

Prussian blue immobilization on various filter materials through Layer-by-Layer Assembly for effective cesium adsorption

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Abstract. Prussian blue (PB) is well known for its excellent Cs⁺ ions adsorption capacity. Due to the high dispersibility of PB in aqueous phase, composite materials imbedding PB in supporting materials have been introduced as a solution. However, building PB particles inside porous supporting materials is still difficult, as PB particles are not fully formed and elute out to water. In this study, we suggest layer-by-layer (LBL) assembly to provide better immobilization of PB on supporting materials of poly vinyl alcohol sponge (PVA) and cellulose filter (CF). Three different PB attachment methods, ex-situ/in-situ/LBL assembly, were evaluated using PB leaching test as well as Cs⁺ adsorption test. Changes of surface functionality and morphology during PB composite preparation protocols were monitored through Fourier transform infrared spectroscopy and scanning electron microscopy. The results indicate that LBL assembly led to better PB attachment on supporting materials, bringing less eluting PB particles in aqueous phase compared to other synthesis methodologies, such as ex-situ and in-situ synthesis. By enhancing the stability of the adsorbent, adsorption capacity of PVA-PB with LBL improved nine times and that of CF-PB improved over 20 times. Therefore, the results suggest that LBL assembly offers a better orientation for growing PB particles on porous supporting materials

Keywords: prussian blue; cesium; polyvinyl alcohol sponge; cellulose filter; layer by layer

1. Introduction

Prussian blue (PB) is well known for its excellent capacity to adsorb cesium ions (Cs⁺). The structure of Prussian blue is a simple lattice in which the cation of the hydrated Cs⁺ ion is bound via electrostatic force in a cage of the PB lattice (Ishizaki *et al.* 2012). Having this special structure, PB was used as adsorbent in the decontamination of radioactive cesium after the Fukushima nuclear plant disaster.

Because of its high Cs⁺ ion adsorption capacity, Prussian blue has been applied in the water treatment field in many studies. However, the attraction force between PB and water leads the particles to be dispersed in water, and this makes it difficult to recover or separate them from the treated water stream due to the few-tens of nanometer size of PB. In order to overcome this size issue, intensive studies have been carried out to immobilize PB in/on the supporting matrix. Especially, PB composites based on organic polymers having numerous pores have recently come to be preferred as supporting material in applications in the water treatment field. PB immobilization technologies using cellulose (Vipin *et al.* 2016), chitin (Vincent *et al.* 2015) and alginate (Vipin *et al.* 2016) as supporting materials have been introduced.

PB immobilization methods can be roughly classified

into ex-situ synthesis and in-situ synthesis. In ex-situ synthesis of PB, pre-synthesized PB is attached on supporting matrix by physical interaction, but it is difficult to deliver PB particles deeply inside the pores (Montazer and Maali Amiri 2014). In this sense, the in-situ synthesis method has been more actively studied in cases of porous supporting materials. PB particles were synthesized in the presence of supporting materials in in-situ synthesis, but this also caused a problem of residue inside pores when the concentrations of precursors were not carefully regulated, which occurs when growing unstable PB particles.

For the in-situ synthesis of PB, two precursor solutions, iron (III) solution and ferrocyanide solution, were used, as suggested in a previous study (Vincent *et al.* 2014, Jang *et al.* 2014, Yang *et al.* 2014). Typically, supporting materials were immersed in iron (III) solution; then, the supporting materials were immersed again in ferrocyanide solution prepared in a separated vessel. However, the amount of immobilized iron (III) was much lower than the initial iron (III) concentration in the solution; therefore, the stoichiometric ratio was not well maintained if the concentration was not well regulated. Due to the deficiency of iron(III) ion, PB prepared by in-situ synthesis would be unstable on the surface of supporting materials.

2. Materials and method

2.1 Materials

Poly vinyl alcohol sponge was obtained from

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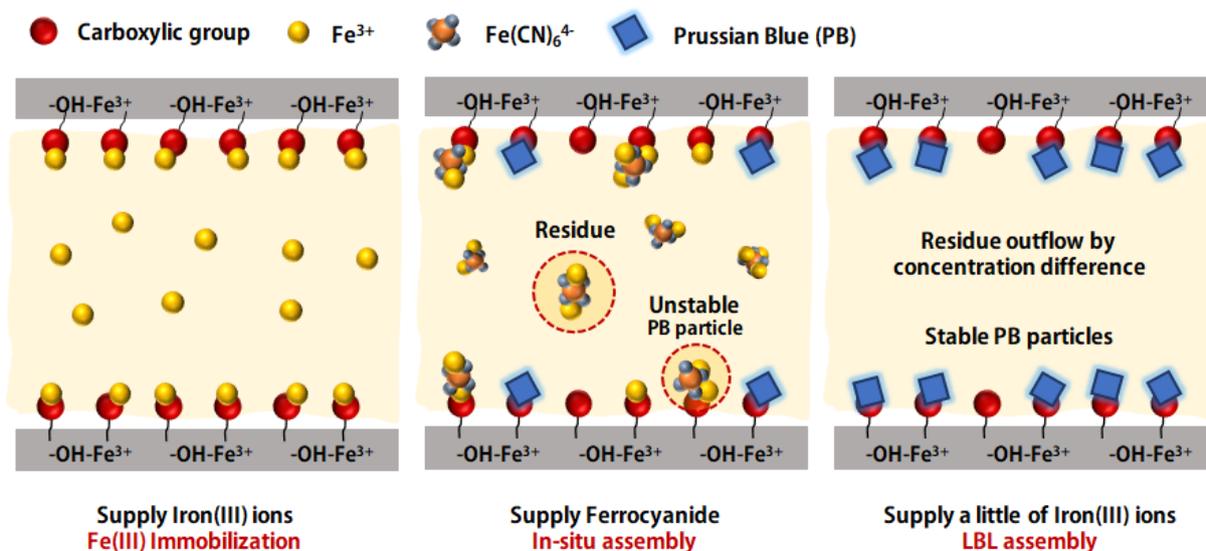


Fig. 1 Schematic of synthesis strategy for PB immobilization by LBL-assembly

Samkwang Trading Company (Daegu, Korea), and Cellulose filter was obtained from Taebong Co. Ltd. (Daegu, Korea). Potassium persulfate (KPS, 99%), and sodium chloride (NaCl, 93%) were purchased from Samchun Chemical Reagent Co. Ltd. (Gyeonggi-do, Korea). Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 97%) and potassium ferrocyanide trihydrate ($\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$, 99%) as precursor for synthesizing Prussian blue were purchased from Duksan Chemical Reagent Co. Ltd. (Seoul, Korea). All chemical reagents and solvents were of extra pure grade. The Cs(I) standard solution (1000 mg/L) at ICP-MS analytical grade was obtained from Kanto Chemical Co. Inc. (Chuo-cu, Japan). Deionized water was used in the preparation of all solutions.

2.2 Preparation of PB adsorbents

Ex-situ PB synthesis was performed using pre-formed PB particles in aqueous solution. FeCl_3 solution (20 mM) and $\text{K}_4\text{Fe}(\text{CN})_6$ solution (20 mM) were mixed to form PB. After PB particles were formed, 250 mg of PVA sponge ($5 \times 5 \times 5$ mm; 125 mm^3)/Cellulose filter (3×3 cm; 9 cm^2) were added to the PB suspension, and reacted for 5 min. Then, the obtained products were stored at 60°C and denoted as E-PVA-PB and E-Cell.-PB.

In-situ PB synthesis was performed by injecting the precursor of PB in series in the presence of supporting materials. 250 mg of PVA sponge ($5 \times 5 \times 5$ mm; 125 mm^3)/Cellulose filter (3×3 cm; 9 cm^2) was added to a 50 ml solution of 20 mM FeCl_3 for 24 h. Then, the supporting materials with immobilized iron(III) were separated from the solution, and the product was reacted with 50 ml of 20 mM $\text{K}_4\text{Fe}(\text{CN})_6$ solution for 5 min. Afterward, the obtained product was stored at 60°C and denoted I-PVA-PB and I-Cell.-PB.

PB growth via LBL assembly is similar to that via in-situ synthesis, but has an additional step of adding ferric chloride solution after in-situ synthesis finishes. At the last step of the in-situ synthesis, PVA and cellulose were

separated from the solution, which was then reacted with 50 ml of 10 mM FeCl_3 solution for 5 min. Afterward, the obtained products were stored at 60°C and denoted as L-PVA-PB and L-Cell.-PB.

2.3 Characterization

In order to monitor changes of functional groups, Fourier-transform infrared (FTIR, TENSOR27, Bruker, Germany) spectra were recorded in the $400\text{--}4000 \text{ cm}^{-1}$ region on the surface of the pristine supporting materials and the supporting materials synthesized by each assembly process.

The morphologies of the different PB composites were monitored by Scanning Electron Microscope and the chemical compositions of the samples were investigated by Energy Dispersive X-ray Spectrometer (SEM/EDS, SU8010, Hitachi, Japan).

2.4 Evaluation of PB leaching

The amounts of PB leached from the synthesized adsorbents during the several washing steps were analyzed using absorbance, showing wavelength value with unique colors of PB, detected at 690 nm by UV-Vis Spectrophotometry (Libara S22, BioChrom Ltd., USA). Prepared adsorbents were further washed in 50 mL of deionized water. Five repetitions of the same approach were performed as a standard washing protocol. The supernatants from each washing step were collected and the PB concentration was measured by absorbance, as described above.

2.5 Adsorption experiments

The adsorption test of cesium ions in aqueous solution was carried out in batch experiments. In a typical batch adsorption equilibrium experiment, 100 mg of each adsorbent was reacted with 50 mL of 5 mg/L Cs^+ aqueous

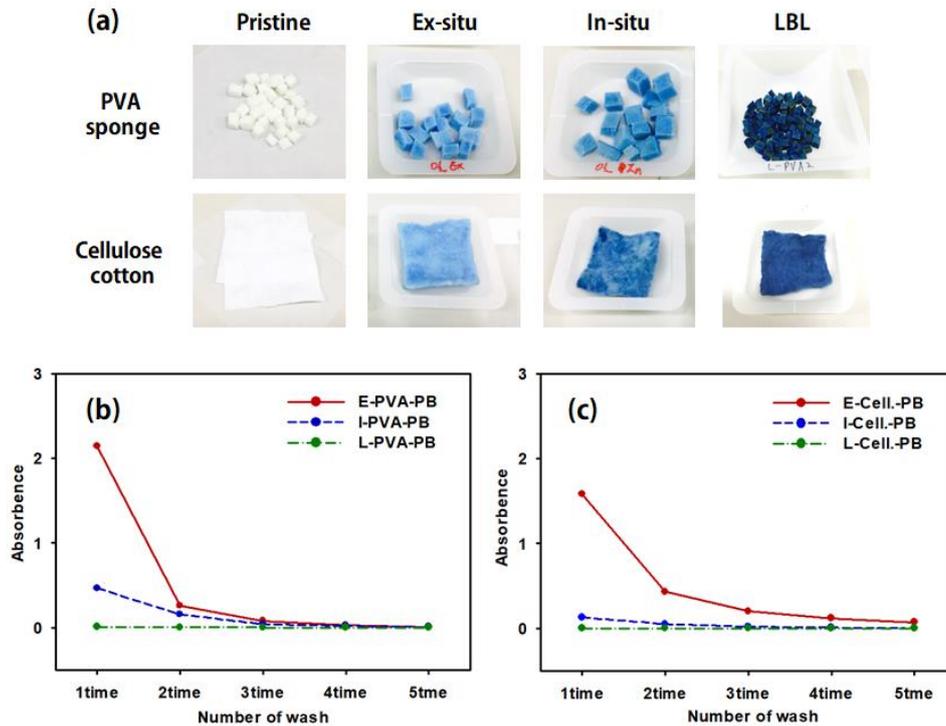


Fig. 2 (a) PB adsorbents prepared by other preparation protocols; and (b-c) PB leaching during washing step measured as absorbance at 690 nm (b) PVA-PB, (c) Cellulose-PB)

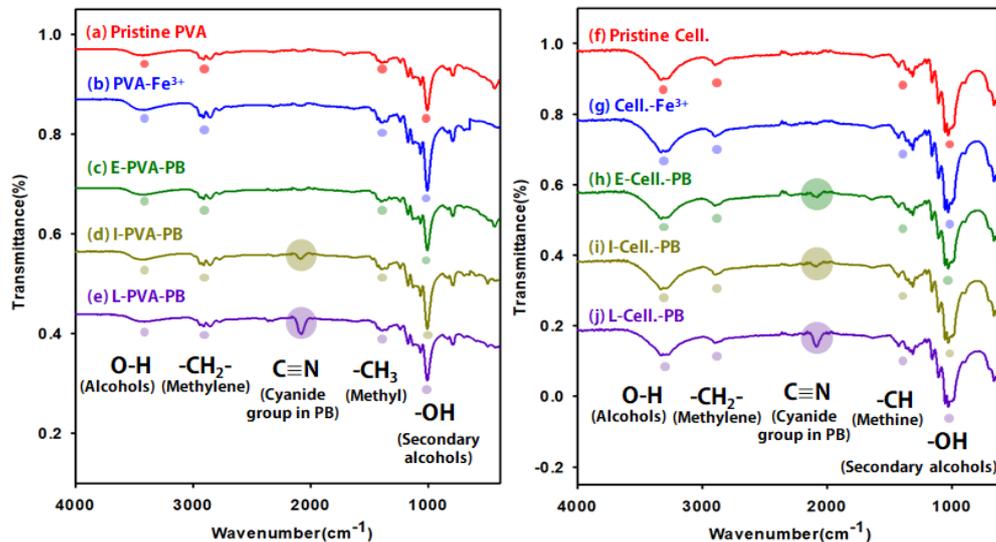


Fig. 3 FTIR spectra of sample with Ex-situ/In-situ/LBL assembly. Distinctive adsorption bands at 3500-3200 cm⁻¹ (O-H, alcohol), 3000-2850 cm⁻¹ (-CH₂-, Methylene), 2100-2080 cm⁻¹ (C≡N, Cyanide), 1320-1000 cm⁻¹ (-CH₃, methyl), 1365 & 1315 cm⁻¹ (C-H stretch), 1050 cm⁻¹ (Secondary alcohols)

solution in a set of conical tubes. The pH of cesium aqueous solution was not adjusted and the sample were shaken at 303 K for 24 h in an agitator. Analysis of residual cesium ion concentration was performed using an inductively coupled plasma mass spectrometer (ICP-MS, NexION 350D, Perkin-Elmer, USA). Afterward, Cs⁺ adsorption equivalent (q_e , mg/g) values were calculated, as follows (Eq. 1) (Lee *et al.* 2017):

$$q_e = (c_o - c_e) \times \frac{V}{m} \quad (1)$$

3. Results and discussion

3.1 PB leaching during washing steps

Fig. 2 (a) provides pictures of the PB composites prepared by different synthesis protocols, ex-situ, in-situ, and LBL assembly. The pristine PVA sponge and cellulose filter were white, but the color changed to blue after PB immobilization due to the color of PB. The degree of color could be a parameter explaining the amount of immobilized

PB. A deeper blue color was achieved in the case of LBL assembly compared to the other synthesis protocols; this directly explains the advantage of LBL assembly for providing stronger interaction with PB during intensive washing steps.

The amounts of PB particles leached from the PB composites during the washing steps were analyzed using UV-vis spectroscopy; the results are shown in Fig. 2 (b-c), respectively. As the apparent blue color of PB particles was detected at 690 nm wavelength, the absorbance at 690 nm directly explains how many PB particles were detached from the composites.

In most cases, leaching out of PB was not observed after 3 times of washing; therefore, we confirmed that 3 times of washing is enough to wash out unattached PB particles from composites for all cases. However, first and second washings were significantly different with respect to the synthesis methods.

In the case of ex-situ synthesized composites (E-PVA-PB and E-Cell.-PB), significant amounts of PB washed out during the first and second washing steps. This indicates that physical immobilization was not successful at binding PB on the supporting materials. In this synthesis method, pre-synthesized nano-sized PB just interacted with the surface of the porous polymeric structure, it did not move inside of the pore structures due to the size of the particles.

Contrary to this, the samples prepared by In-situ or LBL showed lower leaching of PB after a single washing. In these synthesis methods, PB precursor solutions containing ionic form of ferric iron and ferrocyanide were used instead of PB particles; therefore, the ionic species could be more easily transported inside of the porous polymeric structure. The PB particles prepared inside of the porous network benefited from the protective effect of the surrounding structure. Moreover, the sample with LBL (L-PVA-PB and L-Cell.-PB) showed much less loss of PB during the washing step, indicating the stable binding of their pore network.

3.2 Change of functional groups during PB immobilization

Functional groups of each synthesized adsorbents were identified using FT-IR analysis, as presented in Fig. 3. The pristine PVA sponge and cellulose filter indicated that they contain alcohol and hydrocarbon groups, as shown in Fig. 3 (a), (f). It appeared that there was C-O stretch due to alcohol at 1320-1000 cm^{-1} and C-H stretch due to sp^3 at 3000-2800 cm^{-1} (Mansur *et al.* 2008, Garside and Wyeth 2003, Oughlis-Hammache *et al.* 2016).

PB nanocomposites prepared by ex-situ assembly (E-PVA-PB and E-Cell.-PB), shown as green lines in Fig. 3, had the same functional groups as those of the pristine samples, and we could not detect a peak at around 2083 cm^{-1} indicating a cyanide group, which is one of the major chemical structures of PB. However, PB composites prepared by in-situ synthesis contained a weak peak at around 2083 cm^{-1} , as shown Fig. 3. (d), (i). Previous research has reported observing cyanide groups in the PB lattice structure at 2100-2050 cm^{-1} (Itaya *et al.* 1986).

However, the low intensity of the $\text{C}\equiv\text{N}$ peak for I-PVA-PB and I-Cell.-PB has been identified; this was the result of relatively deficient Fe(III) ions that remained in an unstable structure.

Contrary to this, the L-PVA-PB/L-Cell.-PB in Fig. 3 (e), (j) had a much stronger and clearer $\text{C}\equiv\text{N}$ peak in the region compared to the samples prepared by ex-situ and in-situ methods. This confirms that more PB particles were firmly immobilized on the supporting materials. This can be explained as showing that an additional supplement of Fe(III) ion in LBL assembly made the PB particles grow into a lattice structure, largely on the supporting material surface. This reveals that the effect of supplying additional Fe(III) ions is to contribute to a stable structure for growing of PB particles on to hydroxyl groups in supporting materials. Based on these results, LBL assembly is suitable for building PB particles in supporting materials.

3.3 Morphology and elemental analysis

Based on the results of FT-IR, PB adsorbents prepared by LBL assembly showed a higher $\text{C}\equiv\text{N}$ peak, indicating a greater amount of PB particles immobilized than the case for the other PB adsorbents. In order to have better confirmation of the immobilized amounts, SEM/EDS analysis was conducted for the PB composites prepared by LBL assembly, as well as for the pristine supporting materials; the results are presented in Fig. 4 and Table 1.

For the PVA sponge, pore size seems to be tightened after PB immobilization, which indicates the formation of additional PB layers in the PVA sponge pore network. The formation of PB layers was observed inside of the PVA sponge as well as on the outer surface. This is a clear advantage of LBL assembly using precursors of PB, and not PB particles themselves. The ferric ion can penetrate well into the pore network of the PVA sponge; then, PB can form by the reaction with ferrocyanide ion. Therefore, PB can be prepared inside of the pore network. A similar structure was also observed in the cellulose filter. Even small aggregate can be detected on the surface of the cellulose fiber, as shown in Fig. 4(d) (red circles).

The above results mean that supporting materials prepared through LBL assembly protocol can effectively bind PB particles enough to immobilize them. EDS analysis was conducted to investigate the elemental composition of the PB composites prepared; results are presented in Table 1. Pristine materials, PVA sponge, and cellulose filter, showed very similar elemental compositions, mainly consisting of carbon (46-47%) and oxygen (52-53%). On the other hand, PB-adsorbents prepared by LBL assembly showed much higher levels of elemental N and Fe in their materials. Based on the molecular chemical composition of PB ($\text{KFe}[\text{Fe}(\text{CN})_6]$), it can be estimated that iron and nitrogen content are greatly affected by PB immobilization. Both LBL-PVA-PB and LBL-Cell.-PB showed 25-28% of iron content, as well as around 6% of nitrogen content; these values are closely related to the chemical composition of PB. These results clearly demonstrate the successful PB immobilization.

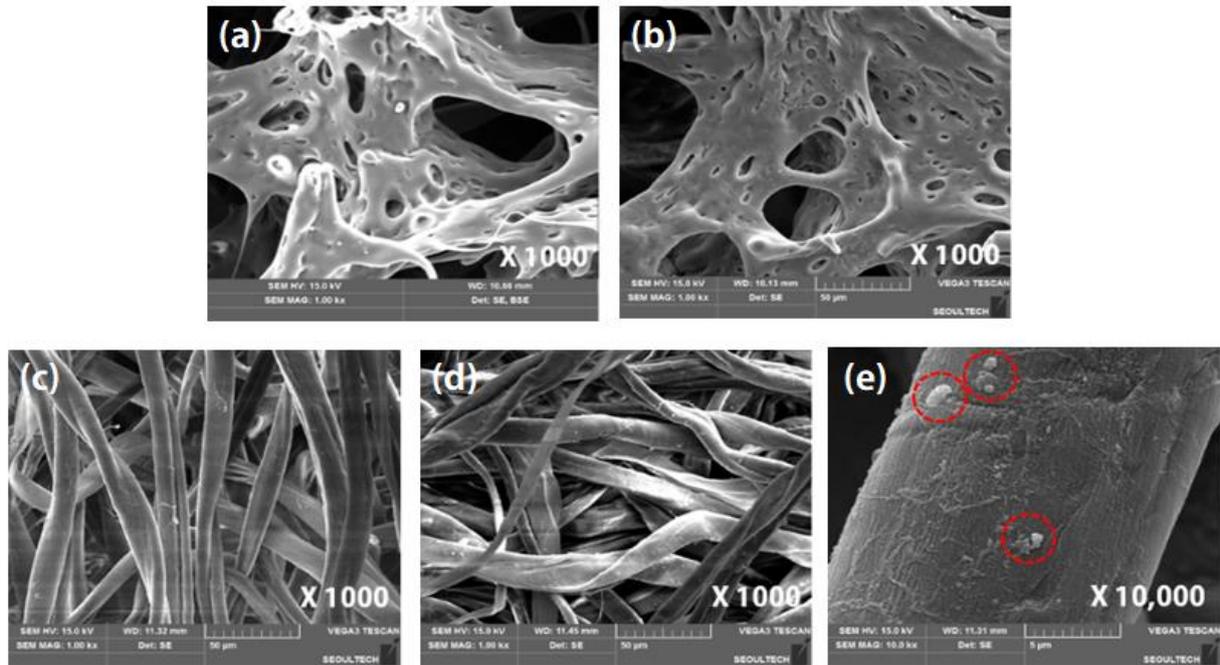


Fig. 4 SEM images (x 1000 magnification) of surface of (a) Pristine-PVA, (b) L-PVA-PB, (c) Pristine-Cellulose, (d) L-Cell.-PB (e) PB particle on Cellulose fiber

Table 1 Weight % of element on total surface of LBL and pristine material

Element Type	C	N	O	K	Cl	Fe
Pristine-PVA	46.05	-	53.95	-	-	-
L-PVA-PB	30.65	6.29	33.9	0.26	0.57	28.33
Pristine-Cellulose	47.44		52.56			
L-Cell.-PB	28.22	6.52	40.12	-	-	25.24

(Unit: Weight %)

3.4 Cs⁺ adsorption capacity

The influence of PB immobilization methods on Cs⁺ adsorption capacity is presented in Fig. 4. First of all, cellulose filter has better Cs⁺ uptake capacity compared to PVA sponge. This could be due to the amount of attached PB as well as to the overall shape of the materials. A cubic shape PVA sponge was used in this study, while a thin layer of cellulose filter was applied. Because of this shape difference, the surface area provided was much higher in the case of cellulose filter, even though the same masses were applied. The thin layer of the cellulose filter enhances the overall mass transfer during PB synthesis, as well as cesium adsorption.

Different levels of Cs⁺ uptake capacity were also observed for different PB immobilization methods. In most cases, PB composites prepared by LBL assembly showed the highest Cs⁺ uptake capacity, while in-situ synthesis was better than ex-situ synthesis. For example, Cs⁺ uptake capacity was significantly enhanced from 0.190 mg/g for I-PVA-PB and to 0.8626 mg/g for L-PVA-PB. Similarly, Cs⁺ uptake capacity was also increased from 0.931 mg/g for I-Cell.-PB and to 2.25 mg/g for L-Cell.-PB. These results

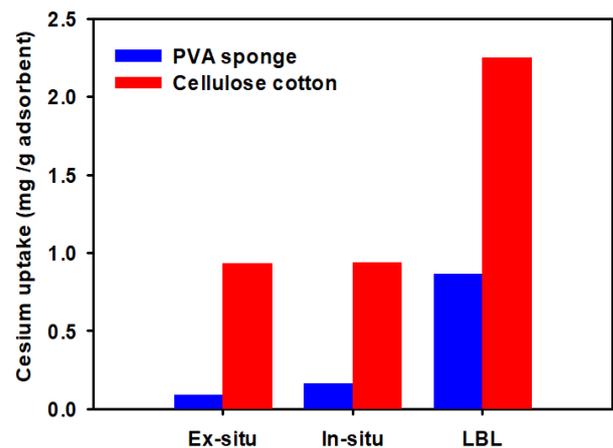


Fig. 5 Cs⁺ adsorption capacity of sample prepared by different synthesis methodologies. (Initial Cs⁺ concentration: 5 mg/L, adsorbent dosage: 2 g/L)

clearly agreed with the results for washing, in that less PB was lost during washing steps; therefore, higher PB content was maintained, which directly influenced the cesium uptake capacity. This can also be well-explained by the results of FT-IR, in which it was seen that growing more PB particles by LBL assembly eventually contributed to increasing Cs⁺ adsorption capacity.

4. Conclusion

Methodologies for PB immobilization on a porous supporting material, ex-situ, in-situ and LBL assembly, were compared for the formation of an effective cesium adsorbent.

- Characterization through FT-IR analysis indicated

that LBL assembly offers more stable growth of PB particles for immobilization on the surface of supporting materials having –OH groups, showing a clear peak in the region of C≡N groups.

- An additional step using iron(III) solution provided suitable stoichiometric condition to produce more PB and stable composition; this method prevented the eluting of PB during washing steps.
- Especially, L-PVA-PB and L-Cell.-PB had almost no leached-out PB particles during washing, because the LBL assembly contributed to the extraction of residues in pores of supporting materials, while at least 3 times of washing was required for other cases.
- The Cs⁺ adsorption capacity of L-PVA-PB improved from 0.910 mg/g to 0.8626 mg/g and the cesium adsorption capacity of L-Cell.-PB also improved from 0.9305 mg/g to 2.2510 mg/g; both improvements are due to the higher content of PB attained by LBL assembly.
- Therefore, LBL assembly will be a highly efficient process for growing PB particles on a porous supporting material.

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