

# PHYSICOCHEMICAL IN-SITU SYNTHESIS OF PRUSSIAN BLUE FOR CESIUM REMOVAL

## FIZIKALNO-KEMIJSKA SINTEZA BERLINSKEGA MODRILA ZA ODSTRANITEV CEZIJA

Woo Jung Lee<sup>1</sup>, Sang Sun Choi<sup>1</sup>, Soon Hong Lee<sup>1</sup>, Kyung Jae Yun<sup>1</sup>, Yeon Ji Cho<sup>1</sup>,  
Joon Hyuk Lee<sup>2\*</sup>

<sup>1</sup>Department of Environmental and Energy Engineering, Anyang University, Anyang 14028, Republic of Korea

<sup>2</sup>Department of Chemical Engineering, Hanyang University, Seoul 04763, Republic of Korea

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Prussian blue (PB) has attracted substantial attention as a potential adsorbent for radionuclides due to its high water-insoluble characteristics. Here, PB-encapsulating activated carbon fibers (ACFs) obtained via a physicochemical in-situ synthesis were introduced for an effective cesium removal. ACFs were used as an anchor platform to hold PB within the pores. The physicochemical synthesis of PB (PB-ACF-B) was done by stirring ACFs in an iron chloride solution. Potassium ferrocyanate was injected during the stirring process. As the counterpart, powdered PB (PB-ACF-A) was prepared with a physical synthesis. Throughout the test, PB-ACF-B revealed a decrease in the specific surface characteristics compared to PB-ACF-A; however, it also experienced an increase in the <sup>137</sup>Cs adsorption. In all the cases, the dosage of the adsorbent and radionuclide was in positive correlation with the adsorption performance. Further, the amount of PB was found to be the key factor for the adsorption of <sup>137</sup>Cs compared to the specific surface characteristics.

**Keywords:** Prussian blue, cesium, adsorption, physicochemical synthesis

Berlinsko modrilo, znano tudi kot pariško oz. prusko modrilo, je v osnovi železov (III) heksacijanoferatni (II) pigment Fe<sub>4</sub>[Fe(CN)<sub>6</sub>]<sub>3</sub>. V zadnjem obdobju je postal, zaradi svoje odlične netopnosti v vodi, zelo zanimiv in atraktiven material kot potencialni adsorbent za radioaktivne elemente. V članku avtorji obravnavajo s pruskim modrilom (PB) obložena aktivirana ogljikova vlakna (ACFs). Opisujejo izdelavo učinkovitega odstranjevalca cezija PB-ACF-B s pomočjo *in-situ* fizikalno-kemijske sinteze. Aktivirana ogljikova vlakna so uporabili kot osnovo in sidrišče za prusko modrilo v porah ACFs. Avtorji so fizikalno-kemijsko sintezo PB-ACF-B izvajali s premešavanjem aktiviranih ogljikovih vlaken v raztopini železovega klorida. Kalijev ferocianat so vbrizgavali v raztopino med premešavanjem. Za primerjavo so pripravljali tudi prašni PBs (PB-ACF-A) s fizikalno sintezo. Rezultati raziskav so pokazali, da ima PB-ACF-B manjšo specifično površino kot PB-ACF-A, vendar pa ima kljub temu boljše lastnosti za adsorpcijo <sup>137</sup>Cs. V vseh primerih, ne glede na dozo absorbenta in radioaktivnega elementa, je obstajala pozitivna korelacija glede sposobnosti za adsorpcijo. Nadalje so avtorji ugotovili tudi, da je v primerjavi s površinskimi lastnostmi vlaken vsebnost pruskega modrila ključni faktor za uspešno adsorpcijo <sup>137</sup>Cs.

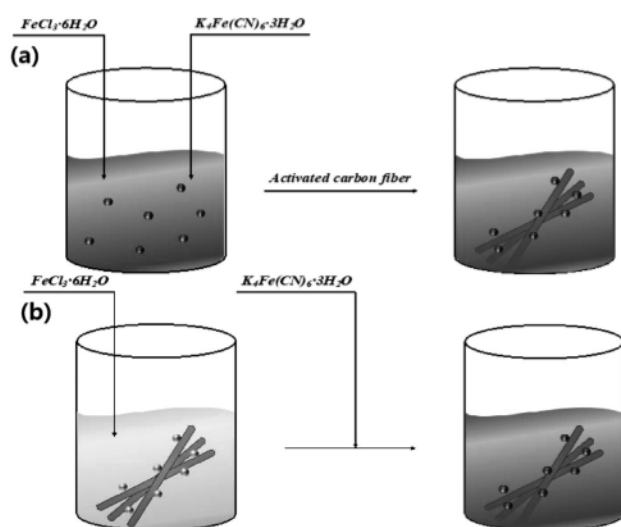
**Ključne besede:** berlinsko modrilo, cezij, adsorpcija, fizikalno kemijska sinteza

## 1 INTRODUCTION

Nuclear energy seems to be one of the most viable alternatives with a low-carbon footprint compared to traditional energy sources. Previous reports indicated that nuclear energy releases a considerably low amount of greenhouse-gas emissions in comparison with carbon-based fossil fuels.<sup>1</sup> Owing to the widespread use of nuclear energy, unfortunate accidents such as the 2011 Fukushima disaster may result in artificial radionuclide releases. Radionuclides are generated during the operation of nuclear facilities, having a negative effect on human health and environment due to their toxicity and radioactivity. Compared to the other radionuclides, cesium-137 (<sup>137</sup>Cs) is known to diffuse more easily over a wide area and dissolve more readily in water. The long-term behavior of <sup>137</sup>Cs with its very long half-life could lead to an accumulation throughout the ecosystem

and the food chain. These factors incentivize the development of <sup>137</sup>Cs uptake using various platforms. At present, using the high ion-exchange capacity of Cs<sup>+</sup> is acknowledged as a mature technology for separating <sup>137</sup>Cs from the surrounding environment. Here, high stability of a platform is crucial as a sample matrix exhibits radioactive and acidic characteristics. Activated carbon fibers (ACFs) are amorphous carbonized fibers with high specific surface areas and functionalized surfaces. ACFs can be produced in a straightforward and convenient manner because of their high carbon yield.<sup>2,3</sup> For the <sup>137</sup>Cs uptake, it is vital to use ACFs, yet challenging if it is done without any surface modification. Metal hexacyanoferrate or Prussian blue (PB) is widely applied in many fields including the uptake of radionuclides. PB has a unique face-centered cubic lattice structure, allowing a preferable ion-sieving capability of hydrated cations. Utilizing this feature, <sup>137</sup>Cs ions can be selectively adsorbed into PB.

\*Corresponding author's e-mail:  
flower@hanyang.ac.kr (Joon Hyuk Lee)



**Figure 1:** Immobilization of PB with a) physical and b) physicochemical syntheses onto ACFs

In the present study, a simple material design was adopted to create a friendly ion-exchange environment between  $^{137}\text{Cs}$  and PB. We hereby employed pitch-based ACFs as the anchor for PB. For the maximized insertion, we synthesized PB directly inside the pores of ACFs via an in-situ method. Physical- and physicochemical syntheses were done separately for comparison. The method introduced in this work was inspired by previous in-situ acidic treatments and PB treatments on different carbonaceous materials.<sup>4–6</sup> The specific surface area, pore-size distribution and adsorption/desorption characteristics of PB were first investigated. Adsorption performance within the designated time frame was assessed after immobilizing PB onto the ACFs. Given that  $^{133}\text{Cs}$  is a radioisotope of  $^{137}\text{Cs}$ ,  $^{133}\text{Cs}$  was employed for the practical evaluation.

## 2 EXPERIMENTAL PART

### 2.1 Preparation of samples

All the materials and chemicals were of analytical grade and used without further purification. Pyrolysis fuel oil was provided by Hyundai OilBank Corp., Republic of Korea. The reaction temperature was set as 600 °C for 1 h at a 1 bar pressure with a heating rate of 6 °C/min.  $\text{N}_2$  gas (4 L/min) was introduced to ensure an inert condition. The prepared pitch was further oxidized, carbonized and activated at 800 °C for 2 h under  $\text{H}_2\text{O}$  gas (0.2 mL/min). The potassium hexacyanoferrate solution was immobilized through the coprecipitation method onto 0.5 g of ACFs as can be seen in **Figure 1**. The physical synthesis was carried out using 20 mM of powdered PB, stirred at 150  $\text{min}^{-1}$  for 2 h to reach the plateau. Following the synthesis, PB was physically trapped in the pores of ACFs. The physicochemical synthesis was done by stirring ACFs in a 20-mM iron chloride solution at

150  $\text{min}^{-1}$  for 1 h and continually injecting, 10 times, 20 mM of potassium ferrocyanate (5 mL/min). After that, the resulting material was washed 5 times and dried at 70 °C for 24 h in a desiccator. In this case, not only iron ions bonded due to the chemical adsorption, but also the iron ions in the aqueous solution were expected to be synthesized into PB, thus they could be trapped in the pores during the immersion time. For convenience, the finalized samples were named PB-ACF-A and PB-ACF-B for the physical and physicochemical syntheses of PB, respectively.

### 2.2 Methodology

The morphology of the samples was characterized using a scanning electron microscope (SEM, SIGMA, Carl Zeiss) coupled with an energy dispersive spectrometer. The samples were coated with Au with a sputter coater (E-1045, Hitachi). The specific surface area and the resulting pore volume were measured with BET and BJH using ASAP2460 (Micromeritics). In order to evaluate the binding stability of PB, the samples were washed 5 times in 50 mL of deionized water. The desorption characteristics of PB at 690 nm were analyzed using an ultraviolet/visible spectrometer (UV-VIS spectrometer, Libra S22, Biochrom). The adsorption of PB onto the samples was measured with inductively coupled plasma mass emission spectroscopy at the end of each period (NexION 350D, PerkinElmer).

## 3 RESULTS AND DISCUSSION

### 3.1 Physicochemical properties of the samples

We first obtained a set of images of the surface characteristics of each sample as shown in **Figure 2**. In **Figure 2a**, a sample before the surface modification reveals a smooth and porous morphology. In the case of synthesized PB-ACFs (**Figures 2b** and **2c**), it was confirmed that PB (white flakes) was successfully doped on the surface. After the physical synthesis, PB was attached to the outer pores and it seems that it bonded to the surface by itself (**Figure 2b**). On the contrary, PB formed inside the pores of PB-ACF-B (**Figure 2c**). Iron ions in the aqueous solution were absorbed into the pores before and after the synthesis, thus allowing more time for PB to be doped on the sample. In this sense, one could assume that the physicochemical synthesis may allow more PB to be distributed onto the surface. An EDS elemental analysis was performed to observe the elemental composition (**Table 1**). The sample before the surface modification showed the highest C- and O- contents due to the C-O bonding in carbonaceous materials. Depending on the synthesis method, PB-ACF-A and PB-ACF-B had different iron amounts. The Fe amount of PB-ACF-B was about 45.11 % higher than that of PB-ACF-A. The content of PB was evaluated using the amount of synthesized iron and the formula for Prussian blue, and it was



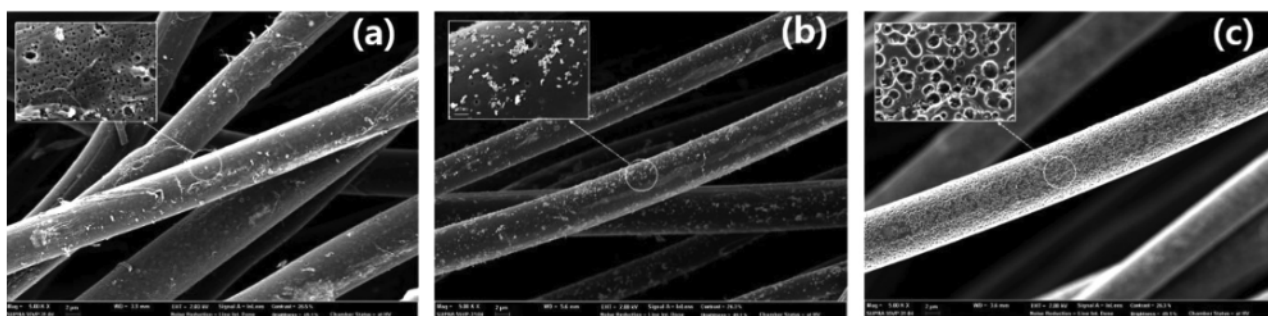


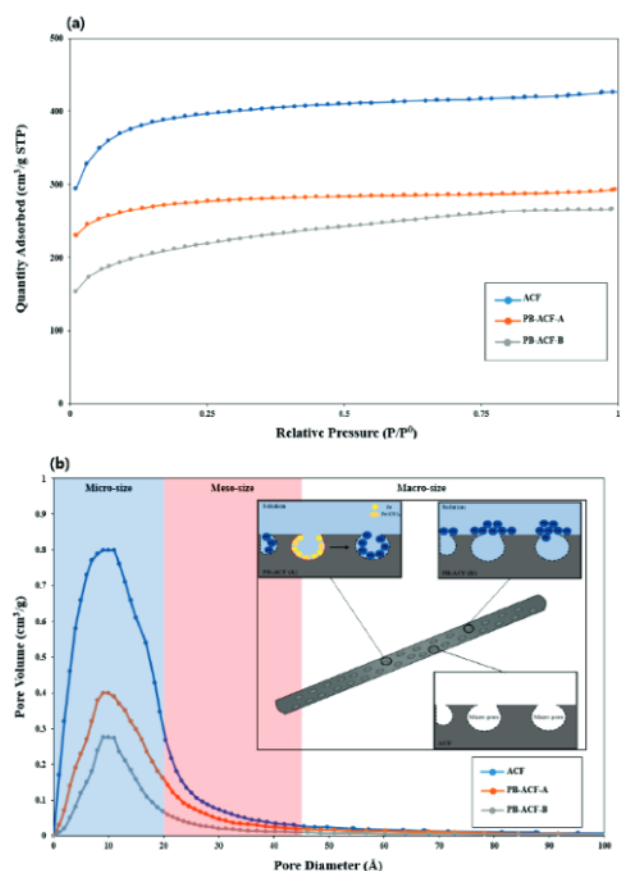
Figure 2: SEM images: a) ACF, b) PB-ACF-A, c) PB-ACF-B

about 4.13 % in the case of PB-ACF-A and about 9.15 % in the case of PB-ACF-B with respect to the total weight of a sample.

Table 1: EDS elemental analysis of the samples

Materials	Elemental composition (w/%)			
	C	N	O	Fe
ACF	97.79	0.56	1.65	–
PB-ACF (A)	95.92	0.55	1.64	1.89
PB-ACF (B)	93.64	0.54	1.63	4.19

Table 2 presents various surface parameters including BET specific surface area, micropore area and exter-

Figure 3: Pore distribution of the samples: a) plotted pore adsorption and desorption isotherms determined by N<sub>2</sub>, b) size difference plotted against pore volume

nal surface area of the samples. Detailed pore characteristics are shown in Figure 3. In all the cases, the introduction of PB led to an inevitable decrease in the specific surface characteristics. Herein, PB-ACF-A and PB-ACF-B showed a 20.03 % and 38.81 % reduction, respectively, in  $S_{\text{BET}}$  compared to ACF. PB-ACF-A was observed to have a minimal decrease in the specific surface characteristics, suggesting that PB is not feasible in the pores when produced via physical synthesis. On the contrary, PB-ACF-B exhibited the lowest specific surface profile, which is in accordance with Figure 2. Following the same principle, rich PB produced via physicochemical synthesis was also responsible for the plots in Figure 4. The leaching of PB declined after the second trial, which was mainly due to the weak bonding between PB and the pores. One important conclusion based on this figure is that the use of PB may have caused an

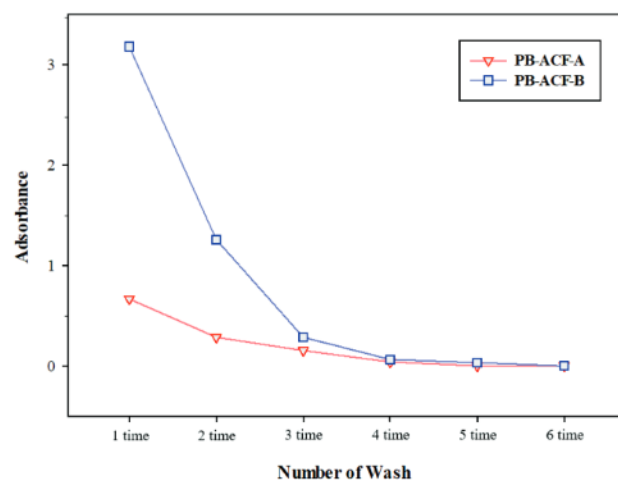


Figure 4: Leaching of PB probed with the UV-VIS spectrometer

Table 2: Specific-surface characteristics of the samples as determined by N<sub>2</sub> isotherms

Classification	$S_{\text{BET}}^a$ ( $\text{m}^2\cdot\text{g}^{-1}$ )	$S_m^b$ ( $\text{m}^2\cdot\text{g}^{-1}$ )	$S_e^c$ ( $\text{m}^2\cdot\text{g}^{-1}$ )
ACF	1495	1161	334
PB-ACF (A)	1050	854	196
PB-ACF (B)	812	706	106

<sup>a</sup>BET specific surface area, <sup>b</sup>micropore area, <sup>c</sup>external surface area

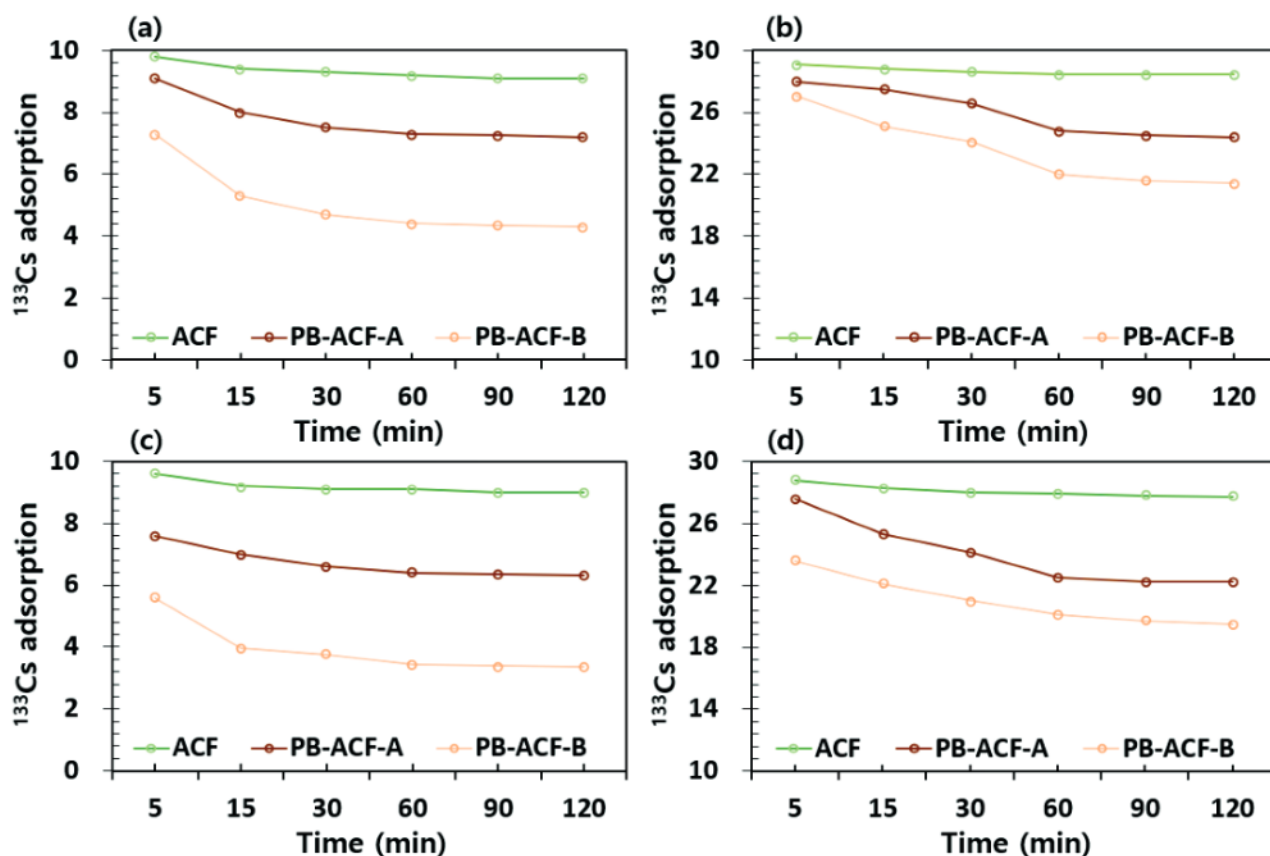


Figure 5: Adsorption of  $^{133}\text{Cs}$  via samples by a) 0.01 g/10  $\mu\text{g}$ , b) 0.01 g/30  $\mu\text{g}$ , c) 0.05 g/10  $\mu\text{g}$  and d) 0.05 g/30  $\mu\text{g}$  of the sample dosage and target radionuclide

efficient uptake of  $^{133}\text{Cs}$ , yet the environmental perspective of reusability should be critically investigated by optimizing the pore design.

### 3.2 Evaluation of $^{133}\text{Cs}$ adsorption performance

Figure 5 shows the effect of increasing the sample dosage and target radionuclide. It is clear from the figure that increasing the aforementioned factors resulted in higher adsorption performance. This is mainly related to the increased adsorption sites and thus, rich pores allow  $^{133}\text{Cs}$  ions to be attached to the pores with the Van der Waals force.<sup>7</sup> Furthermore, the sample dosage is in direct correlation with the total amount of PB. An increase in the ionic strength and region can increase the adsorption capacity of  $^{133}\text{Cs}$  onto samples.<sup>8</sup> The linear nature of the plot confirms that the use of PB is sufficient for the removal of  $^{133}\text{Cs}$ . The adsorption performance of  $^{133}\text{Cs}$  was found to be in the order of PB-ACF-B > PB-ACF-A > ACF. The time gap between PB-ACF-A and PB-ACF-B is mainly due to the amount of PB. These results show that PB is the key factor for the  $^{133}\text{Cs}$  adsorption, preceding the specific surface characteristics, which opens the door to designing a useful carbonaceous platform material for radionuclide removal.

## 4 CONCLUSIONS

PB-ACF-B showed a decrease in the specific surface characteristics and an increase in the  $^{133}\text{Cs}$  adsorption compared to PB-ACF-A. Interestingly, the difference in the  $^{133}\text{Cs}$  adsorption performance of the samples was attributed to the amount of PB. The amount of PB was found to affect the  $^{133}\text{Cs}$  adsorption more than specific surface characteristics. Altogether, a physicochemical in-situ synthesis may be a promising method for the  $^{133}\text{Cs}$  adsorption via carbonaceous materials.

## Acknowledgment

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