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In-situ preparation of iron(III) hexacyanoferrate nano-layer on polyacrylonitrile membranes for cesium adsorption from aqueous solutions

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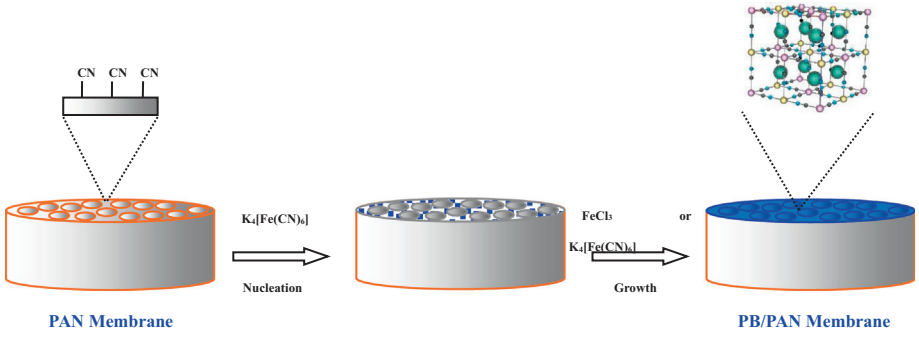
HIGHLIGHTS

- Prussian blue nano-layer was in-situ prepared on porous polymer membranes.
- Immobilization of PB on membrane surface does not deteriorate in adsorption performance.
- The membrane showed high adsorption capacity and selectivity for cesium and rubidium.

GRAPHICAL ABSTRACT



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ABSTRACT

Ion-exchange adsorption is an effective method for separating cesium and rubidium from other alkaline metal ions in aqueous solutions. Herein, we developed a novel and facile method for in-situ preparation of Prussian blue (PB) nano-layer on porous polyacrylonitrile (PAN) membranes by heterogeneous nucleation in potassium ferrocyanide solution and then growth in $FeCl_3$ solution, or potassium ferrocyanide solution as single precursor. The effects of reactant concentrations and reaction time on the PB layer, the static adsorption, dynamic adsorption, desorption and reuse of PB membranes were investigated. The results showed that the maximum adsorption capacity of PB nano-layer for cesium attains 0.714 mmol g^{-1} (25 °C), and the ideal selectivity factor of Cs^+ vs. Li^+, K^+, and Na^+ is found to be 41.76, 35.50, and 23.67 respectively. Compared with the PB powder, the immobilized PB on membrane surface does not deteriorate in the adsorption performance. NH_4Cl aqueous solution exhibits excellent eluting effect, and the membrane can be reused for 5 times without apparent deterioration, indicating practical perspective in adsorption of cesium and rubidium from aqueous solutions.

1. Introduction

Cesium and rubidium, as highly dispersed and precious metal elements, play important roles in many fields such as photocells, spectrographs, health care, scintillation detectors, catalyst, atomic clock, magnetic fluid, etc [1–4]. Under natural conditions, cesium and rubidium exist in the salt lake, geothermal water and oil field brine besides ore minerals. Cesium and rubidium usually coexist with other alkali metals such as lithium, sodium and potassium as accompanying elements in the liquid resources. Radioactive cesium in nuclear waste is also

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of great concern in environment, public health, and safety aspects [5,6].

Separation of cesium and rubidium from other alkali metals has been one of the most difficult problems due to their close similarity in physical and chemical properties. When the metal ion concentration is less than 1 mg L^{-1}, the chemical precipitation, extraction and electrochemical methods are not efficient [7]. In contrary, adsorption is an effective method to extract trace cesium and rubidium from aqueous solutions. Natural and synthetic zeolites [8,9], clay minerals, and synthetic ion-exchangers (e.g. ammonium tungstophosphate, [10] iron(III) hexacyanoferrate and its analogues [11], zirconium tungstate [12],etc.) have been employed for adsorption of cesium and rubidium. Iron(III) hexacyanoferrate (Prussian blue, PB), as an excellent scavenger of Cs^+, is approved by FDA for the removal of radioactive cesium from the creatures' gastrointestinal tract by oral administration [13,14], and has been paid remarkable attentions in the adsorption of cesium and rubidium.

Nevertheless, the synthetic ion-exchangers are usually ultrafine powders, resulting in high resistance in adsorption fixed bed. Therefore, preparation of adsorbent composites by immobilizing the ion-exchangers particles on supporter or matrix is widely employed, such as copper hexacyanoferrate/polyacryloni trile [15], potassium tetraphenylborate/calcium alginate (KB $(C_6H_5)_4$–$Ca(ALG)_2$)[16], PB/alginate calcium [17], magnetic PB/graphene oxide (PB/Fe_3O_4/GO) [18], magnetic PB/graphene oxide alginate calcium [19], PB/pine cone [20], etc. However, the adsorption efficiency of the composites (usually hundreds or thousands of micrometers in size) is usually not satisfied because of large intraparticle diffusion resistance, coating of ion-exchangers by matrix, and agglomeration of ion-exchangers. Membrane adsorption has emerged as a novel adsorption technology in recent years [21]. By incorporating nanosized adsorbents in polymer matrix, the porous adsorptive membranes are employed in removal of trace solutes from aqueous solution [22,23], exhibiting low internal diffusion resistance, and fast adsorption rate [24]. Nevertheless, as some adsorbents are enveloped in membrane matrix, the adsorption efficiency still needs to be further improved [25].

Polyacrylonitrile (PAN) possesses low density, thermal stability, high strength and large elasticity modulus, and is a versatile polymer for producing ultrafiltration membranes, adsorptive membranes[26,27], substrates for reverse osmosis and pervaporation membranes[28]. Herein we developed a novel and facile method to fabricate Prussian blue nano-layer in situ on porous polyacrylonitrile (PAN) membranes for adsorption of cesium and rubidium. In the preparation, PAN membranes were firstly immersed in potassium ferrocyanide solution. As PAN membrane surface possesses huge amounts of cyano (–CN) groups, it has strong affinity to $[Fe(CN)_6]^{4-}$. The $[Fe(CN)_6]^{4-}$ complexes in solution slowly dissociate and generate ferrous ions [29], resulting in the reaction of ferrous ions with $[Fe(CN)_6]^{4-}$ and nucleation of PB on PAN surface. The PB nuclei grow and form PB layer in $FeCl_3$ solution or potassium ferrocyanide solution (as single precursor). Analogous to the electroless plating [30,31], the nucleation and growth process of PB on PAN membrane surface is slow, leading to uniform and robust PB nano-layer. In the adsorption operation, the feeding solution flows through the membrane pores and contacts with the PB layer directly, resulting in low internal diffusion resistance, fast adsorption rates, and high removal efficiency. In this paper, the effects of reactant concentrations and reaction time on PB layer, the static adsorption, dynamic adsorption, desorption and reuse of PB membranes were investigated.

2. Experimental

2.1. Materials

$K_4Fe(CN)_6$, $FeCl_3$, CsCl, RbCl, KCl, NaCl, LiCl, NH_4Cl, $CaCl_2$, and H_2SO_4 were analytical grade, and used as received without further purification. PAN ultrafiltration membrane (MWCO 50,000) was bought from Beijing Saipuruite Company, China. The stock solution of metal chloride (10 mmol L^{-1}) was prepared by dissolving the salt in DI water. To obtain the working solutions, the stock solution was diluted to the desired concentrations.

2.2. In-situ preparation of PB nano-layer

For in-situ preparation of PB with $K_4Fe(CN)_6$ and $FeCl_3$ as reactants, the PAN membranes were firstly immersed in potassium ferrocyanide solution (0.025 mol L^{-1}) for 24 h. Then the membrane was rinsed with DI water for three times and immersed in $FeCl_3$ solutions (0.005, 0.025, and 0.125 mol L^{-1}, containing 0.01 mol L^{-1} hydrochloric acid) respectively for 24 h to form PB layer. For the preparation of PB with $K_4Fe(CN)_6$ as single precursor, the PAN membranes were immersed in 0.025 mol L^{-1} potassium ferrocyanide solution (containing 1.6 mol L^{-1} hydrogen chloride acid) for 3, 6 and 9 days respectively. New prepared $K_4Fe(CN)_6$ and $FeCl_3$ solutions were used in the above experiments. The membranes were weighed with balance prior to and after the growth of PB to measure the PB content.

2.3. Adsorption

The static adsorption was conducted in a sealed conical flask with 50 mL of metal chloride solution (0.075 mmol L^{-1}) under stirring rate of 50 rpm for 24 h. The adsorption capacity (Q_e, mmol g^{-1}) was calculated as,

$$Q_e = \frac{(c_0 - c_e) \times v_0}{w_0} \quad (1)$$

where c_0 and c_e are the initial and equilibrium cation concentration (mmol L^{-1}) respectively, v_0 the solution volume (L), w_0 the PB mass (g) unless otherwise specified. The ideal selectivity factor is defined as $Q_{e,i}/Q_{e,j}$, where i and j represent the cation i and j. The removal efficiency (R, %) was expressed as,

$$R = \frac{c_0 - c_e}{c_0} \times 100\% \quad (2)$$

The desorption rate (DR,%) was calculated as,

$$DR = \frac{c_1 \times v_1}{w_1} \times 100\% \quad (3)$$

where c_1 is the cation concentration in the eluent (mmol L^{-1}), v_1 the eluent volume (L), w_1 the cation adsorbed on the membrane (mmol).

The dynamic adsorption was carried out with a filter (Φ50 mm). The membrane was firstly preconditioned with 3 × 5 mL water, and then 100 mL of aqueous solution (0.06 mmol L^{-1}) flowed through the membrane at the rate of 3.33 mL min^{-1}. The effluent solution was collected at a certain interval and analyzed to determine the residual cation concentrations. In the dynamic desorption, a certain volume of eluting agent flowed through the membrane at a rate of 0.2 mL min^{-1}, and the eluent concentration was measured.

2.4. Characterization

The morphologies of membranes were observed with a field emission scanning electron microscope (SEM, Hitachi S-4800,