

Layer by Layer Assembly for Prussian blue immobilization onto various filter materials for effective cesium adsorption

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ABSTRACT

Prussian blue (PB) has well known for supreme Cs⁺ ions adsorption capacity. Due to the high dispersibility of PB in aqueous phase, the composite materials imbedding PB in supporting materials have been introduced as a solution. However, building PB particles inside a porous supporting materials is still difficult, as PB particles are not fully formed and it elutes out to water. In this study, we suggested layer-by-layer (LBL) assembly to provide better immobilization of PB on supporting materials, 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. The change of surface functionality and morphology during PB composite preparation proctols was monitored through Fourier transform infrared spectroscopy and scanning electron microscope. The results indicated that LBL assembly showed better PB attachment on supporting materials, which bring less eluting PB particles in aqueous phase compared to other synthesis methodologies, ex-situ and in-situ synthesis. By enhancing the stability of the adsorbent, adsorption capacity of PVA-PB with LBL was improved as 9 times and that of CF-PB is over 20 times. Therefore, the results suggested that the LBL assembly offered the better orientation of growing PB particles onto a porous supporting materials.

1. INTRODUCTION

Prussian blue (PB) has well known for adsorbing Cs^+ ions as supreme adsorption capacity. Prussian blue structure had a simple lattice structure where the cation of hydrated Cs^+ ion was bounded as electrostatic force on cage of PB lattice (Ishizaki et al., 2012). Having this special structure, PB was used as adsorbent in decontamination of radioactive cesium after the Fukushima nuclear plant disaster.

For the reason of having a high adsorption capacity of Cs^+ ion, applying Prussian blue into water treatment field has been tried in many studies. However, attraction force between PB and water leads the particles to be dispersed in water, and it makes difficult to recover or separate from treated water stream due to few tens of nanometer size PB. In order to overcome this size issue, intensive studies have been carried out to immobilize PB in/on supporting matrix. Especially, PB composites based on organic polymers having numerous pores as supporting material were recently preferred in applying to water treatment field. PB immobilization technology 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 were roughly classified as ex-situ synthesis and in-situ synthesis. In ex-situ synthesis of PB, pre-synthesized PB was attached on supporting matrix by physical interaction, but it is difficult to deliver PB particles inside pore deeply (Montazer and Maali Amiri, 2014). In this sense, in-situ synthesis method was more actively studied in case of porous supporting materials. On the other hands, PB particles were synthesized in the presence of supporting materials in case of in-situ synthesis, but it also caused a problem of remaining residue on pore when the concentration of precursors were not carefully regulated, which occurs to growing the unstable PB particles to water.

For the in-situ synthesis of PB, two precursor solutions, iron (III) solution and ferrocyanide solution, were used as suggested in 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 separated vessel as following step. However, immobilized iron (III) was much lower than initial iron (III) concentration in the solution, therefore, the stoichiometric ratio was not well maintained if the concentration was well regulated. In term of a point of immobilizing iron(III) ion, which is precursor for PB particles, in-situ synthesis also causes PB to be unstable on only coating ferrocyanide as a deficiency of iron(III) ion.

This study suggested the new methodology for PB growth onto supporting materials by layer by layer assembly (LBL). LBL assembly was well applied as thin film deposition method. It is a pervasive method for coating substrates with polymers, colloids, biomolecules, and even cells, which offers superior control and versatility. Traditionally, LBL assembly was performed by sequentially adsorbing oppositely charged materials

onto a substrate (through enthalpic and entropic driving forces)(Richardson et al., 2016; Lee et al., 2015). In this study, we have introduced the LBL assembly to solve deficiency of iron(III) ion during in-situ PB synthesis as described in Fig. 1. After common in-situ PB synthesis, additional step to react with iron(III) ions again was applied to form more Prussian blue particles as well as to prevent eluting the particles in aqueous. So, this study focused on comparing three different PB attachment methods, ex-situ/in-situ/LBL assembly by evaluated using Fourier-transform infrared spectroscopy (FTIR), PB leaching test as well as Cs⁺ adsorption test.

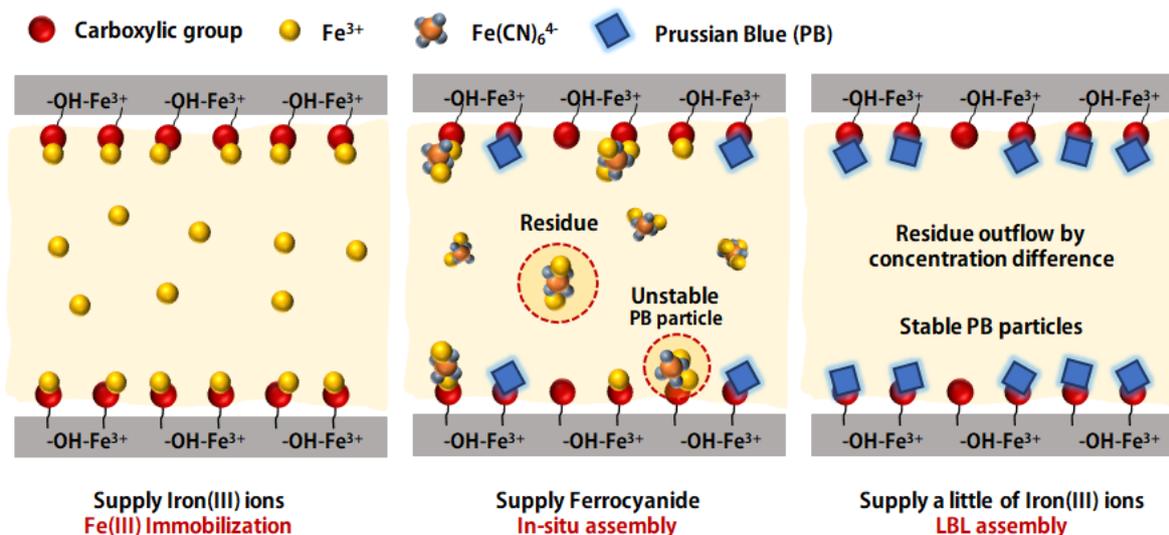


Fig. 1. Schematic of strategy synthesis for PB immobilization by LBL-Assembly

2. MATERIALS AND METHOD

2.1 Materials

Poly vinyl alcohol sponge was obtained from 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 (FeCl₃·6H₂O, 97%), Potassium ferrocyanide trihydrate (K₄[Fe(CN)₆]·3H₂O, 99%) as precursor for synthesizing Prussian blue were purchased Duksan Chemical Reagent Co. Ltd (Seoul, Korea). All of chemical reagent and solvents were of extra pure grade. The Cs(I) standard solution (1000 mg/L) as ICP-MS analytical grade were obtained from Kanto Chemical Co. Inc (Chuo-cu, Japan). The deionized water was used in the preparation of all solutions.

2.2 Preparation of PB adsorbents

Ex-situ PB synthesis was performed with using pre-formed PB particles in aqueous solution. A 50 ml of 20 mM FeCl₃ and 20 mM K₄Fe(CN)₆ solutions were mixed to form PB. After PB particles were formed, 250 mg of PVA sponge (5 x 5 x 5 mm; 125 mm³)/Cellulose filter(3 x 3 cm; 9 cm²) were added into the PB suspension, and let it reacted with that for 5 min. And then, the obtained products were stored at 60 °C and named as E-PVA-PB/E-Cell.-PB, respectively.

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 x 5 x 5 mm; 125 mm³)/Cellulose filter(3 x 3 cm; 9 cm²) was added into a 50 ml solution of 20 mM FeCl₃ for 24 h. And then, the supporting materials with iron(III) immobilized was separated from the solution, and the product was reacted with 50 ml of 20 mM K₄Fe(CN)₆ solution for 5 min. Afterward, the obtained product was stored at 60 °C and named as I-PVA-PB/I- Cell.-PB, respectively.

PB growth as LBL assembly is similar to that with in-situ synthesis, but it contains an additional step as adding ferric chloride solution after in-situ synthesis was finished. On last step of in-situ synthesis, PVA and Cellulose were separated from the solution was reacted with 50 ml of 10 mM FeCl₃ solution for 5 min. afterward, the obtained product was stored at 60 °C and named as L-PVA-PB/L-Cell.-PB, respectively.

2.3 CHARACTERIZATION

In order to monitor a change of functional groups, the Fourier-transform infrared (FTIR, TENSOR27, Bruker, Germany) spectra were recorded in the 400-4000 cm⁻¹ region about surface of the pristine supporting materials and the supporting materials synthesized by each assembly processes.

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

2.4 EVALUATION OF PB LEACHING

The amount of leached PB from synthesized adsorbents during several washing step was analyzed using absorbance, showing wavelength value by unique color of PB which could be detected at 690 nm by UV-Vis Spectrophotometer (Libara S22, BioChrom Ltd., USA). Prepared adsorbents were further washed by adding PVA-PB and CF-PB in 50 mL of deionized water. Five times of same approach was repeated as a standard washing protocol. The supernatant from the 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 using the adsorbents was carried out in batch experiments. In a typical batch adsorption equilibrium experiment, 100 mg of each adsorbents was contacted with 50 mL of 5 mg/L Cs⁺ aqueous solution in a set of conical tube. The pH of cesium aqueous solution was not adjusted and the reaction continued to be shaken at 303 K for 24 h in agitator. Analysis of remaining cesium ion concentration were performed with using inductively coupled plasma mass spectrometer (ICP-MS, NexION 350D, Perkin-Elmer, USA). Afterward, Cs⁺ adsorption equivalent (q_e , mg/g) were calculated as follows:

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

3. RESULTS AND DISCUSSION

3.1 PB LEACHING DURING WASHING STEPS

Figure 2 (a) showed pictures of PB composites prepared by different synthesis protocols, ex-situ, in-situ, and LBL assembly. Pristine PVA sponge and cellulose filter were white, but color was changed to blue after PB immobilization due to the color of PB. The degree of color could be an parameter explaining the amount of PB immobilized. More deep blue color could be achieved in case of LBL assembly compared to other synthesis protocols, which directly explain the advantage of LBL assembly for providing stronger interaction with PB during intensive washing steps.

The amount of leached PB particles from the PB composites during washing steps were analyzed using UV-vis spectroscopy and the results of PVA-PB, Cell.-PB were shown in Fig. 2 (b-c), respectively. As apparent blue color of PB particles was detected at 690 nm wavelength, the absorbance at 690 nm directly explain how much amount of PB particles was detached from 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, washing during first and second was significantly different with respect to the synthesis ways.

In case of ex-situ synthesized composites (E-PVA-PB and E-Cell.-PB), significant amount of PB was washed-out during first and second washing steps. This indicated that physical immobilization was not successful to bind PB on the supporting materials. In this synthesis way, pre-synthesized nano-sized PB was just interact with surface of porous polymeric structure not inside of pore structures due to the size of particles.

Contrary to this, the sample prepared by In-situ or LBL showed lower leaching of PB after single time of washing. In these synthesis way, PB precursor solution containing ionic form of ferric iron and ferrocyanide were used instead of PB particles, therefore, these ionic species could be more easily transported inside of porous polymeric. The prepared PB particles inside of porous network could be benefited as protective effect of surrounded structure. Moreover, the sample with LBL (L-PVA-PB/L-Cell.-PB) showed

much less loss of PB during washing step indicating the stable to binding of their pore network.

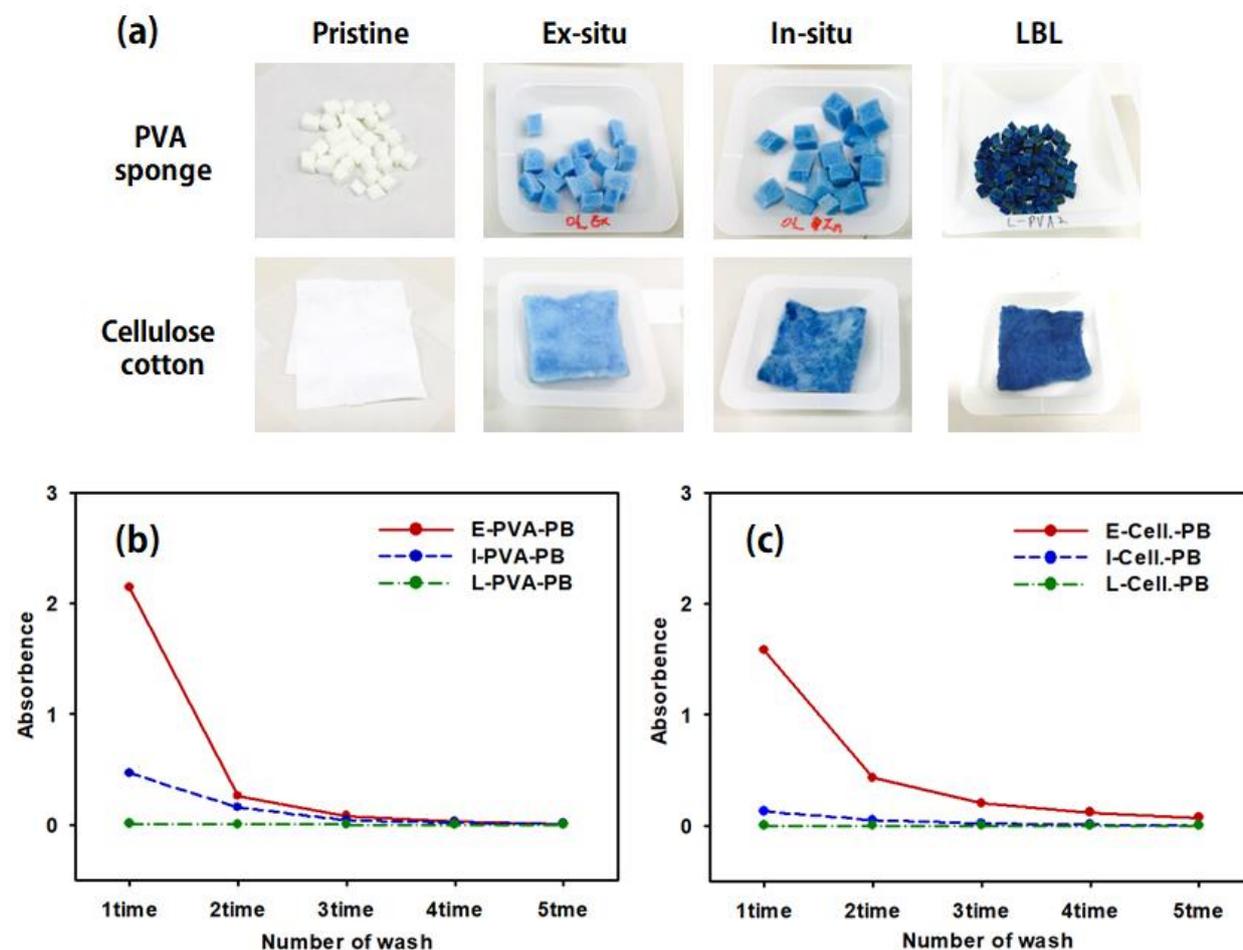


Fig. 2 (a) PB adsorbents prepared by other preparation protocols; and (b-c) PB leaching during washing step measured as absorbance at 690 nm ((b) PVA-PB, (c) Cellulose-PB)

3.2 CHANGE OF FUNCTIONAL GROUPS DURING PB IMMOBILIZATION

Functional groups of each synthesized PVA-PB/Cell.-PB were identified using FT-IR analysis as presented in Fig 3. The pristine PVA and CF indicated that they contains alcohol group and hydrocarbon group as shown in Fig. 3 (a), (f). It appeared C-O stretch as alcohol at $1320-1000\text{ cm}^{-1}$, C-H stretch as sp^3 at $3000-2800\text{ cm}^{-1}$ (Mansur et al., 2008; Garside and Wyeth, 2003).

PB nanocomposites prepared by ex-situ assembly (E-PVA-PB and E-Cell.-PB) as green lines in Fig. 3 had same functional groups of pristine samples, and we could not detect a peak at around 2083 cm^{-1} indicating cyanide group, which is one of the major chemical structure 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

researches has reported observing cyanide group in PB lattice structure at 2100-2050 cm^{-1} (Itaya et al., 1986). However, the low intensity of $\text{C}\equiv\text{N}$ peak for I-PVA-PB/I-Cell.-PB have identified, because a relative deficient Fe(III) ions were remained on a unstable structure.

Contrary to this, L-PVA-PB/L-Cell.-PB in Fig. 3 (e), (j) had a much stronger and more clear $\text{C}\equiv\text{N}$ peak in the region compared to samples with ex-situ and in-situ. It confirmed that more PB particles were immobilized firmly onto supporting materials. This could be explained as an additional supplement of Fe(III) ion in LBL assembly made the PB particles to grow lattice structure largely on supporting material surface. It revealed that the effect of supplying additional Fe(III) ions contribute to be a stable structure for growing PB particles to hydroxyl groups in supporting materials. Based on this results, it indicated that LBL assembly would be suitable to building PB particles in supporting materials.

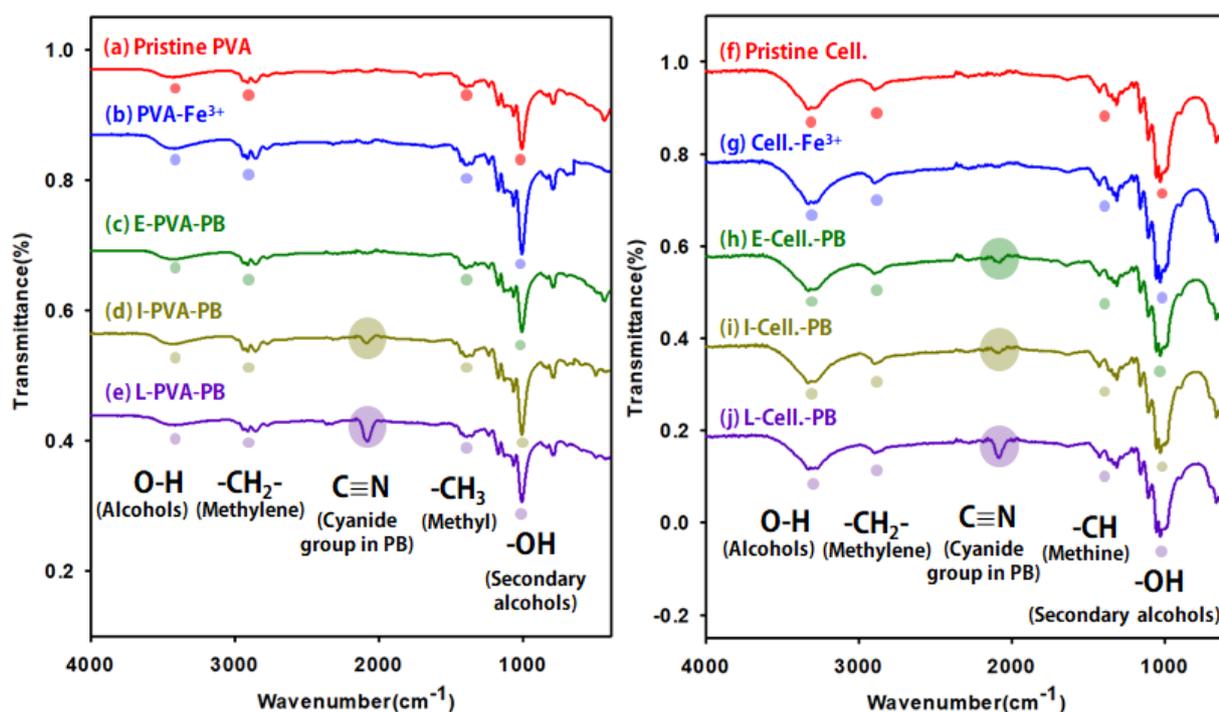


Fig. 3. FTIR spectra of the sample with Ex-situ/In-situ/LBL assembly. Distinctive adsorption bands at 3500-3200 cm^{-1} (O-H, alcohol), 3000-2850 cm^{-1} ($-\text{CH}_2-$, Methylene), 2100-2080 cm^{-1} ($\text{C}\equiv\text{N}$, Cyanide), 1320-1000 cm^{-1} ($-\text{CH}_3$, methyl), 1365 & 1315 cm^{-1} (C-H stretch), 1050 cm^{-1} (Secondary alcohols).

3.3 MORPHOLOGY AND ELEMENTAL ANALYSIS

Based on results of FT-IR, PB adsorbents prepared by LBL assembly showed a higher $\text{C}\equiv\text{N}$ peak indicating more amount of PB particles immobilized than other PB adsorbents. In order to have better confirmation on the immobilized amount, SEM/EDS

analysis was conducted for PB composites prepared by LBL assembly as well as pristine supporting materials, and the results were presented in Fig. 4 and Table 1.

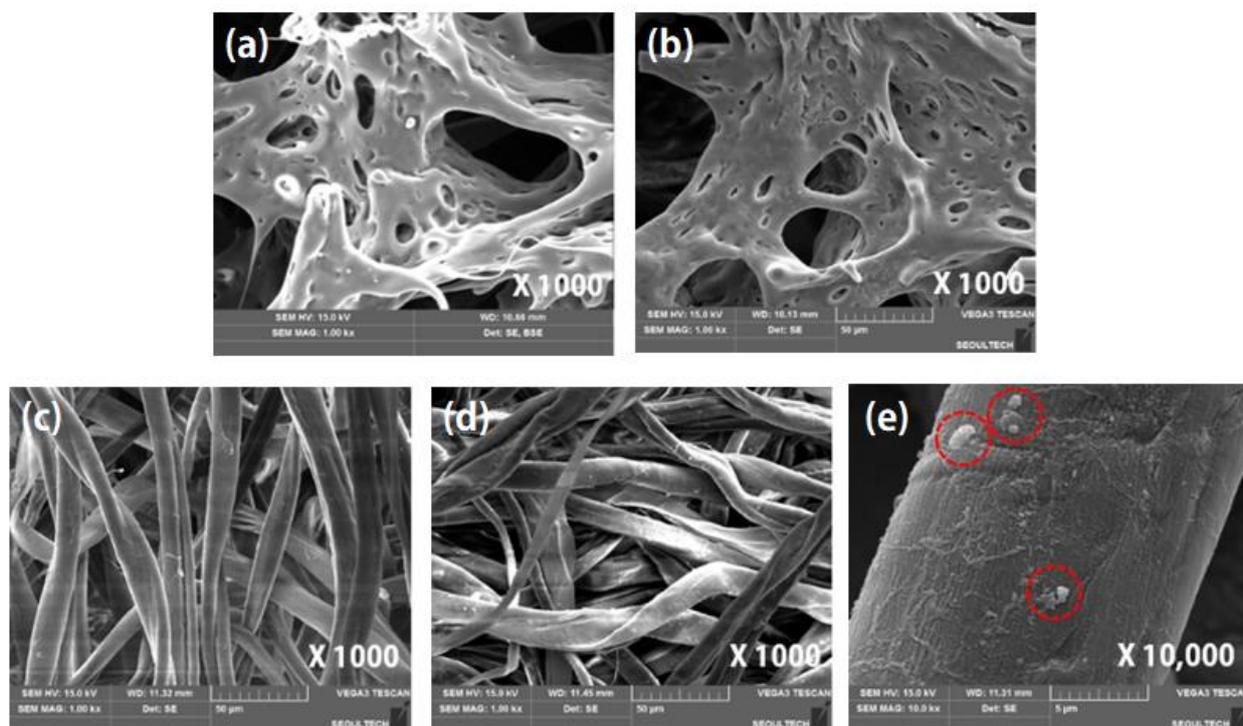


Fig. 4. SEM images (x 1000 magnification) of surface of (a) Pristine-PVA, (b) LBL-PVA-PB, (c) Pristine-Cellulose, (d) LBL-Cell.-PB (e) PB particle on Cellulose fiber, respectively

For PVA sponge, pore size seems to be more tightened after PB immobilization, which indicating the formation of additional PB layer in the PVA sponge pore network. The formation of PB layer could be observed inside of PVA sponge as well as outer surface. This is an clear advantages of LBL assembly using precursors of PB not PB particles itself. The ferric ion could be well penetrate over a pore network of PVA sponge, then PB was formed by the reaction with ferrocyanide ion, therefore, PB could be prepared inside of pore network. Similar structure could be observed also in cellulose filter. Even small aggregate could be detected on the surface of cellulose fiber as shown in Fig. 4(d) (red circles).

Above results mean that supporting materials prepared through LBL assembly protocol could effectively bind PB particles enough to immobilize them. EDS analysis was conducted to investigate the elemental composition of the PB composites prepared as presented in Table 1. Pristine materials, PVA sponge and cellulose filter, showed very similar elemental composition, mainly consist of carbon (46-47%) and oxygen (52-53%). On the other hands, PB-adsorbents prepared by LBL assembly showed much higher N, Fe element in their materials. Based on the molecular chemical composition of PB ($\text{KFe}[\text{Fe}(\text{CN})_6]$), it could be estimated that iron and nitrogen content would be great affected by the PB immobilization. Both of LBL-PVA-PB and LBL-Cell.-PB showed 25-

28% of iron content as well as around 6% of nitrogen content, which is closely related with chemical composition of PB. This result clearly demonstrated the successful PB immobilization.

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

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

(Unit: weight %)

3.3 Cs⁺ adsorption capacity

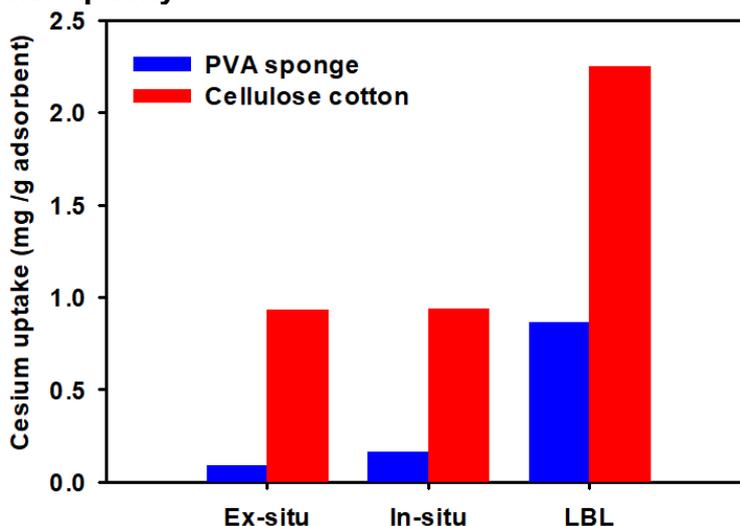


Fig. 5. Difference of Cs(I) adsorption capacity of the sample with each assembly in Cs(I) solution of 5 mg/L (Blue: PVA-PB, Red: Cellulose-PB).

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

The different Cs(I) uptake capacity was also observed for different PB immobilization methods. In most cases, PB composites prepared by LBL assembly showed the highest Cs(I) uptake capacity, while in-situ synthesis was better than ex-situ synthesis. For example, Cs(I) uptake capacity was significantly enhanced from 0.190 mg/g for I-PVA-PB to 0.8626 mg/g for L-PVA-PB. Similarly, Cs(I) uptake capacity was also increased from 0.931 mg/g for I-Cell.-PB to 2.25 mg/g for L-Cell.-PB. This results clearly agreed with results for washing that less PB was lost during washing steps, therefore, higher PB contents could be maintained, which directly influence on cesium uptake capacity. This could be also well explained by result of FT-IR that growing more PB particles by LBL assembly eventually contributed to increasing Cs(I) adsorption capacity.

4. CONCLUSION

PB immobilization methodologies on a porous supporting material, ex-situ, in-situ and LBL assembly, were compared to be an effective cesium adsorbent. The characterization through FT-IR analysis indicated that LBL assembly offers more stable growth of PB particles to be immobilized on the surface of supporting materials having –OH group, showing a clear peak in the region of C≡N groups. Additional step using iron(III) solution provided suitable stoichiometric condition to produce more PB and stable composition, therefore, it prevent eluting of PB during washing steps. Especially, L-PVA-PB and L-Cell.-PB had almost no leached out PB particles during washing, because LBL assembly contributed to extracting residues in pores of supporting materials, while at least 3 times of washing was required for other cases. The cesium adsorption capacity of L-PVA-PB was also improved from 0.910 mg/g to 0.8626 mg/g and the cesium adsorption capacity of L-Cell.-PB was also improved from 0.9305 mg/g to 2.2510 mg/g which is due to higher content of PB by LBL assembly. Therefore, LBL assembly would be a highly efficient process for growing PB particles onto a porous supporting material.

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