

Enhanced Removal of Cesium Ions by Prussian Blue/Calcium Alginate Composite Membranes: Mechanism of Atomic-Level Trapping Elucidated by Combined Experimental and DFT Studies

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Abstract

The efficient removal of radioactive cesium from contaminated water is crucial for environmental safety and nuclear waste management. In this study, we developed a novel composite membrane by embedding Prussian blue (PB) into a calcium alginate (CA) matrix, and elucidated the atomic-level mechanism of cesium removal through a combined experimental and density functional theory (DFT) approach. Batch adsorption experiments demonstrated that the optimal PB/CA membrane with 20% PB loading exhibited a high adsorption capacity toward Cs(I), with a maximum capacity of 29.59 mg/g. In a multi-ion coexisting system, the membrane achieved an exceptional removal efficiency of up to 94.96% for Cs(I), showcasing superior selectivity and strong anti-interference capability. The adsorption process was found to be spontaneous and endothermic, which was best fitted by the pseudo-second-order kinetic and Langmuir isotherm models, indicating a monolayer adsorption mechanism dominated by chemisorption. A combination of characterization techniques (XPS, XRD, Mössbauer spectroscopy) and DFT calculations collaboratively revealed the fundamental adsorption mechanism: Cs (I) is not simply adsorbed on the surface of the material, but specifically embedded into the intrinsic vacancies of the Prussian blue lattice, where it coordinates with cyano nitrogen atoms, causing a lattice contraction of approximately 0.68%.

Keywords: Prussian blue, Alginate composite membrane, Cesium adsorption, Selective separation, Radioactive waste treatment

Introduction

As a clean energy source, nuclear energy has become one of the important directions of global energy development due to its advantages of low carbon emissions, environmental friendliness, and high energy density. However, the generation of radionuclides during nuclear energy production is unavoidable, which may pose potential risks to human health and the environment. Among them, the release of ^{137}Cs has attracted particular attention and has become a global environmental challenge^[1-3]. With long half-life and strong bioaccumulation ability, these radionuclides can migrate and accumulate through the soil – plant – animal food chain, thereby undermining the structural and functional stability of ecosystems and posing a serious threat to the integrity of the human hematopoietic and nervous systems^[4, 5]. Given its persistent environmental toxicity and long-range diffusion potential, the development of efficient and eco-friendly technologies for the separation and remediation of radioactive cesium contamination is of great practical significance for curbing pollution spread, safeguarding ecological security, and protecting human health^[6-8].

At present, the main treatment methods for cesium in radioactive wastewater include chemical precipitation^[9, 10], solvent extraction^[11], adsorption^[7, 12-16], ion exchange^[17], membrane separation^[18-20], biological methods^[21, 22], and electrochemical methods^[23, 24]. Among them, adsorption has become an effective method for treating radioactive wastewater owing to its low cost, simple operation, good scalability, and lack of secondary pollution. Prussian blue (PB) has attracted extensive attention from researchers due to its excellent chemical stability, radiation resistance, high adsorption capacity, and high selectivity^[25-27]. PB is an inorganic material with a face-centered cubic lattice, and its molecular formula can be expressed as $\text{M}[\text{Fe}(\text{CN})_6]$ (where M is Fe^{3+} , Cu^{2+} , Co^{2+} , Ni^{2+} , etc.). PB contains abundant intrinsic vacancies in its structure, with a radius of approximately 3.20 Å, which is close to the hydrated ionic radius of cesium ions (Cs(I) , 3.29 Å), while the hydrated radii of common competing ions (Na^+ , Ca^{2+} , Mg^{2+}) are much larger than 3.2 Å. This constitutes the core structural basis for its highly selective adsorption toward Cs(I) .

Nevertheless, pristine PB is mostly in powder form, which is difficult to recover and easy to leak into the environment, causing secondary pollution. Therefore, it is necessary to prepare composite adsorbents by loading PB onto support materials to solve these problems [28-31]. Gao^[32] et al. prepared a layer-by-layer assembled ferrocyanide composite fiber (ZnFC/PA/PSF) via the coordination of phytic acid (PA) with Zn^{2+} . This composite fiber exhibited favorable stability and reached rapid adsorption equilibrium within 25 min. The maximum adsorption capacity calculated by the Langmuir model was 524.76 mg/g, and it maintained high selectivity for cesium ions even in the presence of interfering ions ($K = 2.5 \times 10^4 \text{ mL/g}$). Chen^[33] et al. proposed a green synthesis method for mesoporous PB assisted by ionic liquid ([Bmim]BF₄). The interaction between [Bmim]⁺ introduced by the ionic liquid and [Fe(CN)₆]⁴⁻, together with the high viscosity, affected the diffusion of precursors and slowed down the crystallization rate of PB. The PB material synthesized by this method achieved a cesium adsorption capacity of 548.7 mg/g and remained stable over a wide pH range. Zhang^[34] et al. fabricated a polyvinylidene fluoride (PVDF) membrane co-doped with PB and graphene oxide (GO). SEM observations revealed that the addition of GO improved the dispersion of PB, and the PVDF-PB-GO membrane achieved the highest Cs(I) removal efficiency (99.6%) at pH 7. Li^[35] et al. developed a reduced graphene oxide aerogel doped with ternary (Ni, Co, Fe) Prussian blue analogues (RGOA/TPBs) via a controlled self-assembly strategy. The unique three-dimensional layered structure endowed RGOA/TPBs with excellent mechanical strength and high specific surface area, facilitating the exposure of adsorption sites and thus promoting cesium adsorption. The maximum adsorption capacity of the composite was 226.98 mg/g, and coexisting ion adsorption experiments confirmed its good selectivity. Although PB-based composites exhibit superior adsorption performance and stability toward Cs(I) and show considerable potential for industrial application, several challenges remain to be addressed. At present, the support materials used for Prussian blue (PB) composite generally have common drawbacks, such as complex synthesis processes, cumbersome preparation steps (e.g., layer-by-layer (LBL) assembly, ionic liquid and graphene oxide (GO) synthesis), high environmental pollution, and poor

compatibility with PB. To address these issues, we synthesized a new PB-based composite adsorbent.

Alginate is a natural anionic polysaccharide derived from seaweed cell walls, featuring non-toxicity, biodegradability, renewability, excellent gel-forming and film-forming properties, and strong metal complexation ability^[36]. It has been widely used for the removal of various heavy metal ions such as Cd(VI), As(III), and Cu(II) from water bodies^[37-41]. Calcium alginate (CA), as a natural polymer gel coating matrix, can effectively alleviate the shortcomings of PB powder such as easy agglomeration, cumbersome separation, and poor mechanical stability. The integration of these two components to prepare PB@CA composites combines excellent adsorption performance with favorable practical applicability.

On the other hand, current studies on the adsorption mechanism of PB toward Cs(I) mostly remain at the level of macroscopic phenomenological speculation, with preliminary hypotheses mainly including ion exchange and physical adsorption in pore channels, lacking direct evidence and systematic interpretation at the atomic-level. For instance, key scientific issues such as how the size matching between the cage-like pores in the PB crystal structure and Cs(I) affects adsorption selectivity, the types and intensity distribution of atomic-level interactions (e.g., hydrogen bonding, van der Waals forces, coordination interactions), the specific binding mode and electron cloud distribution changes of Cs(I) at adsorption sites, and the microevolution of the PB crystal structure during adsorption have not been fully explored. Therefore, while optimizing the preparation process of PB-alginate composites and improving macroscopic adsorption performance, it is particularly important to conduct atomic-scale adsorption mechanism studies to clarify the adsorption pathway, binding mode, and microscopic interaction mechanism of Cs(I)^[42-44].

In this study, we systematically investigated the preparation of Prussian blue/calcium alginate (PB/CA) composite membranes through a facile blade-coating and cross-linking process. Different from conventional reports focusing on adsorption performance, this work combines detailed experimental analysis with density

functional theory (DFT) calculations to achieve multiple objectives: optimizing membrane preparation conditions such as PB loading and thickness; comprehensively evaluating adsorption behavior including kinetics, isotherms, thermodynamics, selectivity, and reusability under various conditions; and ultimately clarifying the atomic-level capture mechanism of Cs(I) via advanced characterization techniques (SEM, XRD, XPS, Mössbauer spectroscopy) combined with theoretical simulations. This integrated approach not only yields an effective and practical cesium decontamination membrane but also deeply reveals the atomic-Level interactions governing the cesium adsorption process, thereby providing new insights for the design of next-generation selective separation materials.

2 Materials and Methods

2.1 Materials

All chemical reagents were used as received without further purification. Prussian blue, potassium ferrocyanide, cobalt chloride, sodium hydroxide, sodium alginate, absolute ethanol, aluminum chloride, magnesium chloride, copper chloride, ferric chloride, and zinc chloride were all purchased from Sinopharm Chemical Reagent Co., Ltd. Nickel chloride, cesium chloride, nitric acid, and hydrochloric acid were obtained from Tianjin Yaohua Chemical Reagent Co., Ltd. Dimethyl sulfoxide was supplied by Shanghai Lingfeng Chemical Reagent Co., Ltd. Barium chloride was purchased from Tianjin Yongda Chemical Reagent Co., Ltd. Calcium chloride was obtained from Aladdin Biochemical Technology Co., Ltd.

2.2 Preparation of Prussian Blue/Calcium Alginate (PB/CA) Membranes

The Prussian blue/calcium alginate (PB/CA) composite membranes were fabricated using a facile blade-coating method followed by ionic cross-linking. The detailed preparation procedure, schematically illustrated in Figure 1. First, 3 g of dried sodium alginate (SA) powder was gradually added to 77 mL of deionized water under constant magnetic stirring at room temperature. The mixture was then heated and stirred continuously until a homogeneous, viscous SA solution was obtained. Subsequently, 20

g of dried Prussian blue (PB) powder was slowly and incrementally added to the prepared SA solution. The mixture was vigorously stirred to ensure uniform dispersion of the PB particles, resulting in a stable, homogeneous casting solution. The resulting casting solution was poured onto a smooth glass plate and spread uniformly using an automatic membrane applicator to achieve a controlled thickness. The glass plate was then immediately immersed in a bath containing a 1 wt% calcium chloride (CaCl_2) solution for cross-linking. The ion exchange between Na^+ in the alginate and Ca^{2+} in the bath facilitated the formation of a stable, insoluble calcium alginate hydrogel membrane embedded with PB particles. The formed PB/CA membrane was thoroughly rinsed with deionized water to remove any residual salts and finally dried in a fume hood for further use.

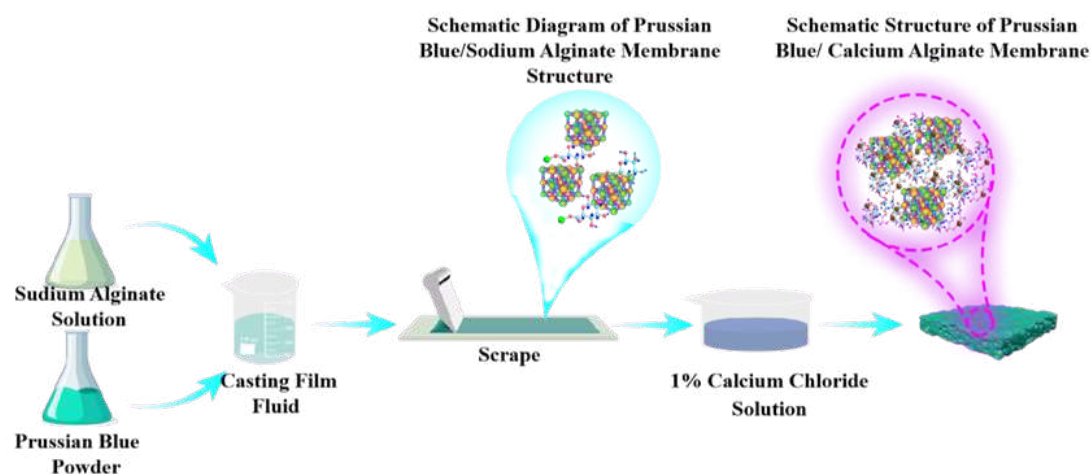


Figure 1 Schematic illustration of the preparation process for the Prussian blue/calcium alginate (PB/CA) membrane

2.3 Characterization Methods

The chemical composition of the materials was characterized using Fourier transform infrared spectroscopy (FTIR, $400 - 4000 \text{ cm}^{-1}$, KBr pellet method). The crystal structure was analyzed by X-ray diffraction (XRD, $\text{Cu-K}\alpha$, $10-80^\circ$, $10^\circ/\text{min}$), while the morphology and elemental distribution (C, N, Fe, Ni, Cs) were examined

using scanning electron microscopy (SEM, 2.0 kV, 2000-5000 $\times$) coupled with energy-dispersive X-ray spectroscopy (EDS).

2.4 Adsorption Test

This study utilized static batch adsorption experiments to explore the adsorption performance of PB/CA membranes towards Cs(I). The experimental procedure was conducted as follows: Initially, a 1000 mg/L cesium chloride stock solution was prepared, which was subsequently diluted to the target concentration in accordance with experimental requirements. The pH value of the solution was adjusted using 1 mol/L hydrochloric acid or sodium hydroxide. A precise mass of PB/CA membrane was accurately weighed and transferred into a 50 mL centrifuge tube, followed by the addition of 40 mL of cesium solution with a specified concentration. The centrifuge tube was then placed on a constant-temperature shaker at 120 rpm for isothermal oscillation. Upon reaching the preset contact time, the solution was filtered through a 0.22 μ m syringe filter. A 1 mL aliquot of the filtrate was pipetted and mixed thoroughly with 4 mL of 2% nitric acid. The concentrations of Cs(I) in the solutions before and after adsorption were determined by inductively coupled plasma mass spectrometry (ICP-MS), based on which the adsorption capacity, removal rate, and desorption rate were calculated. The obtained experimental data were processed using Equations 1, 2, and 3:

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

$$R\% = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

$$Y\% = \frac{C_d \cdot V_d}{m \cdot Q} \times 100\% \quad (3)$$

Q: Adsorption capacity of the adsorbent (mg/g); C_0 and C_e : Initial and equilibrium cesium concentrations in the solution before and after adsorption, respectively (mg/L); V: Volume of the solution (mL); m: Mass of the adsorbent (g); R: Adsorption removal rate of the adsorbent; C_d : Cesium ion concentration in the desorption solution (mg/L); V_d : Volume of the desorption solution (mL); Y: Desorption rate of the adsorbent.

2.5 Related Fitting and DFT Study

Adsorption Kinetics Fitting: In this study, three kinetic models were employed, namely the pseudo-first-order kinetic model, the pseudo-second-order kinetic model, and the Weber-Morris intraparticle diffusion model. Specifically, the pseudo-first-order and pseudo-second-order kinetic models were used to determine the adsorption type, the Weber-Morris intraparticle diffusion model was utilized to characterize the adsorption stages. The specific equations are presented as follows:

(1) Quasi-first-order kinetic model

$$\frac{dQ_t}{dt} = k_1(Q_e - Q_t) \quad (4)$$

Simplifying equation (4) yields:

$$Q_t = Q_e(1 - e^{-k_1 t}) \quad (5)$$

(2) Quasi-Second-Order Kinetic Model

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \quad (6)$$

Simplifying equation (6) yields:

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_2 Q_e^2} \quad (7)$$

(3) Intra-particle diffusion model

$$Q_t = K_{id}t^{\frac{1}{2}} + C \quad (8)$$

Q_e : Equilibrium adsorption capacity(mg/g); Q_t : Adsorption capacity at time t(mg/g); K_1 : Pseudo-first-order kinetic constant (min^{-1}); K_2 : Pseudo-second-order kinetic constant, (g/mg·min); t : Adsorption time (min); K_{id} : Intra-particle diffusion rate constant(g/mg·min^{1/2}); C : Constant related to boundary layer thickness(mg/g)

Adsorption isotherm fitting: The Langmuir and Freundlich models were employed to fit the adsorption of cesium ions onto the as-prepared material in this work.

(1) Langmuir Model

The Langmuir model assumes that the adsorbent forms a monolayer adsorption. Its specific equation is as follows:

$$Q_e = Q_m \frac{K_L C_e}{1 + K_L C_e} \quad (10)$$

In the formula, Q_e and Q_m are the adsorption capacities at equilibrium and the maximum adsorption capacity, respectively, both with units of mg/g; K_L is the Langmuir constant, with units of L/mg; C_e is the concentration of cesium in the solution at adsorption equilibrium, with units of mg/L.

(2) Freundlich Model

The Freundlich model assumes that the adsorption reaction takes place under ideal conditions, and its specific equation is as follows:

$$Q_e = K_F C_e^{\frac{1}{n}} \quad (11)$$

In the formula, Q_e is the equilibrium adsorption capacity, with units of mg/g; K_F is the Freundlich constant, with units of L/mg; n is the heterogeneity factor, representing the uniformity of the distribution of adsorption sites on the adsorbent surface.

Thermodynamic parameter calculation: Based on adsorption isotherm data at different temperatures, the Gibbs free energy change (ΔG_0), enthalpy change (ΔH_0), and entropy change (ΔS_0) are calculated using relevant formulas, in order to determine the spontaneity of the adsorption process, its endothermic or exothermic characteristics, and changes in system disorder. It is subsequently confirmed that the adsorption process is a spontaneous endothermic process.

$$\Delta G^0 = -RT \ln K_d \quad (12)$$

$$K_d = \frac{Q_e}{C_e} \quad (13)$$

$$\ln K_d = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (14)$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (15)$$

In the formula, K_d is the distribution coefficient of the adsorbed substance, with units of L/mg; T is the adsorption temperature, with units of K; R is the ideal gas constant, with a value of 8.314 J/mol·K.

For the geometric optimization of the crystal structure, we initiated the geometry optimization function in the DMol3 module of Materials Studio 7.0. During the optimization steps, all atoms were fully relaxed. The adsorption energy (ΔE_{ads}) was calculated using the following formula

$$E_{ads} = E_{ab} - E_a - nE_b \quad (16)$$

3 Results and Discussion

3.1 Optimization of Membrane Preparation Conditions

The influence of PB content was first evaluated by preparing membranes with PB-to-SA mass ratios ranging from 0% to 20%, while maintaining a constant thickness of 1000 μm . As illustrated in Figure 2a, the removal rate of Cs(I) significantly increased with higher PB loadings. This trend is directly attributable to the corresponding increase in the number of active adsorption sites provided by the PB crystals within the CA matrix. While the pure CA membrane exhibited negligible adsorption, the incorporation of 20% PB yielded the highest performance. However, it was observed that exceeding this ratio compromised the mechanical integrity of the membrane, preventing the formation of a stable freestanding membrane due to an insufficient amount of SA binder to encapsulate the excessive PB particles. Consequently, a PB loading of 20% was identified as the optimal composition and adopted for all subsequent studies.

The effect of membrane thickness on adsorption capacity was examined by fabricating membranes with thicknesses of 500, 750, and 1000 μm . Subsequent adsorption experiments were conducted on these three distinct PB/CA membranes to

ascertain the relationship between membrane thickness and its adsorption efficacy. The experimental findings are presented in Figure 2b.

Variations in membrane thickness exert no significant influence on the removal efficiency of cesium ions from aqueous solution. The high porosity of the calcium alginate (CA) membrane provides sufficient contact interface between Prussian blue (PB) and the aqueous solution, thereby rendering mere adjustments in membrane thickness to have a negligible impact on adsorption performance. Nevertheless, a reduction in membrane thickness compromises the mechanical strength of the composite material; consequently, all subsequent experiments employ Prussian blue/calcium alginate (PB/CA) composite membranes with a thickness of 1000 μ m.

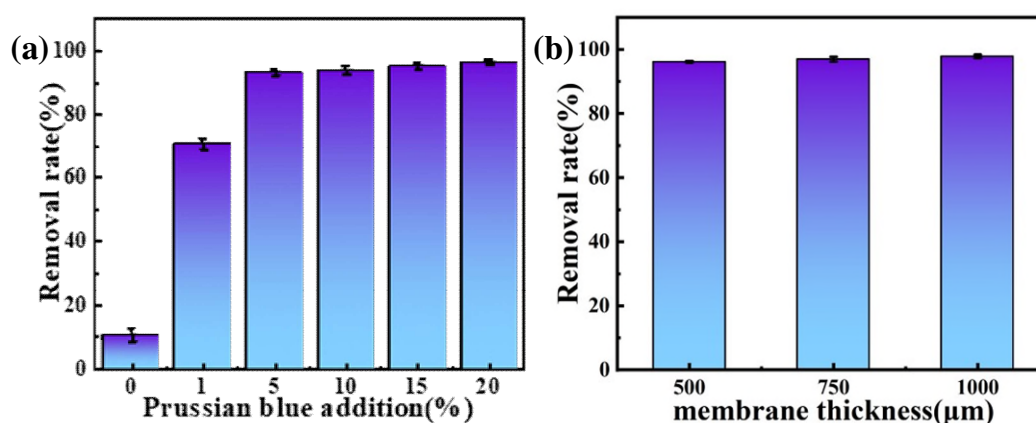


Figure 2: Effects of (a) Prussian blue content and (b) membrane thickness on the adsorption capacity of PB/CA membranes for Cs(I)

The membrane prepared under these optimized conditions (20% PB, 1000 μ m thickness) was further characterized for its mechanical properties using a universal testing machine. The measured tensile strength and elastic modulus were 0.11 MPa and 0.59 MPa, respectively, indicating sufficient mechanical robustness for handling and application in adsorption studies.

3.2 Characterization of the Prepared PB/CA Membranes

The surface morphology of the PB/CA membrane was examined using scanning

electron microscopy (SEM). As shown in Figure 3a and b, which present images at magnifications of 1000× and 2000×, respectively, the membrane exhibits a heterogeneous surface topography with prominent irregularities. At higher magnification (Figure 3b), fine particulate structures are clearly visible, adhering to a relatively smooth substrate region. These particles are uniformly distributed and display characteristic dimensions consistent with Prussian blue (PB) crystals, confirming the successful incorporation of PB into the alginate matrix.

The chemical structure of the prepared materials was characterized by Fourier transform infrared (FT-IR) spectroscopy, as shown in Figure 3c. The spectra of both sodium alginate (SA) and the PB/CA composite exhibit characteristic absorption bands: a broad peak in the range of 3300–3500 cm^{-1} attributed to O–H stretching vibrations, a signal near 2700 cm^{-1} corresponding to C–H stretching, and peaks at approximately 1200 cm^{-1} and 1600 cm^{-1} associated with the asymmetric and symmetric stretching of $-\text{COO}^-$ groups, respectively. A distinct C–O stretching vibration is also observed around 1000 cm^{-1} . Critically, the PB/CA spectrum displays an additional sharp peak at 2086 cm^{-1} , which is absent in the pure SA spectrum. This peak corresponds to the $\text{C}\equiv\text{N}$ stretching vibration of Prussian blue, confirming the successful incorporation of PB into the alginate matrix.

The crystalline structure of the composite membrane was analyzed by X-ray diffraction (XRD). The XRD pattern of the PB/CA membrane (Figure 3d) shows distinct diffraction peaks at 2θ values of 17.50°, 24.84°, 35.42°, 39.76°, 43.74°, 50.95°, 53.47°, 57.49°, 66.51°, 69.37°, and 76.98°. These peaks are indexed to the (200), (220), (400), (420), (422), (440), (531), (620), (640), (642), and (733) crystal planes of Prussian blue, respectively, and align well with the standard reference pattern. The presence of these well-defined diffraction peaks demonstrates that the crystalline framework of PB remains intact throughout the membrane preparation process. This indicates that neither the blade-coating procedure nor the interaction with sodium alginate disrupts the crystal lattice of PB, affirming the successful integration of crystalline PB into the CA membrane.

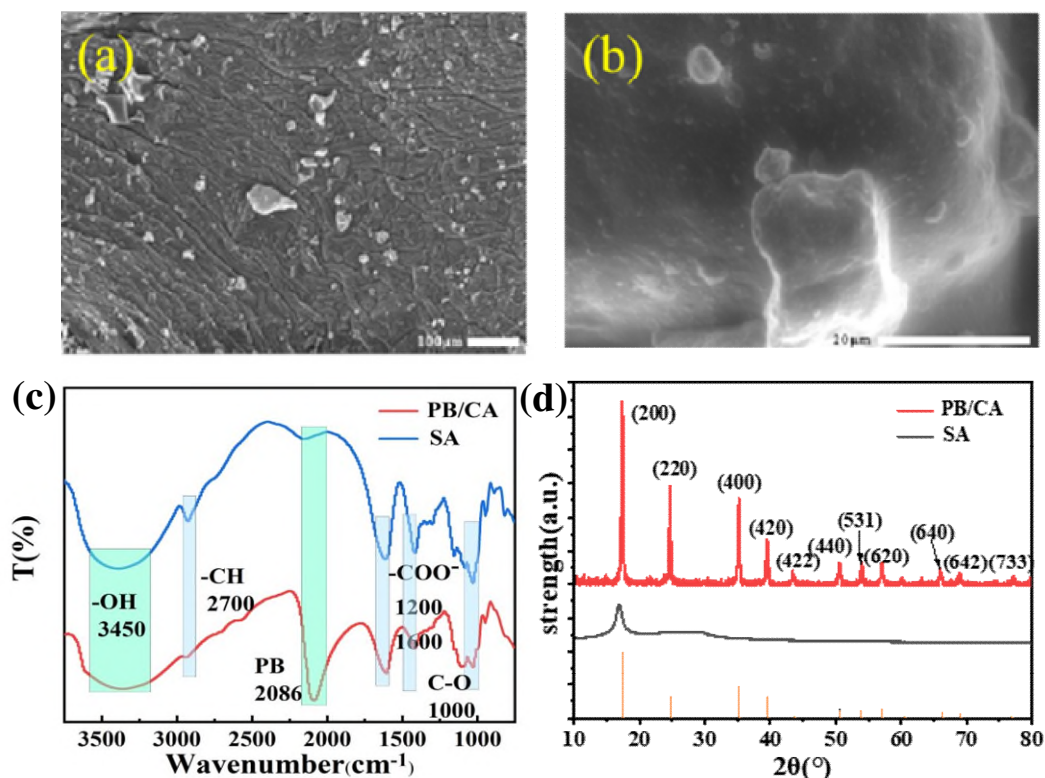


Figure 3 Characterization of the PB/CA membrane: (a, b) SEM images at different magnifications; (c) FT-IR spectra of sodium alginate (SA) and the PB/CA membrane; (d) XRD patterns of the PB/CA membrane and SA.

The chemical composition and surface electronic states of the PB/CA membrane were further probed by X-ray photoelectron spectroscopy (XPS), with sodium alginate (SA) serving as a reference. The survey spectra (Figure 4a) confirm the presence of Fe and N elements in the PB/CA membrane, which are absent in pure SA, providing primary evidence for the successful incorporation of Prussian blue. The C 1s spectrum of SA (Figure 4b) can be deconvoluted into three components at binding energies of 285.13 eV, 286.77 eV, and 288.35 eV, assigned to C-(C/H), C-O, and O-C=O species, respectively. In contrast, the C 1s spectrum of the PB/CA membrane (Figure 4d) exhibits two additional peaks at 284.66 eV and 284.93 eV, characteristic of C≡N and Fe²⁺-C≡N bonds from the cyanide groups in Prussian blue. Correspondingly, the N 1s spectrum of PB/CA (Figure 4c) shows peaks at 397.89 eV and 399.40 eV, attributed to the C≡N and C≡N-Fe³⁺ coordination, respectively. The high-resolution Fe 2p spectrum (Figure 4e) provides definitive evidence, with peaks corresponding to Fe²⁺-C (709.96

eV) and Fe³⁺-N (715.23 eV) coordinations. The presence of these distinct spectral features, alongside the observed charge transfer effects (e.g., σ -electron donation to the π^* orbital of the cyano group to stabilize the structure), conclusively verifies the successful integration of Prussian blue into the alginate matrix.

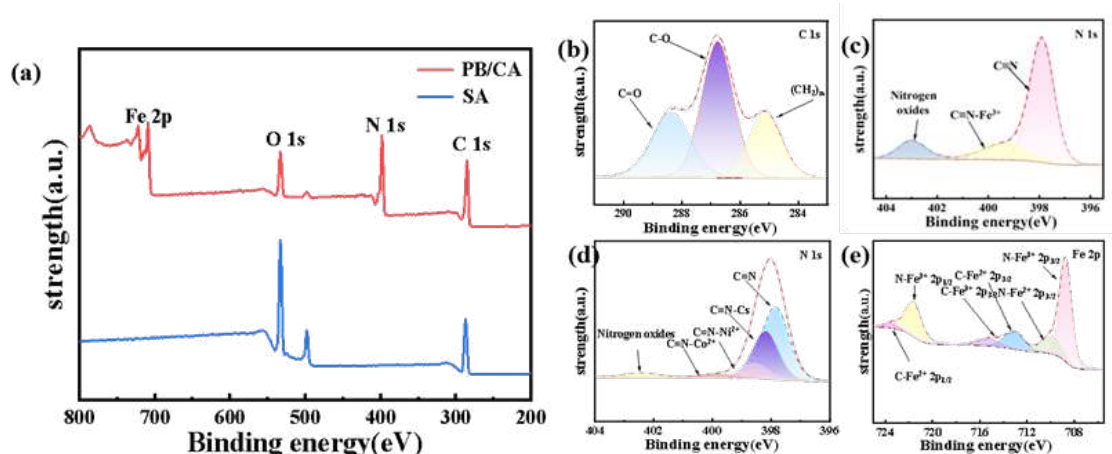


Figure 4 XPS analysis of the PB/CA membrane and sodium alginate (SA): (a) Survey spectra; High-resolution spectra of (b) C 1s of SA, (c) N 1s of PB/CA, (d) C 1s of PB/CA, and (e) Fe 2p of PB/CA.

3.3 Evaluation of Adsorption Performance

3.3.1 Effect of Initial pH of solution

To identify the optimal pH window for Cs(I) removal, the effect of initial solution pH (ranging from 3.0 to 12.0) on the adsorption performance of the PB/CA membrane was investigated. As summarized in Figure 5a, the removal efficiency was strongly pH-dependent. At a strongly acidic pH of 3.0, the adsorption capacity was relatively low. A significant enhancement in Cs(I) removal was observed as the pH increased from 3.0 to 6.0, with the efficiency exceeding 95% at pH 6.0. Notably, across the neutral to alkaline pH range (6.0–12.0), the removal rate remained consistently high and stable, demonstrating the robust performance of the PB/CA membrane under a wide spectrum

of pH conditions. This broad pH adaptability is advantageous for practical applications in treating wastewaters with variable acidity.

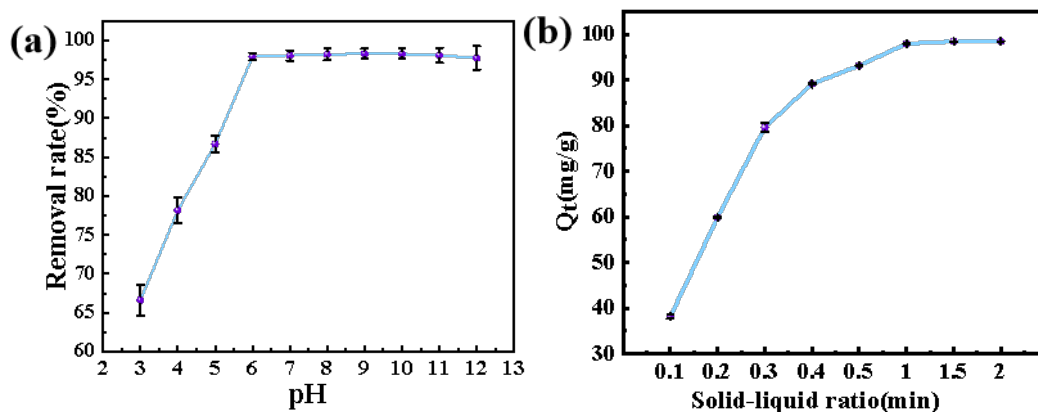


Figure 5 Effects of various parameters on the adsorption and desorption performance of PB/CA membranes for Cs(I): (a) initial pH; (b) adsorbent dosage;

3.3.2 Effect of Adsorbent Dosage

The effect of PB/CA membrane dosage (expressed as solid-to-liquid ratio) on Cs(I) removal was evaluated, as shown in Fig. 5(b). When the dosage increased from 0.1 to 1.0 g/L, the removal efficiency increased sharply, exceeding 97% at 1.0 g/L. This indicates that the active sites provided at this dosage are sufficient to effectively capture most Cs(I) ions from the solution. Further increasing the dosage to 2.0 g/L only resulted in a marginal improvement in removal efficiency, suggesting that the adsorption approaches equilibrium and that additional adsorbent provides diminishing returns. Therefore, a dosage of 1.0 g/L is identified as the optimal value, achieving high removal efficiency while minimizing material consumption.

3.3.3 Adsorption Kinetics

The adsorption kinetics of Cs(I) on the PB/CA membrane are presented in Figure 6a. The removal of Cs(I) exhibited a distinct time-dependent profile, characterized by an initial rapid phase followed by a gradual approach to equilibrium. Specifically,

within the first 180 minutes, the adsorption proceeded rapidly, with the removal efficiency sharply increasing to over 84%. This stage is attributed to the abundant availability of active surface sites. Subsequently, between 180 and 480 minutes, the adsorption rate decelerated significantly as the system approached equilibrium, likely due to the gradual occupancy of active sites and increasing diffusion resistance. After 480 minutes, the removal efficiency remained nearly constant with time, indicating that a dynamic equilibrium between adsorption and desorption was established, corresponding to the saturation of the adsorbent under the given conditions.

To elucidate the adsorption mechanism of Cs(I) onto the PB/CA membrane, the kinetic data were analyzed using pseudo-first-order and pseudo-second-order models. The fitting results are presented in Figure 6b and c. The pseudo-first-order model (Figure 6b) showed a significant deviation between the experimental data points and the theoretical fitting curve, yielding a relatively low correlation coefficient ($R^2 = 0.97$, Supplementary Table 1). In contrast, the pseudo-second-order model (Figure 6c) demonstrated an excellent fit, with the data points closely aligning with the predicted curve and a notably high linear correlation ($R^2 = 0.99$). The superior agreement with the pseudo-second-order kinetics suggests that the adsorption process is primarily governed by chemisorption, likely involving valence forces through the sharing or exchange of electrons between the Cs(I) ions and the functional groups on the PB/CA membrane surface. The intraparticle diffusion model fitting for the adsorption of Cs(I) onto the PB/CA membrane is presented in Figure 6d and Supplementary Table 2. The plot clearly reveals a three-stage adsorption process. In the first stage, Cs(I) ions are rapidly adsorbed onto the readily accessible external surface sites of the membrane. The second stage corresponds to a slower diffusion process, where Cs(I) ions migrate into the internal pores of the PB/CA membrane. Finally, in the third stage, the remaining ions continue to diffuse toward the interior adsorption sites against increasing diffusion resistance, resulting in a gradual decrease in the adsorption rate until dynamic equilibrium is attained.

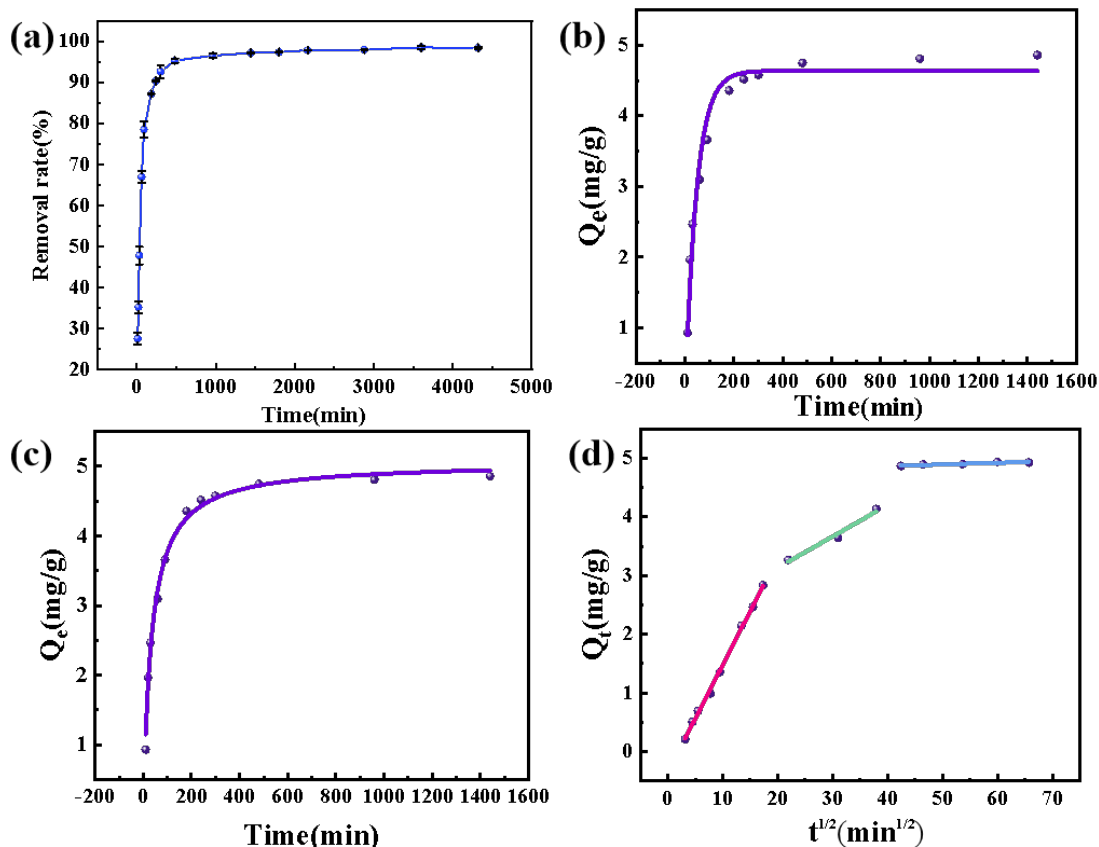


Figure 6 (a)Contact time (Effect of adsorption kinetics on the adsorption and desorption performance of Cs(I)); Model fitting for the adsorption of Cs(I) onto the PB/CA membrane: (b) Pseudo-first-order kinetic model; (c) Pseudo-second-order kinetic model; (d) Intraparticle diffusion model

3.3.4 Adsorption Isotherms and Thermodynamics

The adsorption performance of the PB/CA membrane was evaluated as a function of initial Cs(I) concentration and temperature, as summarized in Figure 7a. The adsorption capacity increased steadily with rising initial Cs(I) concentration, reaching a maximum value of 26.25 mg/g at 80 mg/L. At low initial concentrations (0 – 20 mg/L), the adsorption capacity remained largely unaffected by temperature variation, which can be attributed to the sufficient availability of active sites relative to the low Cs(I) ion concentration. However, at higher initial concentrations, a clear positive correlation between temperature and adsorption capacity was observed, indicating that

the adsorption process is endothermic. The elevated temperature likely enhances the mobility of Cs(I) ions and promotes their interaction with the adsorption sites on Prussian blue, thereby improving the overall adsorption efficiency.

To gain deeper insights into the adsorption characteristics of Cs(I) onto the PB/CA membrane, the equilibrium data were analyzed using the Langmuir and Freundlich isotherm models. The experimental results and corresponding fitting curves are presented in Figure 7b, with the detailed thermodynamic parameters summarized in Supplementary Table 3 and Supplementary Table 4. A comparative analysis indicates that the experimental data exhibit a better fit to the Langmuir model across all tested temperatures, as evidenced by the closer alignment of the data points with the Langmuir fitting curves. This suggests that the adsorption process occurs primarily via monolayer coverage on a homogeneous surface. The maximum adsorption capacity (Q_m) derived from the Langmuir model was determined to be 29.59 mg/g at 298.15 K.

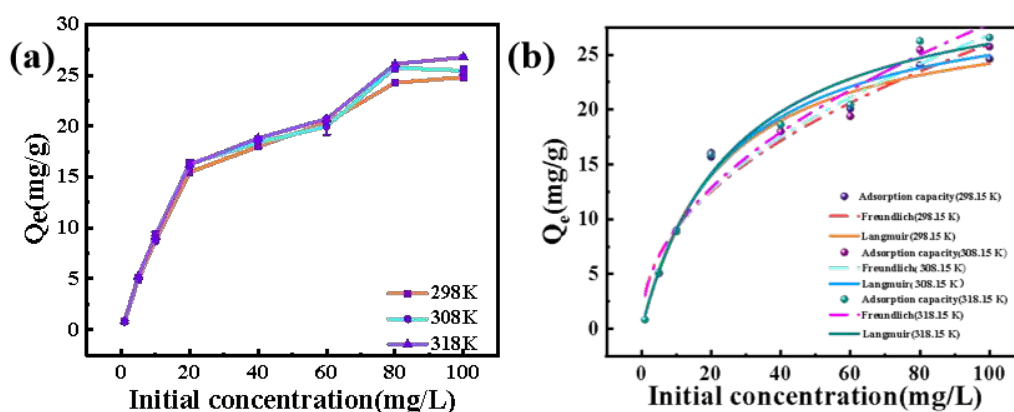


Figure 7 Effects of various parameters on the adsorption and desorption performance of PB/CA membranes for Cs(I): (a) initial concentration and temperature (adsorption isotherms); (b) thermodynamic model fitting;

To further elucidate the nature of the adsorption process, key thermodynamic parameters, including the change in Gibbs free energy (ΔG^0), were calculated and are listed in Supplementary Table 5. The ΔG^0 values at 298.15 K, 308.15 K, and 318.15 K were all negative, confirming the spontaneous nature of Cs(I) adsorption on the PB/CA membrane. Moreover, the ΔG^0 value became more negative with increasing temperature, indicating that the spontaneity of the adsorption process is enhanced at

higher temperatures.

3.3.5 Selectivity and Competitive Adsorption

The selective adsorption performance of the PB/CA membrane for Cs(I) was evaluated in a multi-ion system containing competing cations (Na^+ , Mg^{2+} , K^+ , Ca^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Sr^{2+} , Ba^{2+}). As shown in Figure 8a, the membrane exhibited a pronounced preference for Cs(I), achieving a high removal efficiency of 94.96% despite the presence of these interfering ions. In contrast, the removal rates for most other metal ions were below 40%. Notably, stronger adsorption was observed for K^+ and Ba^{2+} , which can be attributed to the similarity between their hydrated ionic radii and that of Cs(I)^+ (as detailed in Supplementary Table 6, allowing them partial access to the selective sites within the Prussian blue lattice. The maintained high efficiency for Cs(I) highlights the membrane's excellent anti-interference performance, which is fundamentally linked to the precise match between the size of the hydrated Cs(I) ion and the interstitial cavities in the Prussian blue crystal structure.

3.3.6 Regeneration and Reusability

As illustrated in Figure 8b, NH_4Cl demonstrated the highest desorption efficiency among the tested agents. The superior performance of NH_4Cl is likely attributable to the similar ionic radius of NH_4^+ to that of Cs(I), facilitating an effective ion-exchange process for releasing Cs(I) from the adsorption sites. The elution rate increased progressively with higher NH_4Cl concentrations. However, excessively high concentrations (>0.02 mol/L) were found to adversely affect the membrane's mechanical stability, potentially leading to structural damage. Furthermore, high concentrations of NH_4^+ ions may occupy a significant portion of the adsorption sites, thereby reducing the adsorption capacity in subsequent cycles. An optimal concentration of 0.01 mol/L was thus identified, offering a balance between high elution efficiency and preservation of the adsorbent's structural and functional properties.

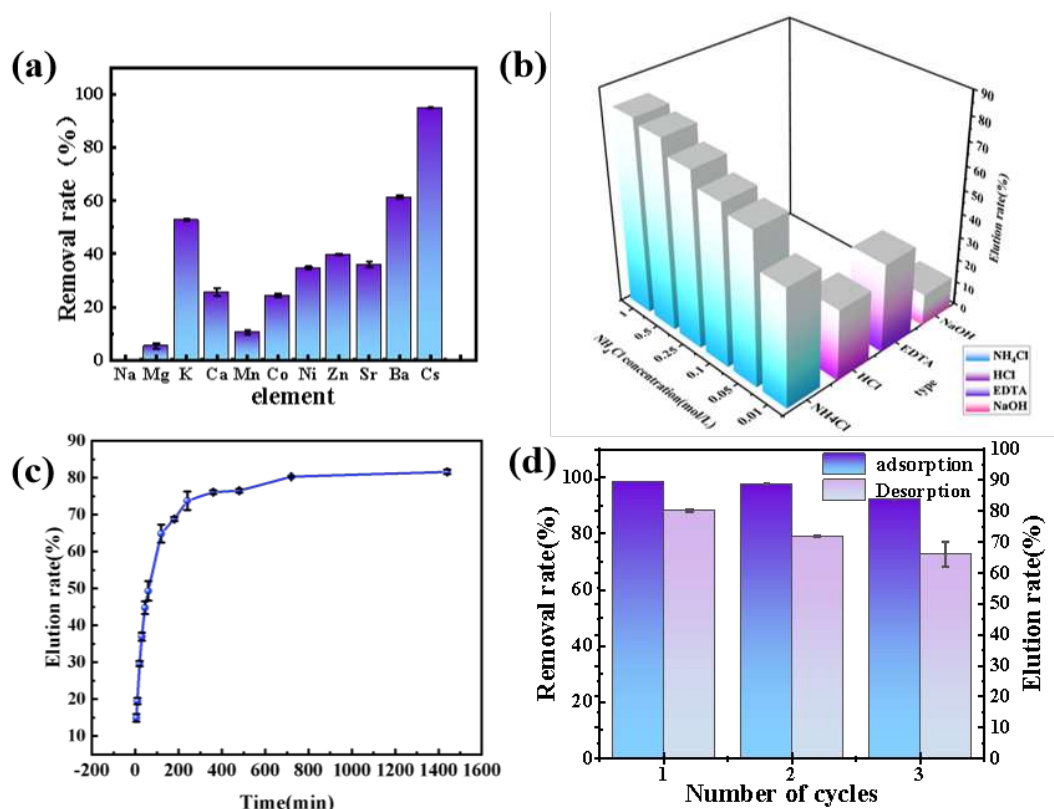


Figure 8 Effects of various parameters on the adsorption and desorption performance of PB/CA membranes for Cs(I): (a) competing ions; (b) type and concentration of desorption agent; (c) desorption time; (d) cycling performance

The effect of desorption time was also examined to determine the kinetics of the elution process. The results, presented in Figure 8c, indicate that the elution rate increased rapidly within the first 180 minutes, showing an approximately linear trend. Beyond 180 minutes, the rate of increase gradually slowed, and the process reached a plateau after 720 minutes, indicating that desorption equilibrium was achieved. Based on these findings, a desorption time of 720 minutes was adopted to ensure near-complete elution while maintaining operational efficiency.

Finally, the cyclic adsorption-desorption performance of the PB/CA membrane was evaluated over multiple cycles under the optimized conditions. As depicted in Figure 8d, the membrane exhibited excellent stability, with only a minor decrease in adsorption efficiency observed after several cycles. In contrast, a more noticeable reduction in the elution rate was recorded in later cycles. This suggests that while the membrane's adsorption capacity remains largely intact, a slight irreversible binding or

pore blockage may occur over repeated use, slightly reducing regeneration efficiency. Nonetheless, the overall performance confirms the good reusability and potential for practical application of the PB/CA membrane.

3.4 Elucidation of the Adsorption Mechanism

To elucidate the mechanism of Cs(I) adsorption onto the PB/CA membrane, a comparative characterization of the membranes before and after adsorption was performed using SEM-EDS. Comparing to pristine PB/CA membrane, after Cs(I) adsorption (Figure 9b), no significant alteration in the overall surface topography is observed, indicating that the adsorption process does not lead to the formation of new surface precipitates or aggregates. This suggests that Cs(I) is not simply deposited on the external surface but primarily incorporated into the internal structure of the Prussian blue crystals within the composite matrix.

Elemental mapping via EDS was conducted to further visualize the distribution of key elements. The corresponding maps for carbon (C, Figure 9c), nitrogen (N, Figure 9d), and iron (Fe, Figure 9e) show a homogeneous distribution throughout the membrane, confirming the uniform dispersion of Prussian blue within the alginate substrate. Most notably, the spatial distribution of cesium (Cs, Figure 9f) after adsorption exhibits a strong correlation with the distribution of Fe. This overlapping pattern provides direct evidence that Cs(I) ions are preferentially adsorbed at sites associated with the Prussian blue component, supporting the hypothesis of lattice-level incorporation rather than superficial deposition.

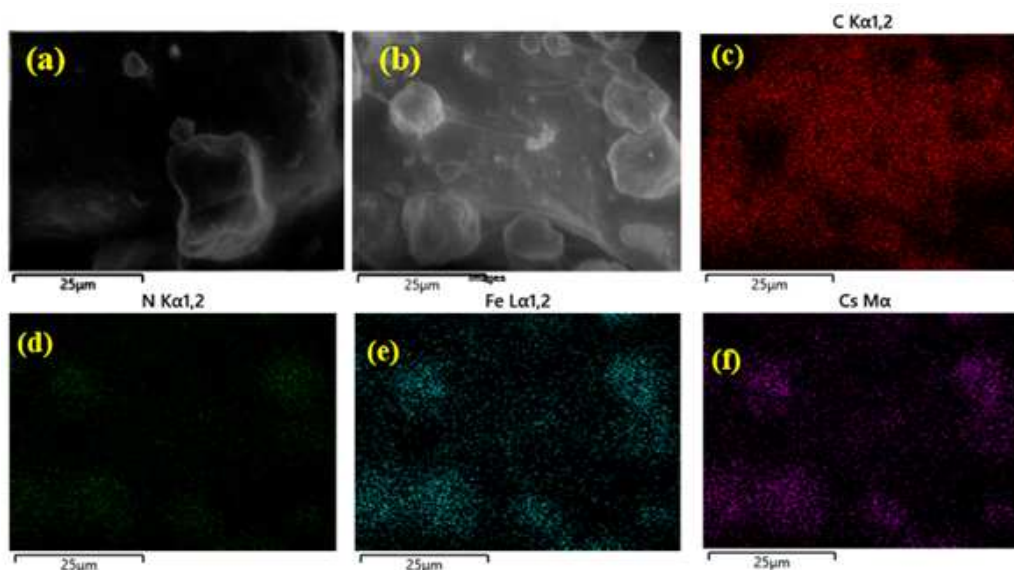


Figure 9 SEM and corresponding EDS elemental mapping images of the PB/CA membrane before (a) and after (b) Cs(I) adsorption, and the distribution of elements (c) C, (d) N, (e) Fe, and (f) Cs

The XRD patterns of the PB/CA membrane before and after Cs(I) adsorption are compared in Figure 10. Following adsorption, a decrease in peak intensity coupled with peak broadening is observed, which can be attributed to lattice distortion induced by the incorporation of Cs(I) ions into the Prussian blue framework. Quantitative analysis of the (200) reflection of the face-centered cubic structure reveals a contraction of the lattice parameter from 5.1093 Å in the pristine membrane to 5.0746 Å after Cs(I) uptake. This lattice contraction, rather than an expansion, provides clear evidence that the adsorbed Cs(I) ions do not substitute for Fe sites within the crystal lattice. Instead, they are incorporated into the interstitial sites, and the observed structural change results from the interaction between the hosted Cs(I) ions and the surrounding Prussian blue lattice.

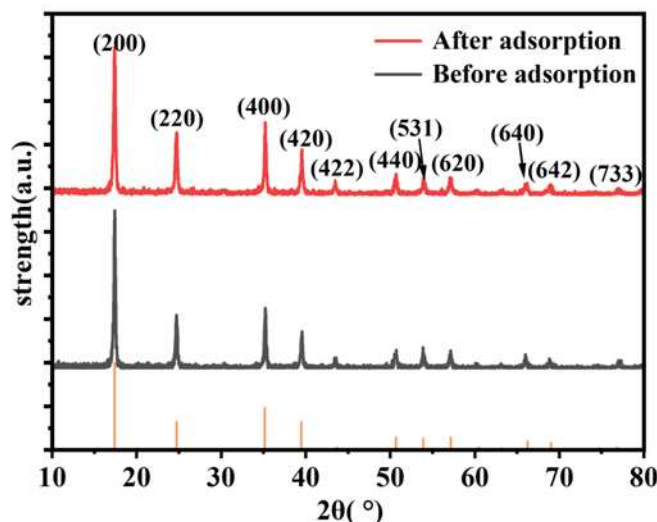


Figure 10 XRD patterns of the PB/CA membrane before and after Cs(I) adsorption

To gain deeper insights into the adsorption mechanism at the electronic structure level, X-ray photoelectron spectroscopy (XPS) analysis was performed on the PB/CA membrane before and after Cs(I) adsorption. The survey spectra (Figure 11a) confirm the successful adsorption of Cs(I), as evidenced by the emergence of distinct Cs 3d peaks in the spectrum of the adsorbed sample, which are absent in the pristine membrane. High-resolution spectra provide further mechanistic insights. The Cs 3d spectrum (Figure 11b) after adsorption displays doublet peaks at binding energies of 724.87 eV (Cs 3d_{5/2}) and 738.77 eV (Cs 3d_{3/2}), confirming the presence of Cs(I) on the membrane.

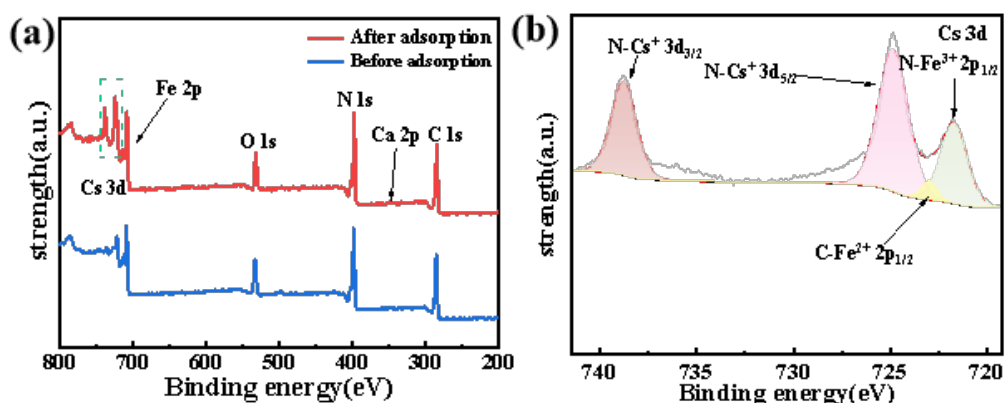


Figure 11 XPS spectra of the PB/CA membrane before and after Cs(I) adsorption: (a) Survey scan; High-resolution spectra of (b) Cs 3d after adsorption

Significant changes were also observed in the spectra of key elements constituting the adsorbent. The C 1s spectrum of the pristine membrane (Figure 12a) was deconvoluted into four components: C-C/C-H (284.78 eV), C-N (284.72 eV), C-O (288.91 eV), and C=O (287.0 eV). After adsorption, the binding energies of the C-N, C-O, and C=O peaks shifted to lower values (284.62 eV, 286.90 eV, and 286.78 eV, respectively), indicating an alteration in the local chemical environment likely due to electron density redistribution upon Cs(I) interaction.

Figure12 Survey scan; High-resolution spectra of (a) C 1s, (b) N 1s, (c) Fe 2p

The N 1s spectrum (Figure 12b) of the pristine membrane featured peaks corresponding to C-N (397.92 eV), C $\equiv$ N (397.92 eV), and C=N (402.39 eV). After Cs(I) adsorption, a new peak emerged at 398.38 eV, which can be attributed to the formation of a C $\equiv$ N-Cs interaction. This suggests that Cs(I) coordinates with the cyanide nitrogen atoms of Prussian blue. Concurrently, the Fe 2p spectrum (Figure 12c) showed a noticeable shift towards lower binding energies after adsorption, reflecting changes in the oxidation state and electronic environment of the Fe centers resulting from the charge transfer associated with Cs(I) incorporation. These electronic structure changes are consistent with the lattice contraction observed by XRD, collectively supporting the mechanism of Cs(I) insertion into the PB crystal lattice.

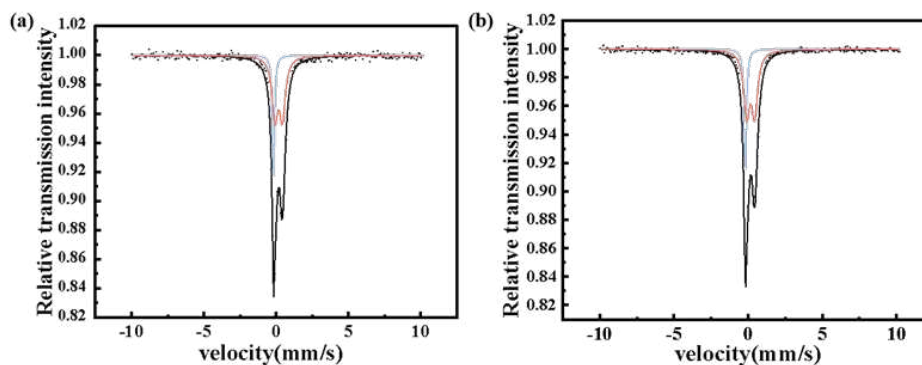


Figure 13 Mössbauer spectra of the PB/CA membrane (a) before and (b) after Cs(I)

The local chemical environment of iron centers in the PB/CA membrane before and after Cs(I) adsorption was probed using Mössbauer spectroscopy, with the corresponding spectra presented in Figure 13. The spectral profiles for both samples consist of two characteristic components: a singlet corresponding to low-spin Fe^{2+} and a doublet representing high-spin Fe^{3+} . The detailed spectral parameters obtained from the fitting are summarized in Supplementary Table 7. Quantitative analysis of the spectral areas reveals a noticeable change in the relative distribution of iron species after Cs(I) adsorption: the proportion of Fe^{2+} increased from 21.0% to 21.7%, while that of Fe^{3+} decreased correspondingly from 79.0% to 78.3%. This subtle but consistent shift in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio suggests a slight electron transfer process, potentially facilitated by σ -electron donation from the cyano groups into the π^* orbitals, which contributes to the stabilization of the mixed-valence Prussian blue framework upon Cs(I) incorporation.

A more pronounced effect was observed in the line widths of the spectral components. After adsorption, the line widths for both Fe^{2+} and Fe^{3+} showed a slight but measurable increase. In a crystalline lattice, the broadening of spectral lines is typically attributed to an increase in the disorder of the local microenvironment surrounding the resonant nuclei. This disorder can be induced by factors such as the presence of point defects, strain, or the incorporation of guest species that perturb the crystal lattice. The observed line broadening provides direct evidence that Cs(I) ions penetrate into the interior of the Prussian blue crystal structure after adsorption. Overall, these findings support an adsorption mechanism in which Cs(I) ions enter the intrinsic vacancies of the PBAs crystal and coordinate with the nitrogen atoms of the cyanide groups, leading to local lattice strain and structural distortion. A schematic diagram of this mechanism is shown in Figure 14.

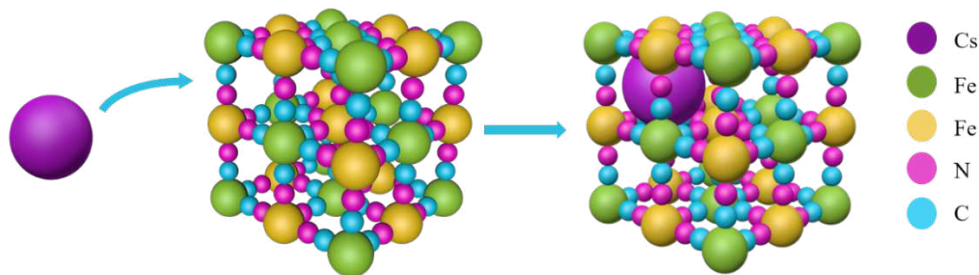


Figure 14 Schematic diagram of Cs ion insertion into the Prussian blue lattice

3.5 Theoretical Calculations via Density Functional Theory (DFT)

3.5.1 Mulliken Charge Analysis

The Mulliken charge distribution within the Prussian blue unit cell, calculated for the PB/CA system before and after Cs(I) adsorption, is presented in Figure 15a and b. The analysis reveals the charge state of individual atoms, providing insight into the electrostatic interactions governing adsorption. As illustrated, the nitrogen (N) and carbon (C) atoms within the cyanide ($\text{C}\equiv\text{N}$) ligands carry significant negative charges. This pronounced anionic character establishes these sites as key anchors for the electrostatic attraction and binding of cationic Cs(I) ions. This computational finding is in excellent agreement with the XPS analysis (Section 3.4), which indicated chemical interaction between Cs(I) and the cyanide groups, thereby corroborating the proposed adsorption mechanism at the electronic structure level.

3.5.2 Adsorption Energy Calculation

CASTEP calculations were modeled using Material Studio. The energy of cesium adsorbed by PB/CA membranes (E_{ads}) is calculated as follows:

$$E_{ads} = E_{ab} - E_a - nE_b \quad (16)$$

where E_{ab} represents the total energy of the PB/CA-Cs complex system, E_a is the energy of the pristine PB/CA membrane, E_b denotes the energy of an isolated Cs atom, and n is the number of adsorbed Cs atoms. A more negative E_{ads} value indicates a thermodynamically more favorable adsorption process and greater stability of the formed complex.

The calculated energy values were as follows: $E_{ab} = -5388.38$ kJ/mol, $E_a = -$

4281.85 kJ/mol, and $E_b = -549.66$ kJ/mol. Based on equation (16), the adsorption energy was determined to be $E_{ads} = -556.87$ kJ/mol (-5.77 eV). The significantly negative value strongly indicates a substantial attractive interaction between the PB/CA membrane and Cs(I), confirming the spontaneous nature of the adsorption process. This result is consistent with a chemisorption mechanism, in full agreement with the experimental findings presented in the previous sections.

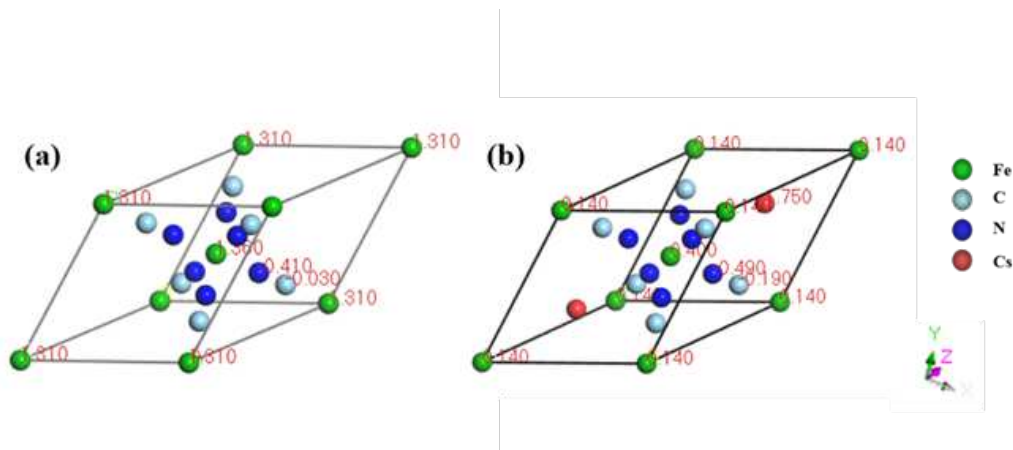


Figure 15 Mulliken charge distribution analysis (a) before and (b) after Cs adsorption (illustrated on the smallest unit cell structure)

4. Conclusion

This study successfully developed a Prussian blue/calcium alginate (PB/CA) composite membrane via a facile and eco-friendly doctor blade coating - crosslinking method, with excellent adsorption selectivity and high efficiency for Cs(I). The optimized membrane demonstrated a high adsorption capacity of 29.59 mg/g and maintained over 94.96% removal efficiency in multi-ion systems, showing excellent selectivity and pH adaptability. Adsorption followed the pseudo-second-order kinetic and Langmuir isotherm models, indicating chemisorption-dominated monolayer adsorption. Thermodynamic analysis confirmed a spontaneous and endothermic process. Through the integrated analysis of XRD, XPS, Mössbauer spectroscopy, and DFT calculations, this study delineates the atomic-level capture mechanism of Cs(I). Rather than merely being adsorbed on the surface, Cs(I) integrates into the interstitial sites of the Prussian blue lattice due to a precise match between its ionic radius and the

PB lattice vacancy (~ 3.20 Å), coordinating with cyanide nitrogen. This integration results in a contraction of the lattice parameter from 5.1093 Å to 5.0746 Å, corresponding to a lattice contraction of $\sim 0.68\%$. Concurrently, there is an increase in the proportion of Fe^{2+} from 21.0% to 21.7% , while the proportion of Fe^{3+} decreases from 79.0% to 78.3% . These changes are accompanied by local electronic rearrangement and structural microstrain. The calculated adsorption energy from DFT stands at -556.87 kJ/mol (-5.77 eV), further confirming strong chemisorption and stable binding. These findings provide a promising material for radioactive cesium removal and a mechanistic insight for designing advanced adsorbents.

CRediT authorship contribution statement

Peng Liu: Funding acquisition, Resources, Supervision. **Wenhui Zhao:** Writing – review & editing, Software. **Haitao Wang:** Methodology. **Keze Du:** Writing – original draft. **Yinuo Zhou:** Data curation. **Fuqiu Ma:** Project administration, Supervision. **Mingbo Ji:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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