A) and Cr^{3+} (B) aqueous solutions; UV-vis absorption spectra of the PVANF-SSRD membrane after being immersed into Hg^{2+} (C) aqueous solutions for 10 min (pH=7)

Fig. 8. Fluorescence spectra of the PVANF-SSRD membrane after being immersed into Fe^{3+} (A) and Cr^{3+}(B) aqueous solutions; PVANF-SSRD membrane after being immersed into Hg^{2+}(C) aqueous solutions (λ_{exc}=525, pH=7)

Fig. 9. Effect of contact time on adsorption of PVANF-SSRD membrane (a) and PVANF membrane (b)

Fig. 10. Adsorption isotherm for Hg^{2+} with contact time 100 min, adsorbent concentration 1g/L

Fig. 11. (A) Langmuir and (B) Freundlich isotherms for Hg ions adsorption on PVANF-SSRD

Fig. 12. Fluorescence intensity change for the PVANF-SRD membrane after alternate treatment by aqueous solution of Fe^{3+}/Cr^{3+} (1×10^{-3} M) and Na_4EDTA and PVANF-SSRD membrane after alternate treatment by aqueous solution of Hg^{2+} (1×10^{-3} M) and Na_4EDTA (λexc = 525 nm)

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ARTICLE TYPE

Poly(vinyl alcohol) electrospun nanofibrous membrane modified with spirolactam-rhodamine derivatives for visible detection and removal of metal ions

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Poly(vinyl alcohol) electrospun nanofibrous membranes (PVANF membrane) which could sensitively detect and adsorb metal ions, were modified with spirolactam-rhodamineine derivatives (PVANF-SRD membrane) and sulfo-spirolactam-rhodamine derivatives (PVANF-SSRD membrane), respectively. Surface chemistry and morphology during functionalization of PVANF membranes were monitored using Fourier transform-infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). These two membranes could display real-time sensing by naked eyes based on ring-opening reaction of spirolactam-rhodamine derivatives induced by corresponding metals. PVANF-SRD and PVANF-SSRD membranes exhibited high selectivity and sensitivity toward Fe^{3+}/Cr^{3+} and Hg^{2+}, respectively. In terms of PVANF-SSRD membrane, adsorption capacity for Hg^{2+} in contaminated water was studied. Freundlich isotherm could better describe the interactions than Langmuir: $K_f = 7.0175$ mg/g ($r^2 = 0.9996$) for Hg^{2+}. The regenerability of these two membranes was investigated via Na_4EDTA solution treatment, and the results demonstrated they had good sustainability in detection and adsorption efficiency.

Introduction

Metal ions play important roles in human body as well as in the ecological system [1]. Some metal ions are essential for keeping health, such as ferric and chromium (III) ions, whereas some other metal ions such as mercury (II) ions could cause serious diseases for central nervous and endocrine systems [2-4]. Therefore, it is urgently needed practical solutions which could easily detect and selectively quick-dispose metal ions. For detective groups, rhodamine B is well-known and extensively used as a fluorochrome due to its remarkable properties such as a high adsorption coefficient, high fluorescent quantum yield, and excitation and emission within visible wavelengths [5]. Especially, non-fluorescent spirolactam-rhodamineine derivatives obtained by the reaction of rhodamine B with primary amine derivatives can respond some particular metal ions to give strong fluorescence emission [6]. Recently, several spirolactam-rhodamineine derivatives based on off-on fluorescent sensors have been developed for sensing metal ions including Cu^{2+}, Hg^{2+}, Fe^{3+} and Cr^{3+} *etc.* [7-18]. All these sensors work by the mechanism of the transition from the spirolactam form to a ring-open form upon the binding of captions, resulting in fluorescence enhancement (550-600 nm).

Although some materials functionalized by spirolactam-rhodamineine derivatives had been prepared to detect metal ions or adsorption purpose [19-25], electrospun membrane adsorption or filtration was probably one of the most attractive methods in wastewater decontamination because of large specific surface areas [26-28]. Electrospinning is a highly versatile method to process fibers with diameters ranging from nanometers to micrometers [29-31]. With different functional groups, electrospun fibers can be fabricated into sensor or adsorption materials with high sensitivity, fast response time and adsorbing capacity for metal ions or molecules in raw sewage [32,33]. Due to the good film-forming ability and abundant hydroxyl groups for easy modification, water-stable poly(vinyl alcohol) (PVA) is one of the promising candidates for fabrication of sensing or adsorption membrane [32-34]. Even though the cross-linking is fully based on reaction with hydroxyl group, there are still abundant active hydroxyls on the surface of nanofibers for the subsequent reactions of functionalizing PVA membranes with specific detective groups. Grafting rhodamine derivatives on the surface of PVA nanofibrous membrane, compared with other matrix such as Fe_3O_4 nanoparticles in peer's reports [19-23], makes fluorescent modified product possible for naked-eye detection. Moreover, PVA membrane grafting rhodamine derivatives could be recycled with aqueous NaOH or Na_4EDTA treatment. The colour changes during adsorption or desorption process which could be observed.

For removal of metal ions, more effective, lower-cost methods to obtain clean water are of great importance. Traditionally, detect and separate metal ions were performed separately. Adsorption material with naked-eye detectable function may save precious time during emergency treatment. In our study, PVA electrospun nanofibrous membrane modified with two different rhodamine derivatives were designed and investigated for the first time. The objective of our work is to develop a facile strategy of practical regenerable materials for naked-eye metal ions sensing and removal with ultra-high sensitivity, selectivity and adsorption ability.

2 Materials and methods

2.1 Materials

Poly(vinyl alcohol) (1799 alcoholysis: 99.8~100% (mol/mol)), Glutaraldehyde (50% in H_2O), Epichlorohydrin were supplied by Shanghai Jingchun industrial Co., chloride salts of metal ion (K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} Cr^{3+}, Fe^{3+}) and a nitrate salt of a metal ion (Ag^+) were purchased from Sigma-Aldrich Co. All chemicals were analytical reagent and used as supplied. As shown in Scheme 1(A), spirolactam-rhodamine derivatives (SRD) and sulfo-spirolactam-rhodamine derivatives (SSRD) were synthesized according to literature and confirmed by ^{1}H NMR and MS. The results were in agreement with previous report [37].

2.2 Preparation of water-stable poly(vinyl alcohol) electrospun nanofiber membrane (PVANF membrane)

PVANF membrane was prepared according to previous report with slight modification [36]. PVA-1799 was dissolved in distilled water and refluxed for 1 h to obtain a homogenous solution with a concentration of 10 wt%. Subsequently, 25 wt% (based on the mass of PVANF) glutaraldehyde (GA) was added into above solution under magnetic stirring for 0.5 h before electrospinning. The resulting solution was placed into a 10.0 mL syringe with a 7-gauge blunt end needle, and the syringe was mounted in a syringe pump (74900-05, Cole-Parmer, USA) to deliver the solution at the speed of 0.5 mL/h. The high voltage and distance between needle tip to the collector were 13 kV and 20 cm, respectively. All fibers were fabricated at 25 °C and relative humidity of 40%. Freshly prepared PVANF/GA nanofibrous membranes were immersed in a mixed solution containing 10 vol% of HCl aqueous solution (37 wt%) and 90 vol% methanol for 9 days to get water-stable nanofibrous membrane.

2.3 Modification of poly(vinyl alcohol) electrospun nanofiber with Rhodamine derivatives(SRD) and sulfo-rhodamine derivatives (SSRD)

A preweighed PVANF membrane was immersed in 100 mL of NaOH solution (pH=9-11). 7.0 mL of epichlorohydrin was added. The mixture was shook in an incubator shaker at 60 °C for 6 h and washed with distilled water thoroughly. Then, the membrane was immersed into water/ethanol (1:1 v/v) solution with 0.3% (w/v) Spirolactam-Rhodamine derivatives (SRD) and sulfo-Spirolactam-Rhodamine derivatives (SSRD), respectively. Subsequently, the pH value of above solution was adjusted to 9-11 via a 10 wt% NaOH solution. The mixture was shook in an incubator shaker at 60 °C for 12 h and then rinsed with distilled water and ethanol three times, dried with nitrogen. Finally, the PVANF-SRD and PVANF-SSRD membrane were obtained.

2.4 Characterization

The overall morphology of nanofibrous membranes was determined via scanning electron microscopy (SEM, S-4800, Hitachi, JPN). The average diameters of the obtained nanofibers were calculated directly with the SEM micrographs using Image Pro Plus 6 software. The BET surface area was obtained from N_2 adsorption-desorption isotherms measured using a surface area and porosity measurement system (TriStar II 3020 V1.03, Micromeritics, US). The fourier transform infrared (FTIR) spectra were characterized on an Affinity-1 FTIR spectroscopy from 4000 to 450 cm^{-1}. X-ray photoelectron spectra were obtained on an X-ray photoelectron spectrometer (XPS, ESCALabMKII, VG Scientific, UK), using Al KαX-ray source (1486.6 eV) as the exciting source. Ultraviolet-visible spectra (UV-vis) were recorded on a UV-1800 (Shimadzu, JPN) at room temperature. Fluorescence spectra were recorded on a RF-5301pc Fluorescence Spectrophotometer (Shimadzu, JPN).

2.5 Metal detection studies

To investigate the selectivity of PVANF-SRD and PVANF-SSRD membranes toward metal ions, various metal ions solutions were prepared in deionized water with the same concentration (1.0×10^{-3} M). The membranes were immersed into each solution for 10 min. After washing thoroughly with water, all membranes were dried with nitrogen, Fluorescence emission measurements were conducted.In order to investigate the sensitivity of PVANF-SRD membrane for Fe^{3+} and Cr^{3+} ions, PVANF-SRD membrane was immersed into different concentration of Fe^{3+} and Cr^{3+} ions respectively for 10 min. Afterwards, the membrane was washed thoroughly with deionized water, the UV-vis absorption spectra and fluorescence spectra were measured. Similar procedures were performed with PVANF-SSRD membrane at different Hg^{2+} ion concentrations.

2.6 Adsorption of Hg^{2+} from Haihe River samples

The adsorption capacities of the modified nanofibrous membranes were assessed by monitoring the residual amount of metal ions in the sewage using inductively coupled plasma mass spectrometry (ICP-MS, Thermofisher, Germany). The water samples from Haihe River (Tianjin, China) were collected. Since no detectable mercury in the samples, 0.2-2 mg of $Hg(NO_3)_2$ was added in 20 ml samples to simulate contaminated water. For Hg^{2+} detection and adsorption, 20 mg of PVANF-SSRD membrane (size around 12*12 cm) was immersed into the samples and agitated on a mechanical shaker between 5-120 min to adsorb Hg^{2+}. After taking out the membrane, the remnant Hg^{2+} was determined by ICP-MS. Equilibrium isotherms required for design and operation of adsorbent to treat Hg^{2+} bearing wastewater was obtained.

The amount of Hg^{2+} adsorbed was calculated according to Eq. (1)

$$q = \frac{C_0 - C_f}{M} V \qquad (1)$$

where q is the amount of Hg^{2+} adsorbed (mg/g), C_f and C_0 are final and initial Hg^{2+} concentrations (mg/L), respectively, V is the volume of Hg^{2+} used (L), and M is the mass of adsorbent (g).

2.7 Reversibility of the PVANF-SRD and PVANF-SSRD membranes samples

For the reversibility (reusability) of the PVANF-SRD and PVANF-SSRD membranes, the membranes were immersed into the saturated Na_4EDTA solution for 10 min, then washed with methanol and water and dried with nitrogen.

3. Results and discussion

Scheme 1(A) showed the synthetic route of spirolactam-rhodamine derivatives (SRD) and sulfo-spirolactam-rhodamine derivatives (SSRD). As shown in Scheme 1(B), functionalization of the PVANF membrane by SRD or SSRD involves two steps. First, epoxy group was grafted onto the PVANF membrane by reacting epichlorohydrin with -OH on the surface of PVANF membrane in alkaline conditions, resulting in PVANF-O membrane. In the second step, the SRD and SSRD reacted with PVANF-O membrane respectively, to obtain the final PVANF-SRD and PVANF-SSRD membranes. The loadage of probe SRD and SSRD onto the PVANF membranes were equivalent to 9.2×10^{-5} M and 9.1×10^{-5} M respectively, which were calculated based on absorbance of the PVANF-SRD or PVANF-SSRD membranes after being immersed into saturated Fe^{3+} or Hg^{2+} solution [25].

3.1 Morphological characterization

The morphologies of the products were observed by SEM. Fig. 1A showed representative SEM image of the PVANF membrane. Fig. 1B, C and D depicted representative SEM images of the intermediate (PVANF-O membrane) and final products (PVANF-SRD membrane, PVANF-SSRD membrane), respectively. The fiber sizes of the membranes were calculated as an average value from 100 measurements using Image Pro Plus 6® software. The average fiber diameters of PVANF-SRD membrane and PVANF-SSRD membrane were 290.11 nm and 287.88 nm respectively, which are of no obvious difference from that of PVANF (271.40 nm) and PVANF-O (270.9 nm). The fiber integrity and porosity were maintained during functionalization. The surface area and pore size of PVANF-SRD membrane were obtained as 18.78 m^2 /g and 143.85 Å. Similarly, the surface area and pore size of PVANF-SSRD membrane were 18.62 m^2 /g and 140.32 Å.

3.2 Fourier transformation-infrared spectroscopy

Functionalization of the PVANF membrane by SRD and SSRD was confirmed by FTIR spectroscopy. Fig. 1 showed the FT-IR spectra of PVANF membrane (a), PVANF-O membrane (b), PVANF-SRD membrane (c), PVANF-SSRD membrane (d) in the 450-4000 cm^{-1} wavenumber range. The peak at 3290 cm^{-1} in spectrum could be assigned to the -OH stretching vibration arising from surface hydroxyl groups of PVANF. The spectrum of PVANF-O membrane showed the peak at 910 cm^{-1}, which was the characteristic peak of epoxide group, indicating the formation of the epoxy group onto PVANF membrane. The peaks at 1420 and 1632 cm^{-1} in the spectrum of Fig. 1(c) were respectively assigned to the C-N and C=O stretching vibration, which Indicated that the PVANF-SRD membrane was successfully fabricated. The increase in the band intensity at 1220 cm^{-1} could be attributed to C=S stretching vibration of SSRD. Therefore, it can be concluded that SRD and SSRD had been grafted successfully on the surface of PVANF membrane respectively.

3.3 Surface composition investigation using X-ray photoelectron spectroscopy

XPS was used to identify the surface composition of both the PVANF-SRD and PVANF-SSRD membranes. Fig. 3 showed the C1s, N1s, O1s, S2s and S2p XPS for PVANF membrane (a), PVANF-O membrane (b), PVANF-SRD membrane (c), PVANF-SSRD membrane (d). The surface of the PVANF-SRD membrane exhibited more apparent N1 content than the PVANF and PVANF-O membrane, which attributed to SRD. Additional S1s and S2s appeared in XPS of PVANF-SSRD membrane can be assigned to SSRD. The result also indicated that SRD and SSRD had been grafted successfully on the surface of PVANF membrane, respectively.

3.4 Selectivity and sensitivity of PVANF-SRD and PVANF-SSRD membrane

Photos were taken when PVANF-SRD membrane were immersed into different metal ions (1.0×10^{-3} M) for 5 min (as shown in Fig. 4A). Significant colour transition from white to pink was easily observed by naked eyes when the membrane was in immersed into solution with Fe^{3+} or Cr^{3+} instantly. As shown in Fig. 4B, photographs of the PVANF-SSRD membranes immersed in the aqueous solutions of various metal ions were taken to present their selectivity and visibility for metal ion detection. Comparatively, the PVANF-SSRD membrane showed high specificity toward Hg^{2+}.

Fluorescence intensity changes of PVANF-SRD membrane after immersed into each ion (1.0×10^{-3} M) for 10 min with an excitation at 525 nm were measured (as shown in fig. 5A). The result clearly demonstrated that the PVANF-SRD membrane had an excellent selectivity toward both Fe^{3+} and Cr^{3+} ions. PVANF-SSRD selectivity and sensitivity for mercury ion sensing were also examined following the similar procedure. (as shown in fig. 5B).

From Fig. 6, it was clearly that the coexistence of most selected metal ions does not interfere with either Fe^{3+} or Cr^{3+} detection of PVANF-SRD membrane. Meanwhile, coexistences had negligible interfering effect on Hg^{2+} sensing by the PVANF-SSRD membrane.

The UV-vis spectrum of the membrane was measured after immersed into different concentration of Fe^{3+} and Cr^{3+} aqueous solutions (Fig. 7A, B). The result indicated that with the increase of Fe^{3+} or Cr^{3+} concentration in aqueous solutions, absorption spectrum at around 560 nm also increased, which coincided with the adsorption of rhodamine. Fig. 8A, B showed the fluorescence spectrum of PVANF-SRD membrane after immersion into different concentration of Fe^{3+} and Cr^{3+} aqueous solutions respectively. It was found that the fluorescence intensity at 593 nm increased steadily as the concentration of Fe^{3+} or Cr^{3+} increased. Fe^{3+} induced stronger fluorescence intensity than that of Cr^{3+}. The results indicated that the PVANF-SRD membrane could be used as a dual responsive sensor with much faster response time for Fe^{3+} and Cr^{3+} detection and the detection limit was approximate 1.0×10^{-6} M for both Fe^{3+} and Cr^{3+}, which was comparable to other materials based on rhodamine derivatives in previous report [25]. UV-vis absorption and fluorescence spectrum of PVANF-SSRD membrane after immersion into different concentration of Hg^{2+} aqueous solutions were showed in fig. 7C and fig. 8C. PVANF-SSRD showed very good selectivity, sensitivity and fast response for Hg^{2+}. Compared with PVANF-SRD membrane, PVANF-SSRD membrane showed more sensitivity for Hg^{2+} with the limit of quantification at approximate 5.0×10^{-7} M.

3.5 Adsorption study

Contact time is a pertinent parameter which could determine the performance of an adsorbent. Adsorption was monitored by immersing 20 mg of electrospun membranes into 20 mL of 0.2 mg $Hg(NO_3)_2$ solution. The amount of Hg^{2+} adsorbed by PVANF-SSRD and PVANF membranes were investigated as a function of contact time, as shown in Fig. 9. A high uptake rate observed for the first 10 min, could be explained by the availability of many adsorption sites in PVANF-SSRD membrane. As Hg^{2+} get attached to these sites with contact time, the amount of adsorbed Hg^{2+} gradually reaches a maximum when no more significant Hg^{2+} were removed. The equilibrium is established.

The equilibrium time for Hg^{2+} was 20and 40 min (Fig. 9), respectively. The PVANF-SSRD membrane showed obvious improved adsorption compared to the PVANF membrane. This is explained by the high number of hydroxyl groups exposed for reaction with SSRD. After reached equilibrium time, the removal of Hg^{2+} was approximately 93%.

Langmuir and Freundlich models are commonly used adsorption isotherms for solid-liquid phase isotherms, which could describe the relationship between Hg^{2+} in solution and PVANF-SSRD membranes. The more appropriate model could reveal the adsorption kinetics, as well as adsorption capacity of the functionalized nanofibrous membranes. It is assumed that every adsorption site is equivalent and the ability of a probe to bind is independent of whether or not adjacent sites are occupied [26, 38].

The Langmuir model is applicable in cases where a monolayer of adsorbed ions is formed at the membrane surface, while Freundlich isotherm model is widely used for heterogeneous surfaces energies. The linearized form of the two adsorption isotherms models is defined by the following equations, respectively.

Langmuir adsorption isotherm (Eq. (2))

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}} C_e + \frac{1}{q_{\max} K_L} \qquad (2)$$

where C_e is the equilibrium concentration of adsorbate ions (mg/L), q_e is the amount of ions adsorbed at equilibrium (mg/g), $q_{\max}$ is the adsorption capacity of adsorbent (mg/g) and K_L is a Langmuir constant related to energy.

Freundlich adsorption isotherm (Eq. (3))

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \qquad (3)$$

where q_e and C_e assume the same quantities as in Langmuir, while K_f and n are adsorption capacity and adsorption intensity constants, respectively [9].

The adsorption kinetics was studied using different concentration for adsorbate metal ions: 25, 50, 75 and 100 mg/L at an adsorbent concentration of 1 g/L. The adsorption isotherms, Langmuir and Freundlich, are represented by Figs. 10 and 11, respectively.

The maximum adsorption ($q_{\max}$) was reported in Table 1. The adsorption capacities of PVANF-SSRD are 222.23 mg/g for Hg^{2+}, compared to 69.93 mg/g for PVANF (Table 1). Moreover, Table 1 showed that the metal uptake data agrees strongly with Freundlich adsorption isotherm model with correlation coefficient (r^2) of 0.9996. This supports the theory that the adsorption concluding probe and physical adsorption. Moreover, the adsorption capacities of Hg^{2+} of PVANF-SSRD membrane were compared with the some adsorbents of recent researchers (Table 2). The table showed that PVANF-SSRD membrane performed good potential for specific heavy metal adsorption in water.

Metal ion	qmax (mg/g)	Langmuir		Freundlich		
		K_L (L/mg)	r^2	K_f (mg/g)	n	r^2
Hg	222.23[a]	0.0255	0.9746	7.0175	1.26	0.9996
	69.93[b]	0.0073	0.9818	3.2446	1.60	0.9837

Table 1 Langmuir and Freundlich isotherm constants for Hg^{2+} of PVANF-SSRD and PVANF membranes

[a] PVANF-SSRD membrane

[b] PVANF membrane

Table 2 A comparison of maximum adsorption capacity (mg/g) of PVANF-SSRD with some adsorbents reported by different researchers

Adsorbent	Hg	Reference
Sulfur-Functionalized Silica Gels	47.8	[39]
Zonal thiol-functionalized silica nanofibers	57.5	[40]
PVA/PVI membrane	118.3	[41]
Organic–inorganic silica membrane (MCM-3T)	234.9	[42]
PVANF-SSRD membrane	222.2	This study

3.6 Regeneration (reversibility) of PVANF-SRD membrane and PVANF-SSRD membrane

To investigate the reversibility and regeneration of PVANF-SRD membrane for Fe^{3+} and Cr^{3+} detection and adsorption, after immersing in Fe^{3+} or Cr^{3+} solutions until reached equilibrium, PVANF-SRD membrane could be restored by exposed in NaOH or Na_4EDTA solution. The red colour faded completely within 10 min. These procedures repeated for ten times and fluorescent emission signal were measured at each stage (Fig. 12A). The open-ring state rhoamine turned back to spirolactam due to its more stability form of SRD under alkaline conditions. Na_4EDTA

could also restore the membrane utilizing its more complexation capacity with Fe^{3+} and Cr^{3+}. PVANF-SSRD membrane could also be reversed by exposing in Na_4EDTA solution and its fluorescent intensity changed with alternately treated with Hg^{2+} ion and Na_4EDTA solution (Fig. 12B). The results clearly demonstrated that these membranes could be reused for several time without significant decrease for detection and adsorption capacities.

Conclusions

In summary, two different spirolactam-rhodamineine derivatives were successfully functionalized on the surface of PVA electronspun nanofibrous membranes respectively for Fe^{3+}/Cr^{3+} and Hg^{2+} sensing and adsorption purpose. These membranes displayed real-time sensing with good sensitivity and selectivity. Due to their large adsorption capacity, these factionalized membrane showed great potential for specific heavy metal adsorption in water purification purpose. It is also worth to note that the material could be recycled without significant decrease in its adsorption capacity. The colour could be changed in the process of adsorption or desorption which is convenient to determine the sewage treatment and reutilization effect. Modifying other metal ion fluorescent probe on the surface of nanofibers with such facile strategy could allow expansion of the range for both detection and adsorption purpose.

Notes and references

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