



Research
Water Pollution Control—Article

Engineering a High-Selectivity PVDF Hollow-Fiber Membrane for Cesium Removal



Shiyuan Ding^{a,b,*}, Lilan Zhang^c, Yang Li^d, Li'an Hou^{d,e,*}

^a Institute of Surface-Earth System Science, Tianjin University, Tianjin 300072, China

^b Tianjin Key Laboratory of Earth Critical Zone Science and Sustainable Development in Bohai Rim, Tianjin University, Tianjin 300072, China

^c State Key Laboratory of Coal Mine Disaster Dynamics and Control, Chongqing University, Chongqing 400044, China

^d State Key Laboratory of Water Environment Simulation, Beijing Normal University, Beijing 100875, China

^e Xi'an High-Tech Institute, Xi'an 710025, China

ARTICLE INFO

Article history:

Received 15 November 2018

Revised 1 February 2019

Accepted 23 April 2019

Available online 31 July 2019

Keywords:

Cesium removal

Composite membrane

Copper ferrocyanide

Polyvinylidene fluoride

ABSTRACT

In this study, a copper ferrocyanide/silica/polyvinylidene fluoride (CuFC/SiO₂/PVDF) hollow-fiber composite membrane was successfully synthesized through a facile and effective crosslinking strategy. The PVDF hollow-fiber membrane with embedded SiO₂ was used to fix the dispersion of CuFC nanoparticles for cesium (Cs) removal. The surface morphology and chemical composition of the composite membrane were analyzed using scanning electron microscopy and X-ray photoelectron spectroscopy (XPS). The composite membrane showed a high Cs rejection rate and membrane flux at the three layers of CuFC and 0.5% SiO₂, and its Cs rejection rate was not affected by variation in the pH (pH = 4–10). The modified membrane could be effectively regenerated many times using ammonium nitrate (NH₄NO₃). The Cs selectivity performance was verified by an efficient Cs rejection rate (76.25% and 88.67% in 8 h) in a solution of 100 μg·L⁻¹ of Cs with 1 mmol·L⁻¹ of competing cations (K⁺ and Na⁺). The CuFC/SiO₂/PVDF hollow-fiber composite membrane showed a particularly superior removal performance (greater than 90%) in natural surface water and simulated water with a low Cs concentration. Therefore, the CuFC/SiO₂/PVDF hollow-fiber composite membrane can be used directly in engineering applications for the remediation of radioactive Cs-contaminated water.

© 2019 THE AUTHORS. Published by Elsevier LTD on behalf of Chinese Academy of Engineering and Higher Education Press Limited Company. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

The release of large amounts of radionuclides into the aquatic environment has attracted worldwide attention after the Fukushima Daiichi nuclear power plant accident in 2011 [1,2]. Among such radionuclides, the concentration of cesium (¹³⁷Cs) is very high because of the long half-life (30.1 years) and high mobility of this element; thus, Cs poses a particular threat to environmental safety and human health [3]. Although there have been many studies on effective removal techniques for trace radionuclides, monovalent Cs removal still faces great challenges due to the highly active biochemical characteristics of Cs, which are similar to those of potassium [4]. Many Cs removal methods have been reported, including adsorption, membrane technology, distillation,

and chemical precipitation [5–9]. Of these methods, adsorption is one of the most effective removal techniques for Cs.

Various types of Cs adsorbents including molybdophosphate, metallic oxides, zeolites, carbon, and other clay minerals have been extensively studied [4,10–14]. However, these adsorbents have a low selectivity for removing Cs from water. Transition metal ferrocyanides (Cu, Fe, Zn, and Ni) are extensively used as adsorbents due to their high selectivity for Cs and low cost [15–19]. These adsorbents always have a lattice spacing size of about 0.32 nm, which is similar to that of the hydrated ion of Cs [20]. In particular, copper ferrocyanide (CuFC) has shown excellent Cs sorption capacity and chemical stability, and has been used to selectively separate Cs from contaminated wastewater [3,15,21–23]. However, CuFC is commonly available in the form of fine particles that are difficult to separate and collect, which limits its practical application [24].

In recent decades, supporting materials with magnetism or high surface areas have been selected to immobilize CuFC [15,22,25,26]. For example, CuFC-type particles can be loaded onto silica (SiO₂) to

* Corresponding authors.

E-mail addresses: dingshiyuan@tju.edu.cn (S. Ding), houlia678@hotmail.com (L. Hou).

improve their mechanical properties, which results in a high Cs rejection rate [27]. The problem of the difficult separation and recovery of the adsorbents has not been solved by fixing them onto the surface of particles. Chen et al. [28] tried to fix transition metal ferrocyanides directly onto a non-woven fabric to solve this problem. To remove heavy metal ions, Efome et al. [29–31] fixed metal-organic framework adsorption materials to a membrane using electrostatic spinning technology in order to effectively solve the problem of nano-materials fixation. However, the efficiency of the adsorption materials may decrease through internal fixation. Recently, transition metal ferrocyanide nanolayers on membranes were engineered to remove Cs from water [32–36]. However, the adsorbent particles directly loaded on the membrane surface blocked the membrane's pores and affected the membrane's filtration efficiency. A substrate with a binding agent can be used in membrane filtration with an acceptable flux and a minimal pressure drop [10,37]. Ding et al. [10] demonstrated an adsorbent-bead structured membrane that was functionalized to effectively eliminate Cs through a filtration adsorption method. Nevertheless, a chemical bonding method can fix the particle substrate on the surface of a membrane more firmly than anchoring through a physical deposition method. Qin et al. [38] reported that the use of chemical bonding to load TiO_2 nanoparticles (NPs) onto a polyvinylidene fluoride (PVDF) membrane greatly improved the membrane flux and increased the stability of the composite membrane. As far as we know, the chemical bonding of transition-metal ferrocyanide-coated NPs onto a hollow-fiber membrane surface for the removal of Cs in water has not been well documented.

In the present work, we synthesized CuFC/SiO_2 -incorporated PVDF ($\text{CuFC}/\text{SiO}_2/\text{PVDF}$) hollow-fiber composite membranes for the effective removal of Cs in water. The physicochemical characteristics of the composite membranes were analyzed and their Cs rejection abilities were studied.

2. Material and methods

2.1. Chemicals and reagents

Non-radioactive cesium nitrate was used as an alternative to ^{137}Cs due to its similar chemical properties. Tetrabutylammonium fluoride (TBAF, 98%) and trimesoyl chloride (TMC, 98%) were supplied by Sigma-Aldrich. SiO_2 NPs modified by amino groups (w/v: 2.5%; particle size: 300 nm) were purchased from Aladdin. Sodium ferrocyanide ($\text{Na}_4[\text{Fe}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$) and other reagents used in this work were provided by Sinopharm. Ultrapure water prepared by the Milli-Q IQ7000 (Millipore, USA) water purification system was used in this study.

2.2. Membrane surface modification

A PVDF hollow-fiber membrane (OriginWater, U100 MF, 0.1–1 μm) was chosen for this study and was further modified by a reported method developed with a minor modification [38]. First, the two terminals of the hollow-fiber membranes were sealed with epoxy resin for 24 h; the membranes were then washed with water for 24 h, and then dried at room temperature after washing with ethanol for 1 h. The membranes were then further modified, as follows: ① Pristine PVDF membrane was immersed in 1 $\text{mol}\cdot\text{L}^{-1}$ potassium hydroxide (KOH) solution with 5 $\text{g}\cdot\text{L}^{-1}$ TBAF for 60 min at 45 $^\circ\text{C}$, and then dipped into 1 $\text{mol}\cdot\text{L}^{-1}$ sodium hydrogen sulfite (NaHSO_3) aqueous solution with H_2SO_4 for 1 h at 45 $^\circ\text{C}$; ② the treated membrane was then immersed by 0.8 wt% TMC hexane solution; ③ the treated membrane was dipped into SiO_2 suspension with a mass concentration of 0.05% and 0.5%, respectively, for 60 min at 100 $\text{r}\cdot\text{min}^{-1}$ and 25 $^\circ\text{C}$. Next, the membrane was heated at 70 $^\circ\text{C}$ for 5 min to improve the grafting reaction. Finally, the membrane was washed and marked as SiO_2/PVDF hollow-fiber composite membrane (Fig. 1).

2.3. $\text{CuFC}/\text{SiO}_2/\text{PVDF}$ hollow-fiber composite membrane preparation

The modified membranes were dipped into 50 mL CuCl_2 (0.5 $\text{mol}\cdot\text{L}^{-1}$) and placed in a shaker with a shaking speed of 120 $\text{r}\cdot\text{min}^{-1}$ for 2 h at 25 $^\circ\text{C}$. The membranes were then transferred into 50 mL of 0.5 $\text{mol}\cdot\text{L}^{-1}$ $\text{Na}_4[\text{Fe}(\text{CN})_6]$ solution and were agitated at 150 $\text{r}\cdot\text{min}^{-1}$ for 4 h at 25 $^\circ\text{C}$. The final CuFC -modified membranes were washed many times to elute any residual solution. The loading process of CuFC was repeated one to three times to grow the crystal. Next, ultrapure water was used to wash the modified membranes. The prepared membranes were dried at 40 $^\circ\text{C}$ and then stored in ultrapure water (Fig. 1).

2.4. Membrane characterization

The surface morphology of the membranes was characterized by scanning electron microscopy, and the element composition of the membrane surface was analyzed by X-ray photoelectron spectroscopy (XPS). The membrane surface was evaluated for the binding performance of the CuFC and SiO_2 NPs via an ultrasonic test for 2 min and then tested again for another 2 min. In the end, the weight and surface morphology of the composite membrane before and after the treatment were determined. Membrane regeneration was carried out by soaking the membrane in a solution of 5 $\text{mol}\cdot\text{L}^{-1}$ ammonium nitrate (NH_4NO_3) at 120 $\text{r}\cdot\text{min}^{-1}$ for 24 h at 25 $^\circ\text{C}$.

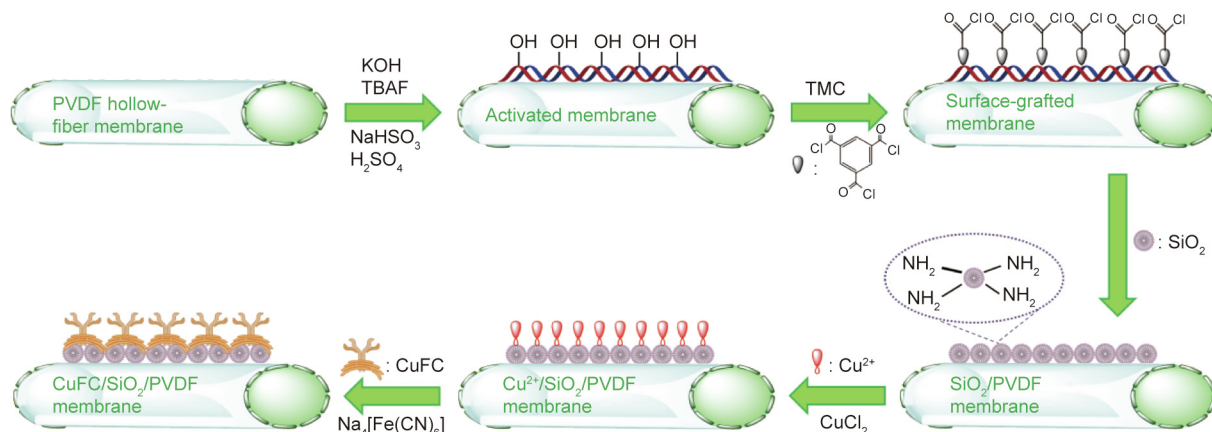


Fig. 1. Schematic diagram of $\text{CuFC}/\text{SiO}_2/\text{PVDF}$ hollow-fiber composite membrane preparation.

2.5. Membrane filtration experiments

Cs solutions of $100 \mu\text{g}\cdot\text{L}^{-1}$ were used to conduct the filtration tests. NaOH or HCl solution was used to maintain the solution at $\text{pH} = 7 \pm 0.1$. One membrane filtration system (Fig. 2) was used to assess the Cs rejection ability and water permeability of the membrane at 90 kPa. The effective membrane area was 12.5 cm^2 . After 1 h of water filtration, the membrane flux was tested and the permeate samples were analyzed.

The effect of the organic matter ($5.0 \text{ mg}\cdot\text{L}^{-1}$ humic acid, HA) and competing cations ($1 \text{ mmol}\cdot\text{L}^{-1} \text{ K}^+, \text{ Na}^+$) on the Cs removal was explored. The physicochemical properties of natural surface water (SW) were tested after filtering through $0.45 \mu\text{m}$ film; the results are displayed in Table 1. Next, $100 \mu\text{g}\cdot\text{L}^{-1}$ Cs solutions in SW and HA solution were used to conduct the filtration experiments. An inductively coupled plasma mass spectrometer was used to test the Cs concentration. The concentrations of cations and anions were analyzed using an inductively coupled plasma atomic emission spectrometer and ion chromatography, respectively.

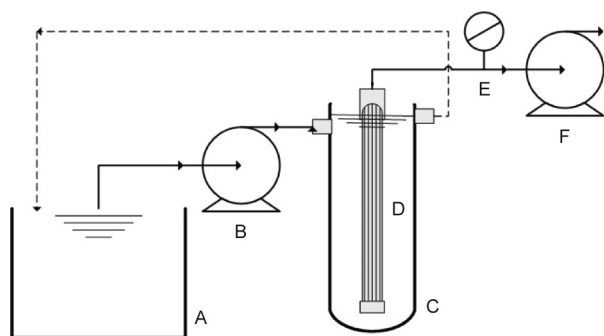


Fig. 2. Schematic diagram of the membrane filtration system. A: feed tank; B: pump; C: membrane element; D: membrane; E: pressure gauge; F: pump.

Table 1
The properties of the SW collected from Wu River (Guizhou, China).

pH	Concentration									
	DOM ($\text{mg}\cdot\text{L}^{-1}$)	Cs ⁺ ($\mu\text{g}\cdot\text{L}^{-1}$)	Na ⁺ ($\text{mg}\cdot\text{L}^{-1}$)	K ⁺ ($\text{mg}\cdot\text{L}^{-1}$)	Ca ²⁺ ($\text{mg}\cdot\text{L}^{-1}$)	Mg ²⁺ ($\text{mg}\cdot\text{L}^{-1}$)	Cl ⁻ ($\text{mg}\cdot\text{L}^{-1}$)	NO ₃ ⁻ ($\text{mg}\cdot\text{L}^{-1}$)	SO ₄ ²⁻ ($\text{mg}\cdot\text{L}^{-1}$)	
7.81	2.37	0.91	4.35	2.79	44.79	13.46	4.74	3.16	45.93	

DOM: dissolved organic matter.

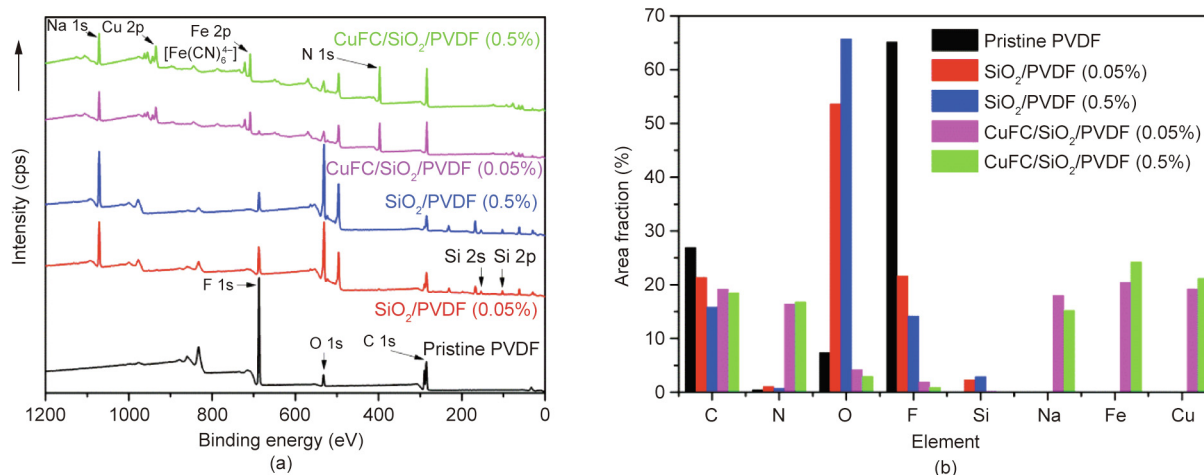


Fig. 3. (a) Elemental composition of membrane surfaces by XPS; (b) area fractions of elements on the membrane surfaces. 0.05% and 0.5% refer to the mass concentrations of SiO₂. Cps: counts per second.

3. Results and discussion

3.1. Properties of PVDF hollow-fiber membranes

The amino-modified SiO₂ NPs were bound with the reactive groups (–COCl) of the pristine PVDF membrane surface, which was formed by pretreating in an alkaline solution and TMC hexane media [38]. The CuFC was then loaded onto the SiO₂ NP surface. As shown in Fig. 1, dehydrofluorination and nucleophilic addition were the two main modification steps. Treatment with KOH solution facilitated the formation of unsaturated double bonds in the pristine PVDF membrane, which was followed by the formation of hydroxyl groups to induce a nucleophilic addition reaction on the polymer chains. XPS was used to test the modification characteristics; the results are shown in Fig. 3. A dramatic change in the XPS wide spectra was seen in the SiO₂/PVDF hollow-fiber composite membranes but not in the pristine membrane. The ratio of oxygen atoms increased, indicating that oxygen-containing groups had been introduced onto the surface of the membrane [38]. Two more peaks of Si 2s and Si 2p appeared in addition to the peaks of C 1s, O 1s, and F 1s, which verified that successful binding of SiO₂ on the PVDF membrane had occurred. A high content of SiO₂ particles facilitated the contact with the pretreated PVDF membrane and promoted the loading of SiO₂ onto the membrane surface through binding with the active group. Furthermore, as shown in Fig. 3, an Fe 2p peak (708.6 eV) and a Cu 2p peak (932.7 eV) appeared on the composite membrane, respectively, in accordance with the presence of Fe(CN)₆⁴⁻ and Cu [39,40], respectively, demonstrating that CuFC was successfully loaded onto the membrane.

The surface morphologies of the PVDF membranes were characterized; the results are shown in Fig. 4. The pristine membrane showed the typical structure of a microfiltration membrane, having a porous skin layer. The results also demonstrated that the amount of SiO₂ NPs increased with the initial concentration used for loading SiO₂ (Figs. 4(b) and (c)). The surface of the CuFC/SiO₂/PVDF (0.05%) showed aggregates of porous platelets (Fig. 4(d)), indicating that CuFC was successfully loaded onto the

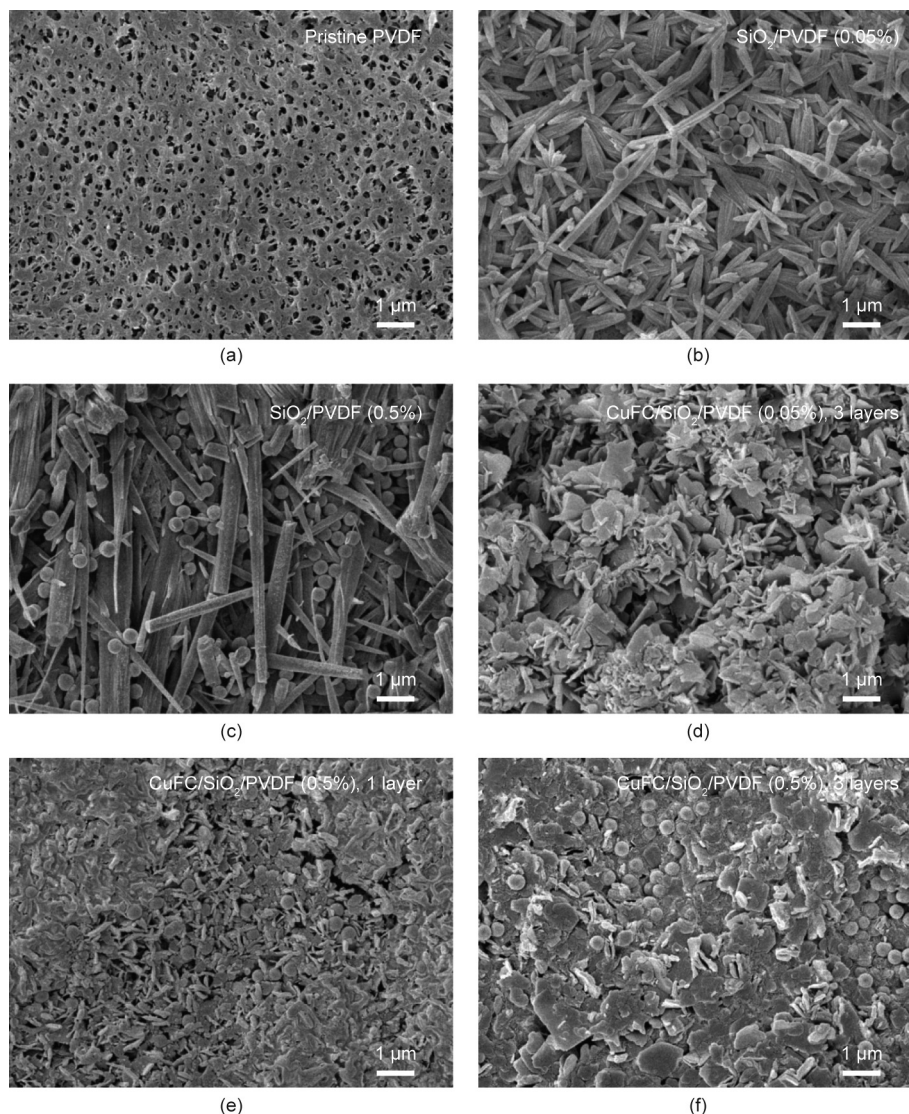


Fig. 4. Surface morphology of the PVDF membranes. (a) Pristine PVDF membrane; (b) and (c) SiO_2/PVDF membranes; (d–f) $\text{CuFC}/\text{SiO}_2/\text{PVDF}$ membranes.

membrane surface [41]. In addition, there was a formed selective CuFC layer (one layer and three layers) on the surface of the composite membrane (Figs. 4(e) and (f)), which might be due to the SiO_2 layer being stabilized on the surface of the membrane.

The Cs rejection rate and flux of these membranes were tested; the results are shown in Table 2. It can be seen that the rejection rate increased and the flux decreased with an increase of the loaded layer. At a concentration of 0.05% SiO_2 , the rejection rate of the composite membrane with three layers of CuFC was higher than 90%, even with decreasing membrane flux. In order to achieve the highest rejection rates, 0.5% SiO_2 -loaded composite membranes were selected in the following experiments.

3.2. Binding stability of modified membrane

As shown in Figs. 4(f) and 5, there was almost no morphological change on the hollow-fiber composite membrane surface before and after physical treatment. It was also demonstrated that the fixation ability of the SiO_2 NPs for CuFC effectively inhibited delamination or peeling between the membrane surface and the CuFC layer. Furthermore, the membrane weight decreased by just 0.2 mg after the physical treatment of the membrane—an amount that could be ignored. Thus, the results of the weight measurements and surface morphology indicated that the binding between the PVDF membrane and the CuFC NPs was strong.

Table 2

Rejection rate and flux of composite membranes with different layers of CuFC and different concentrations of SiO_2 (Cs: $100 \mu\text{g}\cdot\text{L}^{-1}$; pH = 7).

CuFC load layer	Concentration of SiO_2 (%)	Flux ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}\cdot\text{kPa}^{-1}$)	Rejection rate after 1 h (%)	Rejection rate after 6 h (%)
1	0.05	1.61	70.25	49.36
3	0.05	0.30	94.20	89.68
1	0.5	2.92	87.45	78.22
3	0.5	0.49	99.82	94.64

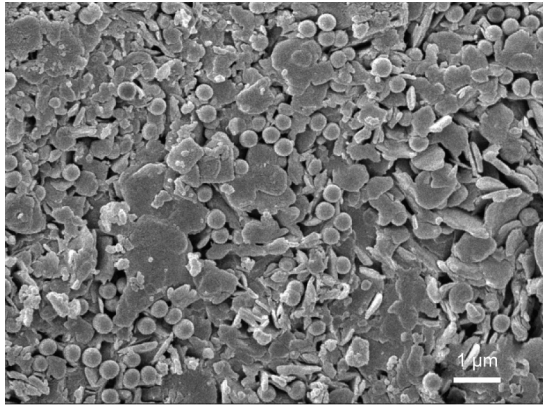


Fig. 5. Surface morphology of the composite membrane after physical treatment.

3.3. Regeneration of modified membrane

It is a major challenge to establish membrane treatment methods that can recover after being used several times. To evaluate membrane regeneration, NH_4NO_3 solution was used to regenerate the filtered composite membrane [42,43]. The Cs rejection rate of the regenerated membrane after being used for 18 h was evaluated. As shown in Fig. 6, the rejection rate of the composite membrane decreased with increasing treatment time. The membrane regeneration was carried out after 18 h. After two cycles of NH_4NO_3 regeneration, the Cs rejection rate was still greater than 98%. Egorin et al. [42] reported that more than 63% of Cs desorption could be achieved from CuFC adsorbent in seawater after regeneration with $5 \text{ mol}\cdot\text{L}^{-1}$ NH_4NO_3 solution. Thus, the composite membrane can be regenerated efficiently by NH_4NO_3 solution many times, giving it potential for practical applications.

3.4. Effect of initial pH

The Cs rejection rate may be affected by the pH of the feed solution; therefore, a series of experiments was carried out over a pH range from acidity to alkalinity. As shown in Fig. 7, the membranes exhibited the maximal rejection rate at pH = 7; the rejection rate decreased at pH = 4 and at a pH higher than 7 (Fig. 7). The phenomenon of decreased rejection rate at low pH might be caused by the competing adsorption of H^+ and Cs onto the $\text{CuFC}/\text{SiO}_2/\text{PVDF}$

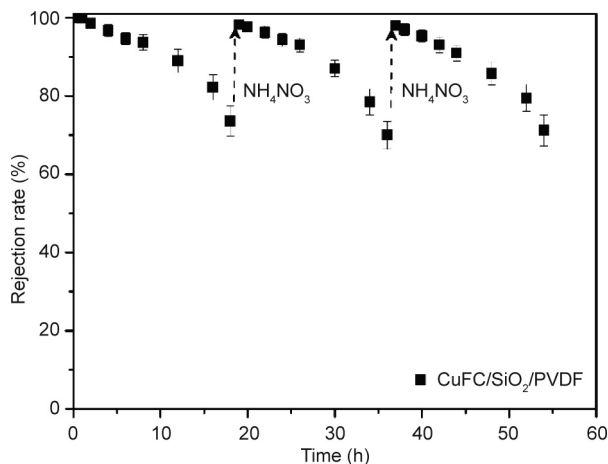


Fig. 6. Loading-regeneration of Cs by the composite membrane.

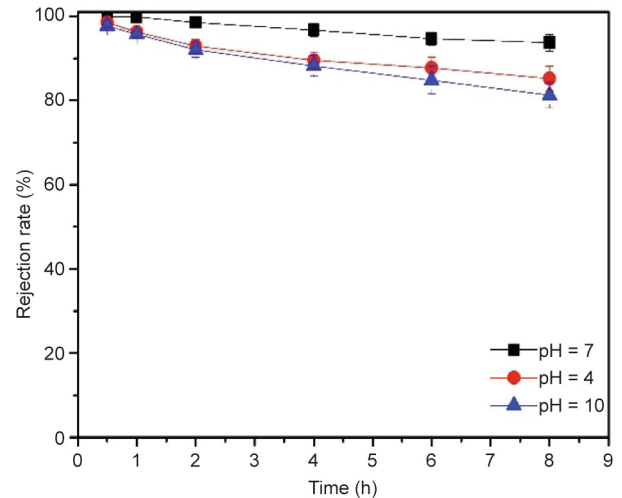


Fig. 7. Effect of initial pH on Cs rejection rate by the composite membrane.

hollow-fiber composite membrane [15,24]. Furthermore, CuFC can decompose in alkaline solution [15,24].

3.5. Effect of competing cations

The chloride salts of K^+ and Na^+ were selected to test the role of competing cations in the Cs rejection rate using composite membranes. As shown in Fig. 8, the rejection rate of the prepared composite membrane was high (99%), but the rejection rate of the pristine PVDF membrane was negligible. The membranes also showed a high rejection rate even after the addition of competing monovalent cations for 8 h. However, the rates decreased with an increase in the duration of the filtration time. Compared with Na^+ , K^+ showed a greater detrimental effect on Cs rejection rate; this might be due to the fact that K^+ has a similar hydration radius (0.331 nm) as Cs^+ (0.329 nm), which could induce competition [3,21]. The Cs rejection rate decreased with an increase of filtration time (Fig. 6), indicating that physical interception by the membrane is not the primary removal mechanism for Cs. As shown in Fig. 8, the Cs rejection rates were not greatly affected by the presence of competing cations, and remained above 90% for the first 2 h of unsaturated adsorption. Adsorption saturation of Cs was gradually reached and the Cs rejection rate was reduced with an increase

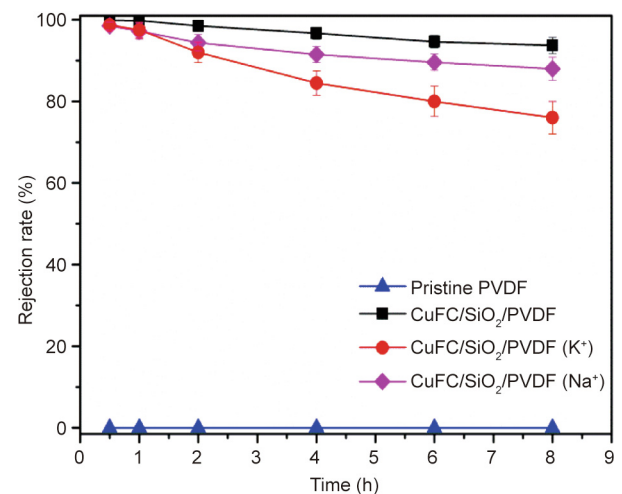


Fig. 8. Effects of competing cations on Cs rejection rate by the composite membrane.

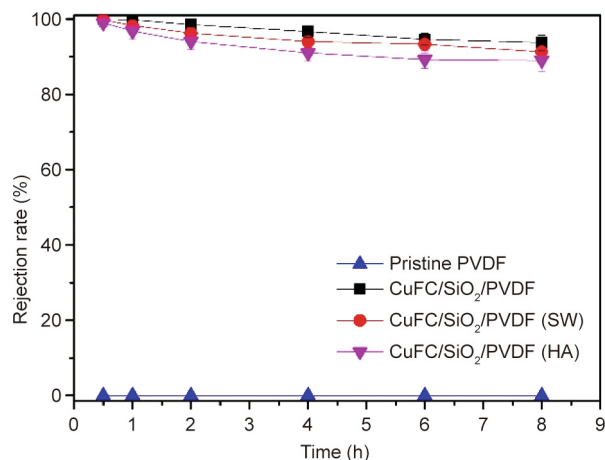


Fig. 9. Effect of organics on Cs rejection rate by the composite membrane.

of filtration time. Thus, the results show that adsorption by the modified membrane is the major mechanism for Cs removal.

3.6. Effects of organics

The effects of organics on Cs rejection rate using composite membrane filtration were tested in an HA solution and in SW; the results are shown in Fig. 9. The membrane continued to have a high Cs rejection rate (> 90%) in both solutions for 8 h. During this period, HA was deposited onto the membrane surface; this might have helped keep the rejection rate high due to size exclusion and Donnan exclusion [6]. Therefore, in addition to adsorption, size exclusion and Donnan exclusion on the membrane surface play an important role in Cs removal. It can be concluded that the composite membrane has excellent application potential for Cs removal.

4. Conclusions

In this work, a hollow-fiber composite membrane was prepared using the facile method of binding CuFC onto a PVDF membrane surface in order to remove Cs from water. SiO₂ NPs were used as an intermediate support layer, and chemical bonding of CuFC to the membrane surface occurred. The CuFC/SiO₂/PVDF hollow-fiber composite membranes exhibited high selectivity toward Cs and membrane flux. The membrane was able to directly and quickly filter out Cs in water, with a rejection rate higher than 99%. Furthermore, Cs rejection rate could be restored to more than 98% using 5 mol·L⁻¹ NH₄NO₃. The rejection rates were slightly affected by the solution pH and by competing cations. In addition, the composite membrane demonstrated good selectivity for water with a low Cs concentration (100 µg·L⁻¹), including SW and simulated water with HA. Overall, the functionalized composite membrane showed excellent potential for the removal of radionuclide Cs.

Acknowledgements

This work was funded by the Major Science and Technology Program for Water Pollution Control and Treatment of China (2015ZX07406006) and the National Natural Science Foundation of China (21677015, 41603109, and 51238006).

Compliance with ethics guidelines

Shiyuan Ding, Lilan Zhang, Yang Li, and Li'an Hou declare that they have no conflicts of interest or financial conflicts to disclose.

References

- [1] Kozai N, Suzuki S, Aoyagi N, Sakamoto F, Ohnuki T. Radioactive fallout cesium in sewage sludge ash produced after the Fukushima Daiichi nuclear accident. *Water Res* 2015;68:616–26.
- [2] Takata H, Kusakabe M, Inatomi N, Ikenoue T. Appearances of Fukushima Daiichi nuclear power plant-derived ¹³⁷Cs in coastal waters around Japan: results from marine monitoring off nuclear power plants and facilities, 1983–2016. *Environ Sci Technol* 2018;52(5):2629–37.
- [3] Kim YK, Kim T, Kim Y, Harbottle D, Lee JW. Highly effective Cs⁺ removal by turbidity-free potassium copper hexacyanoferrate-immobilized magnetic hydrogels. *J Hazard Mater* 2017;340:130–9.
- [4] Khannanov A, Nekljudov VV, Gareev B, Kiamov A, Tour JM, Dimiev AM. Oxidatively modified carbon as efficient material for removing radionuclides from water. *Carbon* 2017;115:394–401.
- [5] Liu X, Chen GR, Lee DJ, Kawamoto T, Tanaka H, Chen ML, et al. Adsorption removal of cesium from drinking waters: a mini review on use of biosorbents and other adsorbents. *Bioresour Technol* 2014;160:142–9.
- [6] Ding S, Yang Y, Li C, Huang H, Hou LA. The effects of organic fouling on the removal of radionuclides by reverse osmosis membranes. *Water Res* 2016;95:174–84.
- [7] Ding S, Yang Y, Huang H, Liu H, Hou LA. Effects of feed solution chemistry on low pressure reverse osmosis filtration of cesium and strontium. *J Hazard Mater* 2015;294:27–34.
- [8] Rana D, Matsuura T, Kassim MA, Ismail AF. Radioactive decontamination of water by membrane processes—a review. *Desalination* 2013;321:77–92.
- [9] Rajib M, Oguchi CT. Adsorption of ¹³³Cs and ⁸⁷Sr on pumice tuff: a comparative study between powder and intact solid phase. *Acta Geochim* 2017;36(2):224–31.
- [10] Ding D, Zhang Z, Chen R, Cai T. Selective removal of cesium by ammonium molybdophosphate-polyacrylonitrile bead and membrane. *J Hazard Mater* 2017;324(Pt B):753–61.
- [11] De Haro-Del Rio DA, Al-Jubori S, Kontogiannis O, Papadatos-Gigantes D, Ajayi O, Li C, et al. The removal of caesium ions using supported clinoptilolite. *J Hazard Mater* 2015;289:1–8.
- [12] Mu W, Yu Q, Li X, Wei H, Jian Y. Efficient removal of Cs⁺ and Sr²⁺ from aqueous solution using hierarchically structured hexagonal tungsten trioxide coated Fe₃O₄. *Chem Eng J* 2017;319:170–8.
- [13] Lee NK, Khalid HR, Lee HK. Adsorption characteristics of cesium onto mesoporous geopolymers containing nano-crystalline zeolites. *Micropor Mesopor Mat* 2017;242:238–44.
- [14] Yin X, Wang X, Wu H, Takahashi H, Inaba Y, Ohnuki T, et al. Effects of NH₄⁺, K⁺, Mg²⁺, and Ca²⁺ on the cesium adsorption/desorption in binding sites of vermiculitized biotite. *Environ Sci Technol* 2017;51(23):13886–94.
- [15] Yang HM, Hwang KS, Park CW, Lee KW. Sodium-copper hexacyanoferrate-functionalized magnetic nanoclusters for the highly efficient magnetic removal of radioactive caesium from seawater. *Water Res* 2017;125:81–90.
- [16] Zhang H, Zhao X, Wei J, Li F. Removal of cesium from low-level radioactive wastewaters using magnetic potassium titanium hexacyanoferrate. *Chem Eng J* 2015;275:262–70.
- [17] Vashnia S, Tavakoli H, Cheraghali R, Sepehrian H. Zinc hexacyanoferrate loaded mesoporous MCM-41 as a new adsorbent for cesium: equilibrium, kinetic and thermodynamic studies. *Desalin Water Treat* 2015;55:1220–8.
- [18] Qing Y, Li J, Kang B, Chang S, Dai Y, Long Q, et al. Selective sorption mechanism of Cs⁺ on potassium nickel hexacyanoferrate(II) compounds. *J Radioanal Nucl Chem* 2015;304(2):527–33.
- [19] Chen GR, Chang YR, Liu X, Kawamoto T, Tanaka H, Kitajima A, et al. Prussian blue (PB) granules for cesium (Cs) removal from drinking water. *Separ Purif Tech* 2015;143:146–51.
- [20] Chen R, Tanaka H, Kawamoto T, Asai M, Fukushima C, Kurihara M, et al. Thermodynamics and mechanism studies on electrochemical removal of cesium ions from aqueous solution using a nanoparticle film of copper hexacyanoferrate. *ACS Appl Mater Interfaces* 2013;5(24):12984–90.
- [21] Kim Y, Kim YK, Kim S, Harbottle D, Lee JW. Nanostructured potassium copper hexacyanoferrate-cellulose hydrogel for selective and rapid cesium adsorption. *Chem Eng J* 2017;313:1042–50.
- [22] Hwang KS, Park CW, Lee KW, Park SJ, Yang HM. Highly efficient removal of radioactive cesium by sodium-copper hexacyanoferrate-modified magnetic nanoparticles. *Colloid Surface A* 2017;516:375–82.
- [23] Yang HM, Lee KW, Seo BK, Moon JK. Copper ferrocyanide-functionalized magnetic nanoparticles for the selective removal of radioactive cesium. *J Nanosci Nanotechnol* 2015;15(2):1695–9.
- [24] Olatunji MA, Khandaker MU, Mahmud HNME, Amin YM. Influence of adsorption parameters on cesium uptake from aqueous solutions—a brief review. *RSC Adv* 2015;5(88):71658–83.
- [25] Michel C, Barre Y, De Windt L, De Dieuleveult C, Brackx E, Grandjean A. Ion exchange and structural properties of a new cyanoferrate mesoporous silica material for Cs removal from natural saline waters. *J Environ Chem Eng* 2017;5(1):810–7.
- [26] Banerjee D, Sandhya U, Pahan S, Joseph A, Ananthanarayanan A, Shah JG. Removal of ¹³⁷Cs and ⁹⁰Sr from low-level radioactive effluents by hexacyanoferrate loaded synthetic 4A type zeolite. *J Radioanal Nucl Chem* 2017;311(1):893–902.
- [27] Sangvanich T, Sukwarotwat V, Wiacek RJ, Grudzien RM, Fryxell GE, Addleman RS, et al. Selective capture of cesium and thallium from natural waters and

- simulated wastes with copper ferrocyanide functionalized mesoporous silica. *J Hazard Mater* 2010;182(1–3):225–31.
- [28] Chen GR, Chang YR, Liu X, Kawamoto T, Tanaka H, Parajuli D, et al. Prussian blue non-woven filter for cesium removal from drinking water. *Separ Purif Tech* 2015;153:37–42.
- [29] Efome JE, Rana D, Matsuura T, Lan CQ. Experiment and modeling for flux and permeate concentration of heavy metal ion in adsorptive membrane filtration using a metal-organic framework incorporated nanofibrous membrane. *Chem Eng J* 2018;352:737–44.
- [30] Efome JE, Rana D, Matsuura T, Lan CQ. Insight studies on metal-organic framework nanofibrous membrane adsorption and activation for heavy metal ions removal from aqueous solution. *ACS Appl Mater Interfaces* 2018;10(22):18619–29.
- [31] Efome JE, Rana D, Matsuura T, Lan CQ. Metal-organic frameworks supported on nanofibers to remove heavy metals. *J Mater Chem A Mater Energy Sustain* 2018;6(10):4550–5.
- [32] Chaudhury S, Pandey AK, Goswami A. Copper ferrocyanide loaded track etched membrane: an effective cesium adsorbent. *J Radioanal Nucl Chem* 2015;304(2):697–703.
- [33] Kim H, Kim M, Lee W, Kim S. Rapid removal of radioactive cesium by polyacrylonitrile nanofibers containing Prussian blue. *J Hazard Mater* 2018;347:106–13.
- [34] Chen R, Tanaka H, Kawamoto T, Asai M, Fukushima C, Na H, et al. Selective removal of cesium ions from wastewater using copper hexacyanoferrate nanofilms in an electrochemical system. *Electrochim Acta* 2013;87:119–25.
- [35] Bang H, Watanabe K, Nakashima R, Kai W, Song KH, Lee JS, et al. A highly hydrophilic water-insoluble nanofiber composite as an efficient and easily-handleable adsorbent for the rapid adsorption of cesium from radioactive wastewater. *RSC Adv* 2014;4(103):59571–8.
- [36] Jia Z, Cheng X, Guo Y, Tu L. *In-situ* preparation of iron(III) hexacyanoferrate nano-layer on polyacrylonitrile membranes for cesium adsorption from aqueous solutions. *Chem Eng J* 2017;325:513–20.
- [37] Ding S, Zhang L, Li Y, Hou LA. Fabrication of a novel polyvinylidene fluoride membrane via binding SiO₂ nanoparticles and a copper ferrocyanide layer onto a membrane surface for selective removal of cesium. *J Hazard Mater* 2019;368:292–9.
- [38] Qin A, Li X, Zhao X, Liu D, He C. Engineering a highly hydrophilic PVDF membrane via binding TiO₂ nanoparticles and a PVA layer onto a membrane surface. *ACS Appl Mater Interfaces* 2015;7(16):8427–36.
- [39] Yatsimirskii KB, Nemoshkalenko VV, Nazarenko YP, Aleshin VG, Zhilinskaya VV, Tomashevsky NA. Use of X-ray photoelectron and Mössbauer spectroscopies in the study of iron pentacyanide complexes. *J Electron Spectrosc Relat Phenom* 1977;10(3):239–45.
- [40] Seah MP, Smith GC, Anthony MT. AES: energy calibration of electron spectrometers. 1—an absolute, traceable energy calibration and the provision of atomic reference line energies. *Surf Interface Anal* 1990;15(5):293–308.
- [41] Loos-Neskovic C, Ayrault S, Badillo V, Jimenez B, Garnier E, Fedoroff M, et al. Structure of copper-potassium hexacyanoferrate(II) and sorption mechanisms of cesium. *J Solid State Chem* 2004;177(6):1817–28.
- [42] Egorin A, Tokar E, Zemskova L, Didenko N, Portnyagin A, Azarova Y, et al. Chitosan-ferrocyanide sorbents for concentrating Cs-137 from seawater. *Sep Sci Technol* 2017;52(12):1983–91.
- [43] Nilchi A, Malek B, Ghanadi Maragheh M, Khanchi A. Exchange properties of cyanide complexes. *J Radioanal Nucl Chem* 2003;258(3):457–62.