Research Article

Prussian Blue Analogues of $A_2[Fe(CN)_6]$ (A: Cu$^{2+}$, Co$^{2+}$, and Ni$^{2+}$) and Their Composition-Dependent Sorption Performances towards Cs$^+$, Sr$^{2+}$, and Co$^{2+}$

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1. Introduction

Increasing demand for nuclear power plants (NPP) has caused a large amount of highly radioactive waste, which brings with it the risk of severe impact on humans and the environment in the event of a nuclear accident [1]. Real-time monitoring and removal of such contaminants are considered an important task upon a NPP shutdown [2, 3]. Radioactive nuclides with long half-life, e.g., $^{137}$Cs (30.2 years) [4–6], $^{90}$Sr (28.8 years) [7], and $^{60}$Co (5.3 years) [8], are the primary species produced in the nuclear reactions and are potentially discharged into the environment during an accident, such as the explosion at the Fukushima Daiichi power plant in 2011 [9]. The isotopes $^{137}$Cs and $^{90}$Sr can be found in radioactive nuclide-contaminated areas, primarily in the aqueous phase, whereas $^{60}$Co is found as an impurity in the stainless steel used in nuclear reactors. $^{60}$Co is also used as a gamma ray source in radiotherapy or used as a disinfectant in the food industry [10]. Thus far, a variety of techniques, e.g., precipitation, extraction, ion-exchange, and adsorption [11–14] have been extensively developed to remove radioactive nuclides from aqueous solutions. Of great interest is the combination of adsorption- and ion-exchange-based approaches because the combined techniques can considerably enhance removal efficiency and selectivity towards the targeted radioactive waste rather than the coexisting competitors or inhibitors [15]. Therefore, it is highly desirable to develop advanced materials with a high degree of porosity and well-established pore size distribution and controllable ion-exchange capability for improved removal efficiency.
In recent years, there have been several classes of porous inorganic materials that match the aforementioned standards, such as clays [16], zeolites [17], and Prussian blue (PB) and Prussian blue analogues (PBAs) [18–20]. In particular, PB and/or PBAs are constructed via coordination bonds between transition metals (e.g., Fe²⁺, Fe³⁺, Cu²⁺, Co³⁺, and Ni²⁺) and CN⁻ ligands. In particular, PBAs can be synthesized in a facile and cost-effective manner. Such materials often exhibit high porosity, excellent thermal, and radiation stability [21], which render them highly applicable in many fields, including information/storage [22], biomedicine [23], and dye [24] or radioactive waste removal. In addition, PBAs have been regarded as one of the most efficient and selective adsorbents for cerium ions. The selective cerium adsorption is attributable to the size matching between PBAs and selective adsorbents for cesium ions. The selective cerium adsorption mechanism of the obtained PBAs.

2. Materials and Methods

2.1. Materials. Standard solutions (Cs⁺ (1000 mg/L), Sr²⁺ (1000 mg/L), Co²⁺ (1000 mg/L), CsCl (99.99%, Meck), SrCl₂ (99.99%, Meck), CoCl₂ (99.99%, Meck), K₄[Fe(CN)₆] (99.99%, Meck), CoCl₂·6H₂O (99.99%, Meck), CuCl₂·2H₂O (99.99%, Meck), and NiSO₄·6H₂O (99.99%, Meck) were used as received. pH was adjusted using HNO₃ (0.01–0.1 N) and NaOH (0.01–0.1 N).

2.2. Synthesis of A₂[Fe(CN)₆]₆. The synthetic protocol for A₂[Fe(CN)₆]₆ (A = Co, Ni, and Co) was slightly modified from previous Therefore reports [26–29]. For the synthesis of Cu₂[Fe(CN)₆]₆, a 250 mL of 0.05 M K₄[Fe(CN)₆] solution was slowly added to a 750 mL of 0.15 M CuCl₂ solution. The reaction mixture was stirred at 1200 rpm and sonicated, prior to heating to 60°C for 4 h. Upon reaction completion, the product was purified by repeated washing with water and centrifugation and dried at 70°C. For the synthesis of Co₂[Fe(CN)₆]₆ and Ni₂[Fe(CN)₆]₆, a CoCl₂ or NiSO₄ solution was, respectively, used in place of CuCl₂ in the aforementioned procedure. The other reaction conditions remained unchanged, unless stated otherwise.

2.3. Adsorption Performance of A₂[Fe(CN)₆]₆ towards Cs⁺, Sr²⁺, and Co²⁺. For the sake of safety, Cs⁺, Sr²⁺, and Co²⁺ used in this study were stable isotopes. A series of reaction flasks containing 50 mL of Cs⁺, Sr²⁺, and Co²⁺ solutions with concentrations of 0.1 mg/L, 1 mg/L, 10 mg/L, 30 mg/L, 50 mg/L, 70 mg/L, 100 mg/L, 150 mg/L, 200 mg/L, 250 mg/L, 300 mg/L, 350 mg/L, 400 mg/L, 450 mg/L, 500 mg/L, 550 mg/L, and 600 mg/L were prepared. To the above solutions, 0.1 g of the as-synthesized A₂[Fe(CN)₆]₆ was added. The pH was adjusted to 7.0, and the mixture was sealed and shaken at 270 times/min for 24 hours at 25°C in order to reach equilibrium. After adsorption completion, the adsorbent was separated by centrifugation (8500 rpm, 10 min), and the remaining solution was filtered through a 220 nm filter for further analysis with TXRF.

The adsorption capacity of A₂[Fe(CN)₆]₆ toward Cs⁺, Sr²⁺, and Co²⁺ is calculated using the following formula:

\[ q = \frac{V \times (C_i - C_f)}{B} \]

where \( q \) is the adsorption capacity of the adsorbent material (mg/g adsorbent), \( C_i \) and \( C_f \) are the concentrations of adsorbate (i.e., Cs⁺, Sr²⁺, and Co²⁺) before and after adsorption, respectively, \( V \) is the volume of the solution, and \( B \) is the mass of the adsorbent used.

Langmuir and Freundlich models were used to assess the adsorption performance of A₂[Fe(CN)₆]₆.

Langmuir adsorption equation \( q_e = \frac{Q_m \times b \times C_e}{1 + bC_e} \),

where \( q_e \) is the amount of Cs⁺, Sr²⁺, and Co²⁺ ions adsorbed by the material (mg/g), \( Q_m \) is the maximum adsorption capacity for Cs⁺, Sr²⁺, and Co²⁺ ions, \( C_e \) is the initial concentration at a point of adsorption (mg/L), and rate constant \( b \) is the adsorption/desorption.

Freundlich adsorption equation \( q_e = K \times C_e^{1/n} \),

where \( q_e \) is the amount of Cs⁺, Sr²⁺, and Co²⁺ ions adsorbed by the material (mg/g), and \( K \) and \( n \) are the adsorption constant at equilibrium.

2.4. TXRF Analyses of the Samples and Cs⁺, Sr²⁺, and Co²⁺ Solution prior to and after Adsorption. After adsorption completion, the adsorbents were washed several times with distilled water and dried at 60°C. The sample elemental contents were analyzed by total reflection X-ray fluorescence spectroscopy (TXRF) to monitor the change in the composition of the material before and after the reaction. The content of Cs⁺, Sr²⁺, and Co²⁺ before and after adsorption remaining in the solution was also measured by TXRF.

2.5. Characterizations. Crystalline structures of A₂[Fe(CN)₆]₆ were investigated by powder X-ray diffraction (PXRD) performed with a Bruker D8 Advance diffractometer using Cu Kα radiation (wavelength 1.541 Å) in focused beam and in the range 10–80°. The morphologies and elemental composition of A₂[Fe(CN)₆]₆ were characterized using field emission transmission electron microscopy (FE-TEM; JEM 2100-Jeol, Japan) and energy dispersive X-ray spectroscopy (EDS; JEM 2100-Jeol, Japan). Gas adsorption isotherms at
The IR spectra of the samples were recorded in the 399-4000 cm\(^{-1}\) range using KBr pellets on a Nicolet iS10 (Thermo Scientific, America). The composition of the material before and after the reaction was analyzed using total reflection X-ray fluorescence (TXRF) S2 Picofox Bruker.

### Table 1: Comparison of the adsorption capacity of Cs\(^+\), Sr\(^{2+}\), and Co\(^{2+}\) ions on different adsorbent materials.

| Adsorbent                              | pH  | Maximum adsorption capacity (mg g\(^{-1}\)) | References |
|----------------------------------------|-----|--------------------------------------------|------------|
| **Cs\(^+\) ion**                       |     |                                            |            |
| Copper hexacyanoferrate (CuHCF)        | 7.0 | 155.60                                     | This research |
| Cobalt hexacyanoferrate (CoHCF)        | 7.0 | 154.46                                     | This research |
| Nickle hexacyanoferrate (NiHCF)        | 7.0 | 120.31                                     | This research |
| Copper ferrocyanide functionalized mesoporous silica | 7.7 | 17.1                                       | [37]       |
| Zeolite A                              | 6.0 | 208.7                                      | [38]       |
| Magnetic PB/GO                         | 7.0 | 55.6                                       | [39]       |
| Montmorillonite-iron oxide composite   | 6.5 | 52.6                                       | [25]       |
| Conjugate adsorbent                    | 7.0 | 77.7                                       | [40]       |
| Ammonium molybdocphosphate-polyacrylonitrile | 6.5 | 81.3                                       | [41]       |
| Cs\(^+\)-imprinted polymer nanoparticle | 9.0 | 50.0                                       | [42]       |
| Poly(AAc-co-B18C6Am) hydrogels         | 6.0 | 74.6                                       | [6]        |
| Prussian blue/Fe\(_2\)O\(_4\)          | 7.0 | 280.82                                     | [43]       |
| CuHCF-cellulose hydrogel               | 7.0 | 309                                        | [44]       |
| CuHCF/MWCNT                            | 7.0 | 310                                        | [44]       |
| MOF/KNiFC                              | 5.0 | 153                                        | [45]       |
| **Sr\(^{2+}\) ion**                    |     |                                            |            |
| Copper hexacyanoferrate(CuHCF)         | 7.0 | 59.95                                      | This research |
| Cobalt hexacyanoferrate(CoHCF)         | 7.0 | 32.73                                      | This research |
| Nickle hexacyanoferrate (NiHCF)        | 7.0 | 29.17                                      | This research |
| Amorphous zirconium phosphates         | 11.4| 134.2                                      | [46]       |
| Zr-MOF                                 | 7.0 | 7.548                                      | [47]       |
| Zirconium phosphate on active carbon   | 6.0 | 2.9                                        | [22]       |
| ZrO\(_2\)-TiO\(_2\)                   | 9.0 | 28.01                                      | [48]       |
| Zirconium phosphate                    | 1.0 | 34                                         | [49]       |
| Fower-like α-ZrP                       | 4.0 | 293.43                                     | [50]       |
| Titanate nanofibers                    | 7.0 | 55.2                                       | [51]       |
| PAN-zeolite                            | 7.0 | 44.43                                      | [52]       |
| Carboxymethylated cellulose            | 4.0 | 108.7                                      | [53]       |
| Graphene oxide                         | 6.5 | 23.83                                      | [54]       |
| ZrP-SO\(_3\)H                         | 4.0 | 183.21                                     | [55]       |
| Nb-doped WO\(_3\)                     | 7.0 | 54.39                                      | [54]       |
| **Co\(^{2+}\) ion**                    |     |                                            |            |
| Copper hexacyanoferrate (CuHCF)        | 7.0 | 62.08                                      | This research |
| Nickle hexacyanoferrate (NiHCF)        | 7.0 | 32.34                                      | This research |
| MWCNT/IO                               |     |                                            |            |
| Silica SBA-15                          |     |                                            | [56]       |
| SiO\(_2\)/Nb\(_2\)O\(_3\)/ZnO        |     |                                            | [58]       |
| Ordered micro- and mesoporous/SiO\(_2\) |     |                                            | [59]       |
| Magnetite-based nanocomposites         |     |                                            | [60]       |
| GO-NH\(_2\)                            |     |                                            | [61]       |

77 K are obtained using TriStar II-Micromeritics, America. The IR spectra of the samples were recorded in the 399-4000 cm\(^{-1}\) range using KBr pellets on a Nicolet iS10 (Thermo Scientific, America). The composition of the material before and after the reaction was analyzed using total reflection X-ray fluorescence (TXRF) S2 Picofox Bruker.

### 3. Results and Discussion

\(A_2[Fe(CN)_{6}]\) (A: Cu, Co, and Ni) was readily synthesized by precipitating Cu\(^{2+}\), Co\(^{2+}\), and Ni\(^{2+}\) salt with \(K_2[Fe(CN)_{6}]\) aqueous solution at 60°C for 4h. The chemical reactions for \(A_2[Fe(CN)_{6}]\) are as follows:
Crystalline properties of the as-synthesized $A_2[Fe(CN)_6]_x$ were examined using PXRD, and the data are shown in Figure 1. Ni$_2$[Fe(CN)$_6$], Co$_2$[Fe(CN)$_6$], and Cu$_2$[Fe(CN)$_6$] exhibit a high degree of crystallinity with a set of diffraction peak characteristic for the PBA family (JCPDS 77-1161) [26, 30, 31]. The respective lattice constant estimated from the PXRD data for Cu$_2$[Fe(CN)$_6$], Co$_2$[Fe(CN)$_6$], and Ni$_2$[Fe(CN)$_6$] is 9.92 ± 0.1 Å, 10.22 ± 0.2 Å, and 10.26 ± 0.2 Å, respectively (Table 2). Although the estimated lattice constants show a slight deviation, presumably due to the size difference among the metal ions, these results are highly consistent with the lattice constant of the face-centered cubic (Pm3m) of PBAs previously reported [26]. The specific surface area of A$_2$[Fe(CN)$_6$] was also characterized using N$_2$ isotherm adsorption at 77 K, and the results were tabulated in Table 3. The surface area of Co$_2$Fe (CN)$_6$ and Ni$_2$Fe (CN)$_6$ is around 60 m$^2$ g$^{-1}$, which are tenfold higher than that of Cu$_2$Fe (CN)$_6$. This could be attributed to the slight aggregation of Cu$_2$Fe(CN)$_6$ as seen by TEM.

The particle size and morphological properties of A$_2$[Fe(CN)$_6$] were examined using transmission electron microscopy (TEM) (Figure 2). Co$_2$Fe (CN)$_6$ shows pseudo-spherical particles with the size varying between 25 and 55 nm (Figure 2(a)). For Cu$_2$Fe(CN)$_6$, the particles are formed from the aggregation of smaller subparticles, resulting in a wider spectrum of distribution. Among the synthesized PBAs, Ni$_2$Fe(CN)$_6$ shows the smallest size, ranging from 15 nm to 35 nm. Essentially, the elemental composition of A$_2$[Fe(CN)$_6$] was confirmed using X-ray energy dispersion spectroscopy (EDX) (Figure 3). The data show that the elements Co, Cu, and Ni were uniformly distributed throughout the examined area in Co$_2$[Fe(CN)$_6$], Cu$_2$[Fe(CN)$_6$], and Ni$_2$[Fe(CN)$_6$], respectively. This further confirms the successful synthesis of A$_2$[Fe(CN)$_6$].

Infrared spectroscopy (IR) is used to investigate the characteristic bonding information within the structure of A$_2$[Fe(CN)$_6$] (Figure 4). In addition to a vibrational band at
590 cm$^{-1}$ and 3450 cm$^{-1}$ corresponding to Fe-C bond [32, 33] and bending mode of H$_2$O [34], all of the A$_2$[Fe(CN)$_6$] exhibit a characteristic peak assigned to the C-N bonding located at around 2000 cm$^{-1}$, which belongs to the CN$^-$ ligand. Principally, the peak position of C-N vibration is indirectly indicative of the bond strength between metal cation and CN$^-$. 

Figure 2: TEM images and the corresponding particle size distribution of (a) Co$_2$[Fe(CN)$_6$], (b) Cu$_2$[Fe(CN)$_6$], and (c) Ni$_2$[Fe(CN)$_6$].
ligands. It is observed that the location of C-N vibration peak in Cu$_2$[Fe(CN)$_6$] is at 2099 cm$^{-1}$, which is slightly higher than those of Ni$_2$[Fe(CN)$_6$] (2097 cm$^{-1}$) and Co$_2$[Fe(CN)$_6$] (2088 cm$^{-1}$), revealing that the contribution of $\pi$-back bonding to the antibonding orbital of CN$^-$ ligand from Cu$^{2+}$ is less significant than those from Ni$^{2+}$ and Co$^{2+}$. In other words, Cu$^{2+}$ within the framework of Cu$_2$[Fe(CN)$_6$] binds less strongly to CN ligand than Ni$^{2+}$ and Co$^{2+}$ do in Ni$_2$[Fe(CN)$_6$] and Co$_2$[Fe(CN)$_6$]. This is an important evidence as it is explicitly correlated with the ion-exchange capacity of A$_2$[Fe(CN)$_6$] discussed later.

The adsorption isotherms of A$_2$[Fe(CN)$_6$] towards Cs$^+$, Sr$^{2+}$, and Co$^{2+}$ were examined at 25°C and pH 7 (Figures 5 and 6). The parameters of the isothermal adsorption of Cs$^+$, Sr$^{2+}$, and Co$^{2+}$ ions on A$_2$[Fe(CN)$_6$] estimated from Langmuir and Freundlich models are shown in Table 4. It is interesting to note that Cu$_2$[Fe(CN)$_6$] shows much higher maximum adsorption capacity (Qm) towards Cs$^+$ (155.60 mg g$^{-1}$), Sr$^{2+}$ (59.95 mg g$^{-1}$), and Co$^{2+}$ (62.08 mg g$^{-1}$) than those of Ni$_2$[Fe(CN)$_6$] (120.31, 29.17, and 32.34 for Cs$^+$, Sr$^{2+}$, and Co$^{2+}$, respectively) and Co$_2$[Fe(CN)$_6$] (154.46 and 59.95 for Cs$^+$ and Sr$^{2+}$, respectively).
Considering crystallographic similarity among the structures of Cu$_2$[Fe(CN)$_6$], Ni$_2$[Fe(CN)$_6$], and Co$_2$[Fe(CN)$_6$], the difference in adsorption capacity can be associated with the ion-exchange capability of the metal nodes in the framework of A$_2$[Fe(CN)$_6$]. More specifically, the metal nodes that bond less strongly to the CN$^-$ ligand are more likely to participate in ion-exchange with adsorbate (i.e., Cs$^+$, Sr$^{2+}$, and Co$^{2+}$). In order to further understand the sorption mechanism, TXRF was used to investigate the solution composition before and after sorption (Figure 7). Figures 7(a)–7(c), respectively, demonstrate the change in the peak intensity of Cs$^+$ (4.3 keV), Sr$^{2+}$ (14.2 keV), and Co$^{2+}$ (6.93 keV) in the solution before and after adding Cu$_2$[Fe(CN)$_6$], Ni$_2$[Fe(CN)$_6$], and Co$_2$[Fe(CN)$_6$] into the solution. As seen, after the sorption reaches equilibrium, the peak intensity corresponding to Cs$^+$, Sr$^{2+}$, and Co$^{2+}$ decreases, revealing the sorption process of those cations by A$_2$[Fe(CN)$_6$]. Interestingly, the peak located at 8.05 keV, which is assigned to Cu K$_\alpha$, is clearly observed after the sorption process in all solutions (Figures 7(d)–7(f)); however, we could not observe
any peaks corresponding to those of Ni$_2^+$ or Co$_2^+$. These data imply that only Cu$_2^+$ cations within the framework of Cu$_2$[Fe(CN)$_6$] meaningfully participate in the sorption via ion exchanging with the adsorbates. This is in concert with the IR data in which Cu$_2^+$ binds less strongly to CN$^-$ ligands, thus readily subjected to readily ion exchange with Cs$^+$, Sr$^{2+}$, and Co$^{2+}$. Ion-exchange-based sorption for removal of radioactive waste was also previously reported for PBAs [35]. In addition, among the tested cations, Cs$^+$ was found to be the most effectively adsorbed PBAs. This is mainly attributed to the size similarity between Cs$^+$ cation (3.25 Å) [25] and the channel window of PBAs (3.2 Å), while the size of Sr$^{2+}$ (4.12 Å) and Co$^{2+}$ (4.23 Å) [36] is comparably larger than the window size. These are important points as these findings can allow for the potential design of adsorbent with designed ion-exchange capacity, so that we could further control the sorption process as well as enhance the selectivity.
### Table 4: Adsorption isothermal parameters of Cs⁺, Sr²⁺, and Co²⁺ by A₃[Fe(CN)]₆ extract from Langmuir and Freundlich models.

| Ion   | Adsorbent material | Qₑ (mg/g) | Langmuir | Freundlich |          |          |
|-------|--------------------|-----------|-----------|------------|----------|----------|
|       |                    |           | Kₑ (L/mg) | R²         | K_f (mg/g) | n     |
| Cs⁺   | Cu₂[Fe(CN)₆]       | 155.60    | 0.996     | 0.927      | 62.69    | 6.797   | 0.907    |
|       | Co₂[Fe(CN)₆]       | 154.46    | 0.010     | 0.954      | 9.44     | 2.269   | 0.890    |
|       | Ni₂[Fe(CN)₆]       | 120.31    | 0.272     | 0.973      | 53.49    | 6.570   | 0.708    |
| Sr²⁺  | Cu₂[Fe(CN)₆]       | 59.95     | 0.068     | 0.980      | 13.65    | 3.804   | 0.871    |
|       | Co₂[Fe(CN)₆]       | 32.73     | 0.008     | 0.961      | 1.79     | 2.233   | 0.953    |
|       | Ni₂[Fe(CN)₆]       | 29.17     | 0.009     | 0.989      | 1.58     | 2.204   | 0.965    |
| Co²⁺  | Cu₂[Fe(CN)₆]       | 62.08     | 0.078     | 0.961      | 18.03    | 4.585   | 0.827    |
|       | Ni₂[Fe(CN)₆]       | 32.34     | 0.028     | 0.935      | 5.81     | 3.523   | 0.914    |

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**Figure 7: Continued.**
4. Conclusions

Prussian blue analogues (PBAs) with different substituted cations (A₂[Fe(CN)]₆ (A: Cu²⁺, Co²⁺, and Ni²⁺)) were successfully synthesized and applied for the removal of Cs⁺, Sr²⁺, and Co²⁺, which are commonly found in radioactive waste. It was found that Cu₂[Fe(CN)]₆ exhibits the highest sorption capacity towards Cs⁺, Sr²⁺, and Co²⁺ compared with those of Co₂[Fe(CN)]₆ and Ni₂[Fe(CN)]₆. IR and TXRF data reveal that the cation-exchange ability of substituted metal within the framework of PBAs has a significant impact on the sorption performance of PBAs. In addition, the similarity between the Cs⁺ size and the channel window size of PBAs leads to a preferential sorption of Cs⁺ over Sr²⁺ and Co²⁺.

Data Availability

The data has been provided by the DaLat University.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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