Research Article

Novel One-Pot Solvothermal Synthesis of High-Performance Copper Hexacyanoferrate for Cs⁺ Removal from Wastewater

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Efficient removal of radioactive cesium from complex wastewater is a challenge. Unlike traditional precipitation and hydrothermal synthesis, a novel vast specific surface area adsorbent of copper hexacyanoferrates named EA-CuHCF was synthesized using a one-pot solvothermal method under the moderate ethanol media characterized by XRD, SEM, EDS, BET, and FTIR. It was found that the maximum adsorption capacity towards Cs⁺ was 452.5 mg/g, which is far higher than most of the reported Prussian blue analogues so far. Moreover, EA-CuHCF could effectively adsorb Cs⁺ at a wide pH range and low concentration of Cs⁺ in geothermal water within 30 minutes, and the removal rate of Cs⁺ was 92.1%. Finally, the separation factors between Cs⁺ and other competitive ions were higher than 553, and the distribution coefficient of Cs⁺ reached up to $2.343 \times 10^4$ mL/g. These properties suggest that EA-CuHCF synthesized by the solvothermal method has high capacity and selectivity and can be used as a candidate for Cs⁺ removal from wastewater.

1. Introduction

Nuclear power plays a significant role in transitioning the energy supply [1]. However, the accidental leakage of the nuclear power plant could cause considerable harm to humans [2–4]. ¹³⁷Cs is one of the most dangerous isotopes. Its long half-life, high energy β/γ emission, and high solubility could make its way into the human body, leading to an increased incidence of cancer, leukemia, and genetic diseases [5–10]. For example, the Chernobyl accident in 1986 and the Fukushima accident in 2011 led to the accidental release of large amounts of ¹³⁷Cs [9, 10]. As a result, the surrounding regions and waters have been seriously polluted. From environmental restoration and human health, it is essential and urgent to remove radioactive cesium from wastewater efficiently [11–15].

Adsorption is one of the most concerning methods for cesium removal, particularly suitable for the separation at trace levels. It is an effective technique for large-scale and efficient cesium separation due to its high adsorption efficiency, low cost, easy operation, and negligible secondary pollution [16–19]. To date, a variety of adsorbents have been developed, such as clay minerals, ammonium molybdo-phosphate, metal sulfides, and metal hexacyanoferrates (MHCFs) [20–25]. Among them, MHCFs, also known as Prussian blue (PB) or Prussian blue analogues (PBAs), presented superior selectivity and adsorption capacity due to their unique cesium affinity [13, 26–32]. Moreover, this family of compounds is low cost, chemically stable, and low toxicity, so they have been extensively investigated. However, the limited direct use of MHCFs made it attractive to immobilize MHCFs onto substrate materials, which severely reduced cesium adsorption capacity. Therefore, a variety of approaches have been taken into account to maximize the performance of MHCFs, mainly focusing on the immobilization form or structure of composites [33–37]. An outstanding MHCF could also make a breakthrough in the adsorption performance of composite adsorbents.
Generally, the precipitation method is used to synthesize MHCFs of targeted size or structure based on mixing of $M^{n+}$ and $[M'(CN)_{6}]^{-n}$ by adding a protective agent or controlling the precursor concentration as well as the addition rate [38–40]. However, the overquick reaction rate of the precursors may cause the obtained MHCFs to be compact and aggregated, which are adverse to sufficiently exposing active sites and accessibly reacting with Cs$^+$. To date, solvothermal and hydrothermal methods have been explored to improve Cs$^+$ adsorption capacity by effectively constructing different structures, morphologies, and sizes of PBAs with high surface areas [41–43]. For example, the hydrothermal method has been applied to inhibit PB aggregation with ordered hollow structures, improving the maximum adsorption capacity from 29.3 mg/g to 262 mg/g. It can be explained that the hollow structure of PB ($S_{BET} = 338 \text{ m}^2/\text{g}$) provided more channels for Cs$^+$ penetration and adsorption. In comparison, the commercial PB ($S_{BET} = 84 \text{ m}^2/\text{g}$) with aggregated fine nanoparticles might only adsorb Cs$^+$ on the external surface [42]. Similarly, a hierarchical PB composed of ultrathin nanosheets (HPBN, $S_{BET} = 246 \text{ m}^2/\text{g}$) was prepared by the solvothermal method with improved Cs$^+$ uptakes of 200 mg/g because of exposure micropores of the rearranged structure [43]. Therefore, it is reasonable to assume that changing solvent or reaction temperature could alter the reaction process. To the best of our knowledge, it has been studied scarcely on synthesizing nanostructured adsorbents with high surface areas except for PB (FeHCF), even though PB shows the lowest capacity among the MHCFs.

In this study, the solvothermal method was experimentally studied to synthesize porous CuHCF for cesium removal. As excepted, the results of adsorption capacity indicate that all the tested factors (solvent, reaction temperature, and precursor ratios) impact the adsorption performance of CuHCF, and the optimal conditions were selected for fabricating targeted EA-CuHCF. Furthermore, the effects of pH, contact time, temperature, competitive ions, and initial concentration on the adsorption performance were investigated systematically, while XRD, SEM, FTIR, and BET were conducted to reveal the structure and surface properties. The results indicated EA-CuHCF could be considered as a promising candidate for $^{137}$Cs removal from wastewater.

2. Experimental

2.1. Materials. It is of particular concern to avoid the harmful effects of radioactive cesium ($^{137}$Cs). Therefore, nonradioactive cesium ($^{133}$Cs) with similar chemical and physical properties was used. CsCl, $K_3[Fe(CN)_6]$ and CuCl$_2$·3H$_2$O were purchased from J&K Scientific Ltd. Methanol, ethanol, and ethylene glycol were brought from Sinopharm Chemical Reagent Co., Ltd. Geothermal water was sampled from a bore well in the Tibet autonomous region. The stock Cs$^+$ solution of 100 mg/L was prepared by dissolving 0.1267 g CsCl in 1000 mL deionized water, and a specific concentration of Cs solution was obtained by quantitative dilution. All reagents used in the experiment were analytical grade without further purification.

2.2. Synthesis of CuHCF. CuHCF was synthesized by the solvothermal method under various conditions. In a typical experiment, 2.0 mmol CuCl$_2$, 0.5 mmol $K_3Fe(CN)_6$, and 20 mL ethanol (EA) were added into a 50.0 mL hydrothermal kettle. Then, the hydrothermal kettle was put into an oven at 100°C for 24 h. After centrifugation, the product was washed thoroughly with anhydrous ethanol and deionized water. After drying, the desired CuHCF was obtained, named EA-CuHCF. The synthesis procedure is shown in Figure 1. On this basis, solvent (methanol (MA), ethanol (EA), and ethylene glycol (EG)), reaction temperature (80, 100, and 120°C), and precursor ratios ($\text{CuCl}_2$ : $K_3Fe(CN)_6 = 1:2$, $1:1$, $2:1$, $3:1$, $4:1$, $5:1$, and $6:1$) were changed successively to synthesize different CuHCF, testing adsorption capacity as the criteria.

2.3. Characterization. ICP-OES (VISTA MPX, USA) was used to determine the concentrations of cesium ions in the solutions before and after adsorption. Scanning electron microscopy (SEM, JSM-IT300LV, Japan) was conducted to observe the surface morphologies of EA-CuHCF before and after adsorption. Powder X-ray diffraction (XRD) was collected on an X-ray diffractometer using Cu Ka radiation over a 2θ range of 5–75° and X-ray power of 36 kV/20 mA at a scan (MSAL XD-3, Beijing Purkinje General Instrument Co., Ltd., China). The BET surface area was measured by an Auto-sorb-iQ3200-4 (Quantatech Co.). FTIR spectra were performed in the range of 4000–400 cm$^{-1}$ with an accumulation of 16 scans (Tensor27, Germany).

2.4. Adsorption Experiments. Batch experiments were conducted to estimate the adsorption performance of the developed adsorbents for Cs$^+$. The adsorption capacity ($q_e$ mg/g), removal rate ($R$ %) distribution coefficient ($K_d$, mL/g), and separation factor ($\alpha_{Me}$) were calculated according to the following formulas [4].

$$q_e = \frac{(c_0 - c_e) \times V}{m},$$

$$R = \frac{c_0 - c_e}{c_0} \times 100\%,$$

$$K_d = \frac{c_0 - c_e}{c_e} \times \frac{V}{m},$$

$$\alpha_{Me} = \frac{K_d \times (Cs)}{K_d \times (Me)}.$$

where $c_0$ (mg/L) is the initial concentration, $c_e$ (mg/L) is the equilibrium concentration, $V$ (mL) is the volume of the solution, $m$ (g) is the weight of the adsorbent, and Me represents the other alkali metal ions.
2.4.1. Effect of pH. The effect of pH on the adsorption performance was investigated by adjusting pH values of Cs solutions from 2 to 10 with 0.1 mol/L NaOH and 0.1 mol/L HCl. In an experiment, 0.05 g CuHCF and 100 mL of 100 mg/L CsCl solution were successively added into a 250 mL beaker and then stirred on a magnetic stirrer for 30 min. After adsorption, the Cs⁺ concentration of the residual solution was determined.

2.4.2. Effect of Competing Ions. In order to find out the selectivity of CuHCF, the influence of competitive ions on the adsorption performance was investigated, using geothermal water as the complex system containing high concentrations of various ions. 0.05 g CuHCF and 100 mL of geothermal water were added into a 250 mL beaker and then stirred on a magnetic stirrer for 30 min. The adsorption experiment was carried out at room temperature and natural pH.

2.4.3. Adsorption Kinetics. Adsorption kinetics was determined by studying the effect of contact time on Cs⁺ adsorption. 0.05 g CuHCF and 100 mL of 100 mg/L CsCl solution were mixed and stirred at room temperature in natural pH. Samples were taken at 15, 30, 60, 120, 180, 240, and 600 min, respectively.

In order to evaluate the kinetic mechanism of Cs⁺ adsorption on CuHCF, the most commonly used models of pseudo-first-order and pseudo-second-order equations are introduced to analyze the experimental data. The equations are expressed as follows [40]:

\[
q_t = q_e \left(1 - e^{-k_1 t}\right),
\]

\[
q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t},
\]

where \(q_e\) and \(q_t\) are the adsorption capacities (mg/g) of CuHCF for Cs⁺ at equilibrium and a specific time \(t\) (min), respectively. \(K_1\) (min⁻¹) and \(K_2\) (g·mg⁻¹·min⁻¹) are the rate constants of pseudo-first-order and pseudo-second-order equation models.

2.4.4. Adsorption Isotherm. Adsorption isotherm was tested by changing the initial concentrations of Cs⁺ solution (60, 150, 250, 650, and 1300 mg/L). 0.05 g CuHCF was added to 100 mL CsCl solutions with different concentrations of Cs⁺, and a series of adsorption experiments were studied for 30 min at room temperature and natural pH.

In order to further study the adsorption characterization of Cs⁺ by CuHCF, two isothermal models, namely, linear Langmuir and Freundlich adsorption models, were used to analyze the adsorption data. The equations are expressed as follows [7]:

\[
\frac{c_e}{q_e} = \frac{1}{q_m K_L} + \frac{c_e}{q_m},
\]

\[
q_e = K_F c_e^{1/n},
\]

\[
\ln q_e = \ln K_F + \frac{\ln c_e}{n},
\]

where \(q_e\) (mg/g) and \(c_e\) (mg/L) are the equilibrium quantities of adsorption capacity and concentration, respectively, \(q_m\) (mg/g) is the maximum adsorption capacity, \(K_L\) (L/mg) and \(K_F\) (mg/g) are the constants of Langmuir and Freundlich isotherms, and \(n\) is related to adsorption strength.

3. Results and Discussion

3.1. Optimization of Reaction Conditions. The synthesis of CuHCF under different reaction solvents, such as methanol, ethanol, and ethylene glycol, was studied. The influence of varying reaction solvents on Cs⁺ adsorption capacity is shown in Figure 2(a). It was found that the tested solvents affected adsorption performance inconspicuously, and the most significant disparity was only 9.0%. When considering the cost and low toxicity of solvents, ethanol was selected as the reaction solvent for further study.

Different reaction temperatures of 80, 100, and 120°C were then investigated, respectively, and the capacities are shown in Figure 2(b). Similarly, the tested temperatures had little influence on adsorption capacity, and generally, the materials synthesized at higher temperatures presented relatively better adsorption performance. So, the reaction temperature was determined to be 100°C.
Finally, different ratios of precursors were investigated, and the results are plotted in Figure 2(c). It can be seen that with the increased molar ratio of CuCl2 to K3Fe(CN)6, the Cs⁺ adsorption capacity first increases and then decreases. The molar ratio of precursors 4:1 (CuCl₂: K₃Fe(CN)₆₈ = 4:1) demonstrated the maximum Cs⁺ adsorption capacity. As mentioned above, the optimum conditions of the solvothermal method fabricating CuHCF have controlled precursor ratios of 4:1 at 100°C using ethanol as a solvent in the following experiments. The satisfying material was named EA-CuHCF.

3.3. Effect of pH Value on Adsorption. The effect of pH on Cs⁺ adsorption was conducted at various pH values with an initial Cs⁺ concentration of 100 mg/L and a liquid-solid ratio of 2000:1. As the results are shown in Figure 6(a), the adsorption capacities of EA-CuHCF remained at a high level over a wide pH, indicating that it has a more negligible effect on pH. So, it is believed that EA-CuHCF could be used in Cs removal from diversified aqueous solutions. For convenience, the subsequent experiments were carried out in a natural pH environment.

3.4. Effects of Competing Ions on Adsorption. The adsorption of Cs⁺ could be hindered by other coexisted alkali metal ions [30]. In order to evaluate the selectivity of EA-CuHCF, the experiments were carried out using geothermal water in the presence of high concentrations of Na⁺, K⁺, and Li⁺. The relevant parameters of the main interfering ions in geothermal water are presented in Table 1. According to the concentrations before and after adsorption, the adsorption efficiency of Cs⁺ was calculated to be 92.1%, while those for Na⁺, K⁺, and Li⁺ were negligible. It was worth saying the concentration of K⁺ was higher than that in initial geothermal water, which could be attributed to the ion exchange between K⁺ and Cs⁺, and the molar ratio of the released K⁺ to adsorbed Cs⁺ was approximately 1. Besides, it is observed that distribution coefficients (Kd) are as high as 2.343 × 10⁴ mL/g for Cs⁺ and separation factors (αNa/K) are in high levels, meaning that EA-CuHCF has favorable adsorption selectivity for cesium ions. From this point of view, EA-CuHCF can be a suitable adsorbent for Cs⁺ even in complex solutions.
Figure 3: SEM images of EA-CuHCF before (a) and after (b) adsorption.

Figure 4: X-ray diffraction patterns of EA-CuHCF (a) and FTIR spectra of EA-CuHCF before and after adsorption (b).

Figure 5: N$_2$ adsorption-desorption isotherms (a) and corresponding BJH pore size distribution curve (b) of EA-CuHCF.
3.5. Effect of Contact Time and Adsorption Kinetics.

As a function of contact time, the EA-CuHCF adsorption capacity is presented in Figure 6(b). Accordingly, the adsorption capacity of EA-CuHCF increased rapidly within the beginning 15 min and reached a maximum within 30 min, achieving adsorption equilibrium. The rapid adsorption rate might be attributed to the existing numerous active sites of the adsorbent in the initial stage, in which Cs\(^+\) is occupied with the ongoing adsorption process, and the adsorption equilibrium is reached.

\[
q_e = 215.37 \text{ mg/g, } k_1 = 0.20795, R^2 = 0.9989
\]

\[
q_e = 217.98 \text{ mg/g, } k_2 = 0.00506, R^2 = 0.9998
\]

**Figure 6:** Effect of pH value on adsorption capacity (a). Influence of contact time on Cs\(^+\) adsorption (b). Nonlinear fitting diagrams of the adsorption kinetic model (c) \((c_0 = 110 \text{ mg/L, } m/V = 0.5 \text{ g/L, } T = 298\text{ K})\). Effects of initial concentration on Cs\(^+\) adsorption (d). Linear fitting diagram of Langmuir (e) and Freundlich (f) isotherm models \((c_0 = 60–1300 \text{ mg/L, } m/V = 0.5 \text{ g/L, } t = 0.5\text{ h})\).

**Table 1:** The selectivity parameters of Cs\(^+\) against the coexisted ions.

|          | Na | K  | Li | Cs   |
|----------|----|----|----|------|
| \(c_0\) (mg/L) | 720.02 | 169.44 | 24.62 | 14.62 |
| \(q_e\) (mg/L) | 715.93 | 173.03 | 24.11 | 1.15  |
| \(R\) (%)   | 0.59 | —   | 2.07 | 92.10 |
| \(K_d\) (mL/g) | 11.43 | —   | 42.31 | 2.34 \times 10^4 |
| \(\alpha^{Me}\) | 2050.30 | —   | 553.73 | 1.00  |

—, not available.

3.5. Effect of Contact Time and Adsorption Kinetics. As a function of contact time, the EA-CuHCF adsorption capacity is presented in Figure 6(b). Accordingly, the adsorption capacity of EA-CuHCF increased rapidly within the beginning 15 min and reached a maximum within 30 min, achieving adsorption equilibrium. The rapid adsorption rate might be attributed to the existing numerous active sites of the adsorbent in the initial stage, in which Cs\(^+\) is occupied with the ongoing adsorption process, and the adsorption equilibrium is reached.
Further investigation was conducted by fitting the pseudo-first-order model and pseudo-second-order model to adsorption kinetic data. As shown in Figure 6(c), the higher correlation coefficient ($R^2 \approx 0.9998$) suggests that the pseudo-second-order model is more suitable than the pseudo-first-order model ($R^2 \approx 0.9989$), indicating chemical adsorption played a considerable role. Therefore, combing the molar ratio of released K$^+$ to adsorbed Cs$^+$, ion exchange is the most probable adsorption mechanism.

### 3.6. Effect of Cs$^+$ Concentration and Adsorption Isotherm

Effects of initial Cs$^+$ concentration on the adsorption process are shown in Figure 6(d). Typically, Cs$^+$ adsorption capacity increased sharply when the initial concentration was less than 150 mg/L, then raised slowly, and reached 450 mg/g with the initial concentration increased to 1300 mg/L. The rapidly increased adsorption capacity was owed to the great accessible Cs$^+$ adsorption sites and increased initial concentration leading to a high driving force for mass transfer. In contrast, the slightly increased adsorption capacity was attributed to the available adsorption sites tending to be occupied, confirmed by the decreased removal rate. Briefly, EA-CuHCF can effectively adsorb Cs$^+$ in a wide initial concentration range, especially in low concentrations, further demonstrating its possible application in Cs$^+$ removal from wastewater of low concentration.

Adsorption isotherm on Cs$^+$ adsorption was fitted to clarify the adsorption mechanism with nonlinear Langmuir and Freundlich isotherm models, and the results are shown in Figures 6(e) and 6(f), respectively. The higher correlation coefficient ($R^2 = 0.9789$) demonstrates that the adsorption is more likely to follow the Langmuir model, suggesting monolayer adsorption formed on the surface of absorbent uniformly, without interacting with each other, calculated maximum adsorption capacity is 452.5 mg/g.

### 3.7. Comparison with Other Adsorbents of Prussian Blue Analogues

When compared EA-CuHCF with other PBA adsorbents, the maximum uptakes of some previously reported PBAs as well as their composites, such as hollow PB nanoparticles, hf-TiFC, and bulk CuHCF, are summarized in Table 2. Meanwhile, the BET surface area and synthetic method are also presented. As given in Table 2, the adsorption capacity of EA-CuHCF was much higher than most of the reported materials, including substrate-loaded PBAs, such as PB/Fe$_2$O$_4$ (280.82 mg/g) [45] and MOF/KNiFC (155 mg/g) [46], and different kinds of PBAs, such as hollow PB nanoparticles (262 mg/g) [42] and bulk CuHCF (251.4 mg/g, coprecipitation) [46]. Therefore, it is believed that solvothermal is an effective way to synthesize EA-CuHCF with excellent potential to remove Cs$^+$ from contaminated outflows.

### 4. Conclusion

In this study, it is the first time to synthesize a crystalline porous adsorbent EA-CuHCF by the solvothermal method for Cs$^+$ removal. Adsorption isotherm results indicated the maximum adsorption capacity reached up to 452.5 mg/g, which was much higher than most reported PBA absorbents. Moreover, kinetics results suggested that the adsorption equilibrium could be reached within 30 min, and the adsorption was more likely to be ion exchange. At the same time, EA-CuHCF material had excellent selectivity to Cs$^+$ according to the results obtained in geothermal water. We believe that EA-CuHCF has tremendous potential for Cs$^+$ removal in wastewater.

### Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

### Conflicts of Interest

The authors declare that they have no conflicts of interest.

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