



Surface modification of poly(vinyl alcohol) sponge by acrylic acid to immobilize Prussian blue for selective adsorption of aqueous cesium

Hyobin Wi ^a, Hyowon Kim ^a, Daemin Oh ^b, Sungjun Bae ^c, Yuhoon Hwang ^{a,*}

^a Department of Environmental Engineering, Seoul National University of Science and Technology, 232 Gongneung-ro, Nowon-gu, Seoul, 01811, Republic of Korea

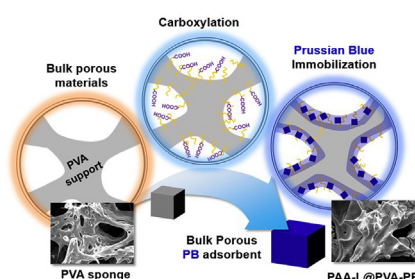
^b Department of Land, Water and Environment Research, Korea Institute of Civil Engineering and Building Technology, 283 Goyang-daero, Ilsanseo-gu, Goyang-si, Gyeonggi-do, 10223, Republic of Korea

^c Department of Civil and Environmental Engineering, Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul, 05029, Republic of Korea

HIGHLIGHTS

- PB was immobilized on a porous PVA sponge for selective cesium adsorption.
- The AA functionalization contributed to stable PB formation and reduced PB leaching.
- PAA-PVA-PB showed 5.7 times higher cesium adsorption capacity than Pure-PVA-PB.
- Effect of water matrix was not severe indicating selective adsorption ability.
- The PAA-L@PVA-PB can be effectively used as column filling material.

GRAPHICAL ABSTRACT



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ABSTRACT

Prussian blue (PB) is known to be an effective cesium adsorbent, but the direct application of PB is limited by the difficulty of its recovery from solution. In this study, PB was immobilized on a porous support media, poly(vinyl alcohol) (PVA) sponge, for use as a selective material for cesium adsorption. The commercially available PVA sponge was functionalized by the addition of poly(acrylic acid) (PAA) (i.e., PAA-PVA) to enhance the PB immobilization, which increased both PB loading and binding strength. The AA functionalization changed the major functional groups from hydroxyl to carboxylic, as confirmed by Fourier-transform infrared spectroscopy. PB was further synthesized in the PAA-PVA using layer-by-layer (LBL) assembly, which contributed to more stable PB formation, and reduced detachment of PB during washing. The prepared adsorbent, PAA-L@PVA-PB, was tested for cesium adsorption capability. Cesium adsorption was equilibrated within three hours, and the maximum cesium adsorption capacity was 4.082 mg/g, which was 5.7 times higher than Pure-L@PVA-PB. The observed decrease in solution pH during cesium adsorption inhibited overall cesium uptake, however, this was minimized by buffering. The prepared PAA-L@PVA-PB was used as a column filling material and its potential use as a counter-measure for removing radioactive cesium from a contaminated water stream was demonstrated.

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* Corresponding author.

E-mail address: yhhwang@seoultech.ac.kr (Y. Hwang).

1. Introduction

As energy demand grows globally and concerns about climate change increase, many countries are using nuclear energy as an alternative to fossil fuels, given its advantages of being economically and reliably available (Forsberg, 2009). Nuclear energy accounted for 19.3% of the total electricity production in OECD countries, and 12 non-member countries, including China, Brazil, India, and Russia, also produce electricity by nuclear power (International Energy Agency, 2018). As of 2014, nuclear energy accounted for 30.1% of Korea's total electric power production. However, nuclear energy has risks, as evidenced by the accident in Japan's Fukushima Daiichi nuclear power plant in 2011. In that event, ^{136}Cs and ^{137}Cs leaked into the Pacific Ocean along with a large amount of other radioactive isotopes, and remediation efforts are still in progress (Buesseler et al., 2012; Ebihara et al., 2012; Tsuji et al., 2014).

Cesium-137 (^{137}Cs) is one of the typical radioisotopes released during a nuclear accident. Because it has chemical properties similar to sodium and potassium, it is easily taken up by organisms if it enters the environment (El-Kamash, 2008). When it enters into the body, it is not readily released, meaning its β decay results in continuous radiation exposure to the body (Jia and Wang, 2017). In addition, its hydration radius is smaller and diffusion coefficient is higher than other radioactive materials, so it is very difficult to remove it after it enters a water system (Ma et al., 2017).

Among the various methods for removing radioactive cesium, adsorption is economical, a relatively simple process, and advantageous in that no additional treatment is required after removal of the target element (El-Kamash, 2008; Long et al., 2013). According to some previous studies, Prussian blue (PB) is known to be highly effective for removing cesium due to its lattice structure, which can capture the cesium ion (Delchet et al., 2012; Haas, 1993; Kong et al., 2014). PB is a type of metal hexacyanoferrate, a cubic lattice structure surrounded by cyanide and metal ions (Ishizaki et al., 2013). Cs-adsorption by metal hexacyanoferrate was governed by three mechanisms, (a) mainly ion-exchange between Cs^+ and K^+ , (b) percolation of Cs^+ cations through vacancy sites from the surface, and (c) proton-exchange with Cs^+ . The excellent selectivity of Cs in adsorption was also explained by the complete dehydration of alkali cations (Takahashi et al., 2018).

However, PB particles rapidly disperse in aqueous systems, which makes it difficult to recover or remove them from the water after being used as an adsorbent. Studies of methods to immobilize PB on supporting materials has steadily progressed toward application as a practical water treatment process. Various types of supporting materials have already been tested as supporting materials for PB attachments, including nonwoven fabrics (Chen et al., 2015; Yasutaka et al., 2013), carbon nanotubes (Jun et al., 2014), graphene, alginate (Basu et al., 2018), chitosan (Vincent et al., 2015), and magnetic nanoparticles (Yang et al., 2016). However, carbon nanomaterials and magnetic materials have a disadvantage in that they are expensive and very fine materials, which can hardly apply to real contaminated sites owing to the collection problem after their use.

In our previous study (Wi et al., 2019a), we developed a protocol to functionalize commercially available supporting materials to immobilize PB and made it stable for contaminated water remediation. Polyvinyl alcohol (PVA) sponge, which can be easily obtained in the market for cleaning purposes, was used as the supporting material. Its porous nature allows water to penetrate into the sponge and provides room for PB synthesis. Moreover, this commercial filter material has already proven mechanical strength and stability. One of the major hurdles to the application of PB immobilized adsorbents in water remediation is the leaching out of

immobilized PB during use. In the previous study, poly(acrylic acid) (PAA) was suggested for the surface functionalization of the PVA sponge (PAA-PVA) to convert hydroxyl groups into carboxylic groups for better PB attachment. This phenomenon can be explained by the HSAB theory. Carboxylates are hard Lewis base, therefore, it forms a strong bond with hard Lewis acids including Fe^{3+} . This concept is commonly used in the field of MOF (metal organic framework) research (Yuan et al., 2018). Because acrylic acid (AA) includes a double bond, and carboxylic groups have a negative charge, AA is capable of trading electrons to alkali metals (Smuleac et al., 2010). This approach overcomes the weak bonding of hydroxyl groups in previous studies, and the method can be applied to various supporting materials that contain hydroxyl groups (Yang et al., 2014; Ge and Wang, 2017). However, the PB leaching during the washing step was not fully prevented by the PAA functionalization.

To minimize PB leaching during the washing step, we suggested a layer-by-layer (LBL) assembly strategy, which adds one more step in PB synthesis. The advantage of LBL assembly was reported in our second previous study (Wi et al., 2019b). In this second work, we did use pristine PVA without any functionalization in order to investigate the effect of LBL. The LBL assembly could significantly decrease PB leaching during washing. However, the effect of LBL assembly on PB synthesis in case of PAA functionalized PVA is still unknown.

The aim of this work was to develop an approach to produce a PB based composite adsorbent for radioactive cesium uptake. This approach includes using commercial materials as a supporting matrix and functionalizing by simple chemical reaction to obtain carboxylic groups, and synthesizing PB by layer-by-layer (LBL) assembly. The overall procedures we suggest showed higher loading of PB and stronger stability to prevent leaching of PB in aqueous solution. Cesium adsorption ability was evaluated through adsorption kinetics and isotherm tests. The effect of pH and water matrix was also evaluated to determine the adsorption mechanism. Lastly, a column filled with our PB based composite showed feasibility for use as a water treatment process to remediate aqueous cesium.

2. Materials and methods

2.1. Materials

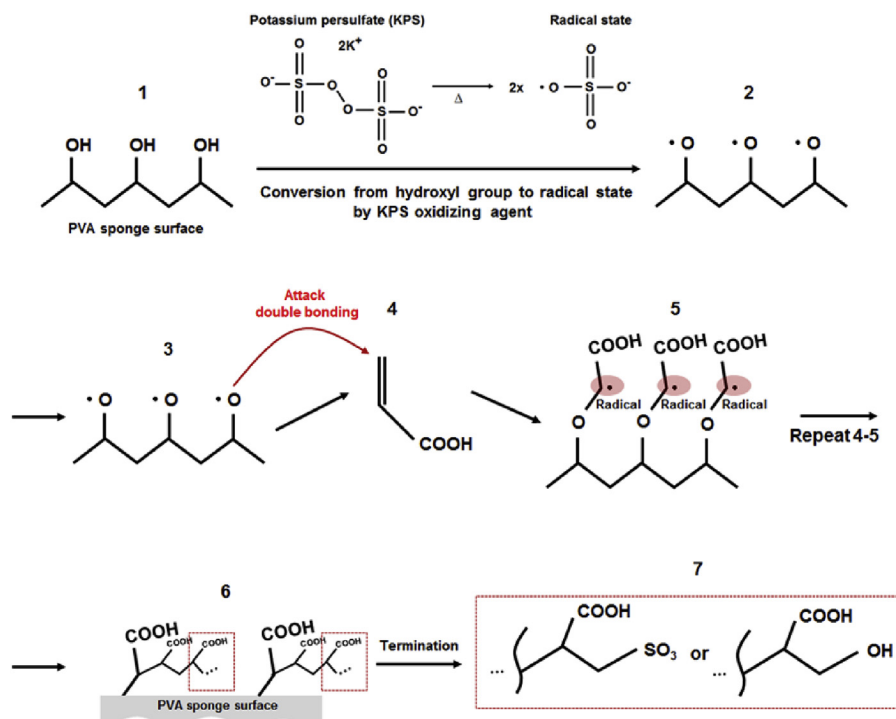
Polyvinyl alcohol (PVA) sponge was obtained from Samkwang trading company (Daegu, Korea). The porosity of PVA sponge was 85–89%, and the average pore size was reported as 60 μm . The tensile strength and permeability coefficients are 3.8 N/cm² and 0.093 cm/s, respectively. Acrylic acid (AA, 99%), potassium persulfate (KPS, 99%), sodium chloride (NaCl, 93%), and ethanol (99%) were purchased from Samchun Chemical Reagent Corporation 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 a precursor for PB synthesis were purchased from Duksan Chemical Reagent Corporation Ltd. (Seoul, Korea). All of the chemical reagents and solvents were of the extra pure grade. The Cs(I) standard solution (1000 mg/L) ICP-MS analytical grade was obtained from Kanto Chemical corporation Inc. (Chuo-cu, Japan). Deionized water was used to prepare all solutions.

2.2. Preparation of PAA-PVA-PBs

2.2.1. PVA surface modification by AA

The overall scheme of preparation is presented in Fig. 1. The PVA modification by AA is a type of radical polymerization. Free radicals on the PVA backbone can be formed by the chemical initiator. The

(a)



(b)

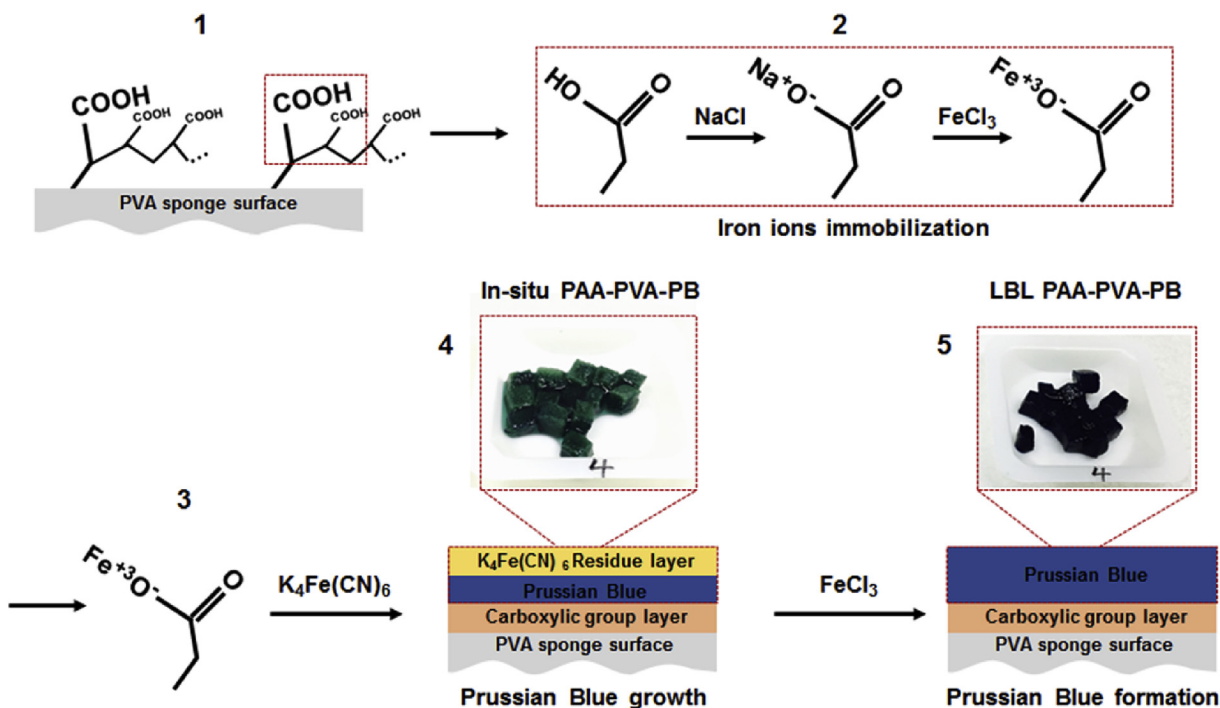


Fig. 1. (a) Schematic of PVA surface modification by AA, (b) LBL assembly for stable PB growth by adding precursor as a final step.

free radicals thus formed can add to monomers to form a covalent bond between the monomer and the PVA. The propagation of the branch continues until termination occurs (Roy et al., 2009). The

major reaction mechanism on the PVA surface modification with the AA by the grafting reaction was well explained in the literature (Mishra et al., 1999; Kurkuri et al., 2006). In this study, we used

potassium persulfate (KPS) as an initiator. The hydroxyl group of PVA as then reacted with the initiator to form a radical state. The acrylic acid monomer is then grafted on the radical site of PVA.

A polymer solution was prepared using 60 mg of KPS and 10 ml of acrylic acid solution dispersed into 50 ml of deionized water in a vessel. Afterward, cubical $5 \times 5 \times 5 \text{ mm}^3$ PVA sponges were immersed in the polymer solution. To remove oxygen dissolved in the vessel, a vacuum oven was filled with nitrogen gas and the reaction conducted at 70°C for 6 h. After the reaction ended, the PAA-PVA was washed with a mixed solution including a ratio 1:1 of ethanol and deionized water until the solution became transparent. Lastly, the prepared PAA-PVA sponge was dried at 60°C . The reaction conditions for AA modification and the FTIR results of PAA-PVA can be found in our previous study (Wi et al., 2019a).

2.2.2. PB immobilization

PB immobilization on modified PVA (PAA-PVA) and unmodified PVA (Pure-PVA) was performed using three different procedures, designated the ex-situ, in-situ and layer-by-layer (LBL) methods. These different immobilization procedures were designed to investigate the PB synthesis mechanism. Ex-situ PB synthesis was performed using pre-formed PB particles in aqueous solution. 50 ml of 20 mM FeCl_3 and 20 mM $\text{K}_4\text{Fe}(\text{CN})_6$ solutions were mixed to form PB. After the PB particles were formed, 250 mg of PVA sponge ($5 \times 5 \times 5 \text{ mm}$; 125 mm^3) was added to the PB suspension and reacted for 5 min. Then, the obtained products were stored at 60°C and denoted PAA-E@PVA-PB and Pure-E@PVA-PB.

In-situ PB synthesis was performed by injecting the precursor of PB in series in the presence of the supporting materials. 250 mg of PVA sponge ($5 \times 5 \times 5 \text{ mm}$; 125 mm^3) 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 PAA-I@PVA-PB and Pure-I@PVA-PB.

PB growth via LBL assembly is similar to the in-situ synthesis but has an additional step of adding ferric chloride solution after the in-situ synthesis has finished. At the last step of the in-situ synthesis, I@PVA-PBs 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 PAA-L@PVA-PB and Pure-L@PVA-PB.

2.3. Evaluation of PB elution

The prepared materials were dried at 60°C for 24 h and washed 5 times (2 min each) in 50 ml of deionized water to evaluate the stability of the immobilized PB. After the washing experiment, the water was analyzed for PB at 690 nm using UV–Visible spectroscopy (UV–Vis, Libra S22, Biochrom).

2.4. Characterization of PVA-PBs

The effect of functionalization was evaluated by monitoring the changes in the functional groups on the surface of the PVA-PBs using Fourier-transform infrared spectroscopy (FTIR, TENSOR27, and Bruker, Germany) recorded in the $400\text{--}4000 \text{ cm}^{-1}$ region. A scanning electron microscope with energy dispersed spectroscopy (SEM/EDS, JSM-6700F, JEOL, and Japan) was used to visualize surface modifications as well as analyze the chemical composition qualitatively. Thermogravimetric analysis was also conducted to obtain information regarding thermal decomposition of the PBA-PBs as well as their chemical composition. Thermograms of the sample were recorded in the temperature range $30\text{--}1000^\circ\text{C}$ with a heating rate of $10^\circ\text{C}/\text{min}$ in a nitrogen atmosphere, with a

thermogravimetric analyzer (TGA, TG-DTA, Bruker, Germany).

2.5. Adsorption experiments

2.5.1. Adsorption isotherms and kinetics

Adsorption isotherm testing was performed to evaluate the overall cesium adsorption capacity of PAA-L@PVA-PB, together with Pure-L@PVA-PB as a test control. 100 mg of the PVA-PBs was mixed with 50 mL of cesium aqueous solutions with different initial concentrations ranging from 0.5 to 20 mg/L in a sealed conical polyethylene (PE) tube. The pH of the cesium aqueous solution was not adjusted and the solution was continuously shaken at 303 K for 24 h in an agitator. The cesium ion concentration in the supernatant was measured with an ICP-mass spectrometer (ICP-MS, NexION 350D, Perkin-Elmer, USA).

The sorption isotherm study of the adsorbed cesium ion at equilibrium (q_e) was calculated using the Langmuir isotherm (Eq. (1)) and Freundlich isotherm (Eq. (2)) equations (Foo and Hameed, 2010; Hameed et al., 2009):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

where q_e is the quantity of adsorbate adsorbed per unit weight of solid adsorbent, q_m is the maximum sorption capacity of the adsorbent (mg/g), C_e is the equilibrium concentration of the adsorbate in solution (mg/L), and K_L is the Langmuir affinity constant.

$$q_e = k C_e^{1/n} \quad (2)$$

where k and $1/n$ are constants indicating the adsorption capacity and the adsorption intensity, while the other terms have the same meaning as in Eq. (1).

The adsorption kinetics of PVA-PBs were investigated in a 10 mg/L Cs solution, similar to the isotherm test, except that several samples were taken at given time intervals (5 min, 30 min, 1 h, 3 h, 10 h and 24 h). The adsorption result was then fitted using pseudo-first-order kinetics suggested by Lagergren and pseudo-second-order kinetics suggested by Ho and McKay, respectively (Ko et al., 2017). The linear forms of the two kinetics are formulated as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

where q_e and q_t are the adsorbed amounts of cesium ions (mg/g) at time t and k_1 is the rate constant of the sorption ($1/\text{min}$)

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right) \quad (4)$$

where K_2 is the rate constant ($\text{g}/\text{mg} \cdot \text{min}$), and the other terms have the same meaning as in Eq. (3).

2.5.2. Effect of initial pH and water matrix

The effect of initial pH was investigated using 20 mg/L cesium solution at different initial pH of 4, 6, 8, and 10. Initial pH was controlled by adding 1 M HCl and NaOH solution. The effect of the water matrix on cesium adsorption was investigated using two types of synthetic stream waters, soft and hard water, as suggested by the literature (Smith et al., 2002). The characteristics of the soft and hard water are presented in Table S1.

2.5.3. Column test

A water filtration column was designed to evaluate the feasibility of using PAA-L@PVA-PB in a real water treatment scenario.

The column was prepared by filling a 2.5 cm diameter and 30 cm length of glass column with PAA-L@PVA-PB. The applied mass of PAA-L@PVA-PB was 0.9 g and the effective length was determined to be 10 cm. A 200 µg/L concentration cesium solution was then introduced into the column in an upward direction. The flow rate was maintained at 2 mL/min, and the linear velocity was around 2 cm/min. Therefore, the contact time was around 5 min. Samples were periodically collected by fraction collector and the cesium concentration in the effluent was analyzed by ICP-MS.

3. Results and discussion

3.1. PB stability during washing depending on PB synthesis methodologies

Fig. 2 shows the variations in the UV–vis absorbance of washing water at 690 nm after washing different PVA-PBs (i.e., E@PVA-PB, I@PVA-PB, and L@PVA-PB) with DIW. Overall, the maximum absorbance of washing water for the Pure-PVA-PB was around 5.5 at the first washing step (Fig. 2 (a)), which was much higher than PAA-PVA-PB (Fig. 2 (b)). The maximum absorbance of washing water for PAA-PVA-PB was around 0.65. This result indicates the effectiveness of surface functionalization on the stability of PB immobilization.

Next, we compared the three PB immobilization methodologies, ex-situ, in-situ and LBL assembly. In the cases of both Pure-PVA-PB and PAA-PVA-PB, ex-situ and in-situ PB immobilization led to leaching out of some PB during the first few washing steps. For example, Pure-E@PVA-PB showed the highest absorbance at the first washing step, 5.5, then it decreased to around 1 at the second washing step. Finally, no color was detected after three times of washing. Similar results were obtained for Pure-I@PVA-PB, PAA-I@PVA-PB, and PAA-E@PVA-PB.

On the other hand, clearly different results were obtained for both samples prepared by LBL assembly, Pure-L@PVA-PB and PAA-L@PVA-PB. The absorbance of the washing solution at the first washing step was less than 0.03, which was significantly lower than the other cases. After this first washing step, almost no color was detected in the following washing step, which indicated the PB immobilization was much more stable.

In the ex-situ synthesis of PB, pre-synthesized PB is attached to the supporting matrix by physical interaction, therefore, it can be easily released to the wash water (Montazer and Maali Amiri,

2014). In contrast, in the in-situ synthesis, PB particles were synthesized in the presence of the supporting materials, but this also caused a problem of residue on the inside of pores when the concentrations of precursors were not carefully regulated, which occurs when growing unstable PB particles. For the in-situ synthesis of PB, the supporting materials were immersed in Fe^{3+} solution; then, the supporting materials were immersed again in ferrocyanide solution prepared in a separated vessel (Hornok and Dékány, 2007). However, the amount of immobilized Fe^{3+} was much lower than the initial Fe^{3+} concentration in the solution; therefore, the stoichiometric ratio was not well maintained if the concentration was well regulated. In terms of immobilizing Fe^{3+} , which is the precursor for the PB particles, in-situ synthesis also causes PB to be unstable. It contained the only ferrocyanide because of the deficiency of Fe^{3+} .

This study suggests a new methodology for PB growth on supporting materials via layer by layer assembly (LBL). LBL assembly has been well applied as a thin film deposition method. It is a pervasive method for coating substrates with polymers, colloids, biomolecules, and even cells, and 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) (Lee et al., 2015; Richardson et al., 2016). In this study, we have introduced the LBL assembly to solve the problem of Fe^{3+} ion deficiency during in-situ PB synthesis, as shown in Fig. 1(b). After the common in-situ PB synthesis, an additional step to react with Fe^{3+} ions was applied to form more Prussian blue particles, as well as to prevent the subsequent eluting of the particles in aqueous solution.

3.3. Characterization of PVA-PBs

3.3.1. FTIR

In order to track changes in the functional groups during PB immobilization, FTIR analysis was conducted for PVA- Fe^{3+} and PVA-PBs in both Pure-PVA and PAA-PVA (Fig. S1). We concluded that the L@PVA-PB was the best methodology in terms of PB stability during washing, therefore, further characterization was done only for L@PVA-PBs. Furthermore, the change of the functional groups by AA modification was reported in our previous study (Wi et al., 2019a). The FTIR result was well agreed with the reported article regarding PAA-PVA synthesis and characterization (Kurkuri et al., 2006).

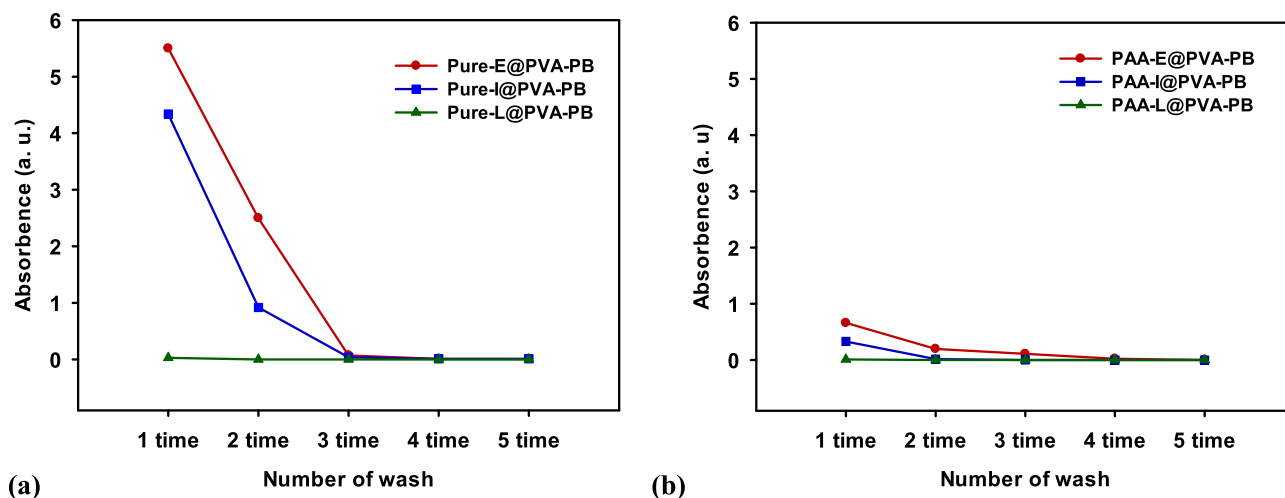


Fig. 2. PB elution of (a) Pure-PVA-PBs, and (b) PAA-PVA-PBs washed by deionized water.

From the spectra of Pure-L@PVA-Fe³⁺ (red line, above), the sharp presence of the C-O of alcohol at 1320–1000 cm⁻¹ and the O-H of alcohol at 3500–3200 cm⁻¹, and the C-H of alkane at 3000–2850 cm⁻¹ can be attributed to the intrinsic PVA sponge (Kharazmi et al., 2015). When PB particles formed as an LBL assembly on Pure-PVAs (Pure-L@PVA-PB), the FTIR spectra did not change much except for a slight change in the peak at 2070 cm⁻¹ (C≡N stretch). This result indicates that PB attachment was not successful when surface functionalization by AA was not conducted.

In contrast, significant iron attachment on surface functionalized PVA (PAA-L@PVA-Fe³⁺) was confirmed by new peaks at 1584 cm⁻¹ and 1413 cm⁻¹ indicating an interaction between the Fe³⁺ and carboxylic groups (Fan et al., 2017). Once PB was formed on the PAA-PVAs, a strong peak at 2070 cm⁻¹ (C≡N) was observed in the PAA-L@PVA-PB, which indicates how surface functionalization by PAA affects PB attachment (Hu et al., 2012; Zhang et al., 2010).

3.3.2. SEM-EDS

The morphologies of the PAA-PVA-PBs were observed using SEM-EDS analysis, as presented in Fig. 3. The elemental analysis results obtained by EDS are presented in Table S2. The pure-PVA showed the very porous nature of the PVA sponge, with large pores around 70 μm in size together with small pores around 5–20 μm in size. Only carbon and oxygen were detected by EDS analysis, which agrees with the molecular structure of the PVA. The Pure-L@PVA-PB had a structure similar to Pure-PVA except for a thin deposition of PB on the surface of the Pure-PVA. Due to the deposition of PB, Fe and N were newly detected by EDS analysis, contributed by the molecular structure of the PB. A slight amount of K was also detected, from the potassium ferrocyanide solution used for PB synthesis.

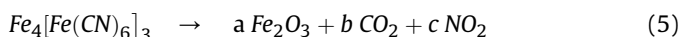
PAA-L@PVA-PB showed significant changes in morphology compared to the other samples analyzed. The small pores, of around 5–20 μm size, were almost blocked and only large pores remained. A very thick layer on the PVA surface was monitored, which might be PAA and PB. It had a relatively higher Fe weight percentage (38.74%) than the other samples, indicating the effect of surface functionalization by AA on PB immobilization. The cross-section SEM images of Pure PVA and PAA-PVA were also provided as Fig S2. The pore blockage by the formation of PAA layer on PVA network could be found.

3.3.3. TGA analysis

The PB content (%) in PAA-L@PVA-PB was investigated by thermogravimetric (TG) analysis as presented in Fig. S3. The Pure-PVA started to lose weight at 380–450 °C (red dashed line), which indicates the thermal decomposition of PVA ((C₂H₄O)_n) into carbon

dioxide and water. After PVA decomposition in this temperature region, almost no weight remained, which indicates this sample contained pure PVA.

PAA-L@PVA-PB showed the decomposition of PVA in the same temperature region. The early decomposition of PAA-L@PVA-PB was due to the decomposition of AA. However, a significant difference was observed after PVA decomposition at 450 °C. There was still around 25% of weight remaining at 450 °C, while the Pure PVA showed complete decomposition, and this weight was further decreased as temperature increased. The remaining weight could be immobilized PB, and the decrease in weight at high temperature can be explained as the degradation of PB particles, as reported in a previous study (Jiang et al., 2015). It was reported that PB particles could be degraded through a collapse of bonding between Fe (II, III) iron and cyanide groups, by converting C≡N into N₂O and CO₂ as shown in Eq (5) (Jiang et al., 2015). Based on the remaining amount after decomposition, the Fe content was calculated to be 7.0% and the PB content was calculated from molecular composition to be 15.4%.



3.4. Adsorption study of PAA-L@PVA-PB

3.4.1. Adsorption kinetic study

An adsorption kinetic experiment was conducted to determine the equilibrium time between PAA-L@PVA-PB and the cesium solution. Fig. 4 (a) presents adsorption capacity with respect to time and solution pH at the time of sampling. The adsorption data were fitted by pseudo-first-order kinetics (Eq. (4)) and pseudo-second-order kinetics (Eq. (5)). The obtained kinetic parameters are given in Table S3.

The adsorbed cesium increased rapidly in the first 3 h, then it was almost stabilized at 24 h. The solution pH showed an inverse pattern to the cesium adsorption. Initial pH was around 5.8 and it decreased quickly during the first three hours, then it stabilized. The final pH was around 4.6. The decrease in pH can be explained by the cation exchange between the aqueous cesium ions and hydrogen ions in the PB lattice structure, as already introduced as Eq. (1).

Both kinetic models, pseudo-first-order and second-order, interpret the experimental data well. The correlation coefficients (R^2) of the two models were 0.9918 and 0.9849, which indicates chemisorption and physisorption occurred simultaneously, and this is in good agreement with previous reports on cesium adsorption by PB (Jang et al., 2015). The pseudo-first-order and pseudo-

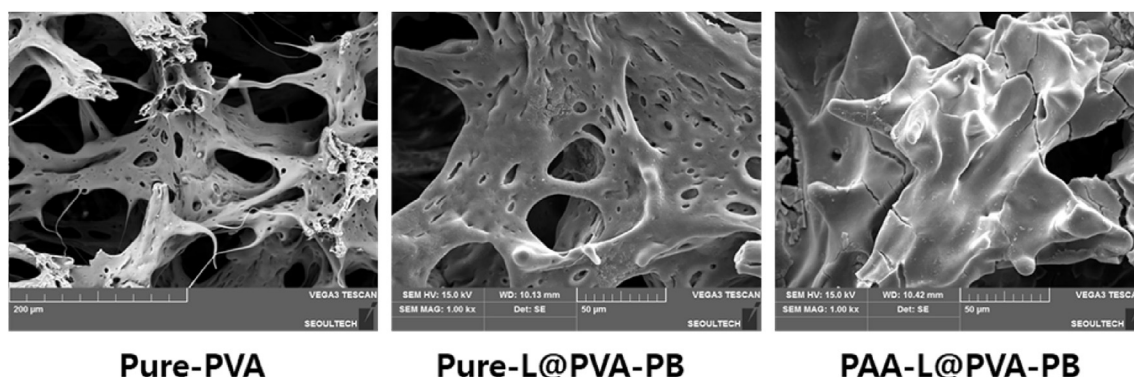


Fig. 3. SEM images of Pure-PVA (×500 magnification), Pure-L@PVA-PB and PAA-L@PVA-PB (×1000 magnification).

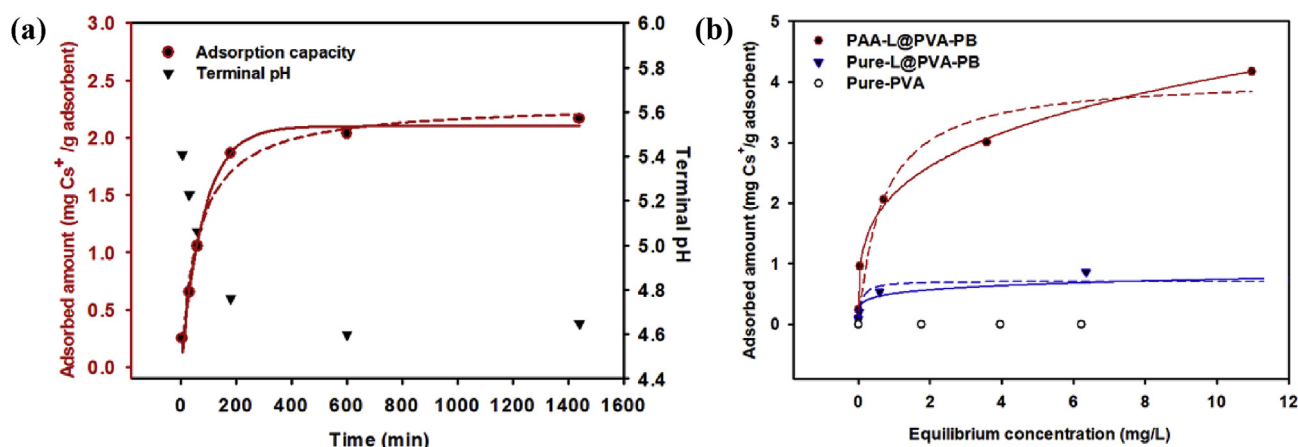


Fig. 4. (a) Kinetics of cesium adsorption of PAA-L@PVA-PB fitted by pseudo-first-order kinetic model (red line) and pseudo-second-order kinetic model (dashed red line). (Initial cesium concentration was 10 mg/L, PAA-L@PVA-PB dosage 2 g/L.) (b) Cesium adsorption isotherm of PVA based adsorbents (Pure-PVA, Pure-L@PVA-PB, and PAA-L@PVA-PB). Note that the adsorption experiments data have been fitted with isotherm models (dashed line: Langmuir, solid line: Freundlich). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

second-order kinetic constants were 0.0121 min^{-1} and $0.00683 \text{ g mg}^{-1} \cdot \text{min}^{-1}$, which is comparable to previous reports (Basu et al., 2018; Yang et al., 2018). Since the adsorption equilibrium could be achieved after 3–6 h of adsorption time, we used 24 h of adsorption time for further equilibrium experiments.

3.4.2. Adsorption isotherms study

Adsorption isotherm experiments were conducted to compare the cesium adsorption capacities of PAA-L@PVA-PB and Pure-L@PVA-PB as shown in Fig. 4 (b). A control experiment with Pure-PVA and PAA-PVA was also conducted in parallel. The pure-PVA and PAA-PVA did not show any cesium adsorption while Pure-L@PVA-PB and PAA-L@PVA-PB showed cesium adsorption capabilities. This result indicates that the cesium adsorption ability of the prepared PVA-PBs is due to the addition of PB, not the supporting materials, PVA, or grated PAA.

When the cesium adsorption capacities of Pure-L@PVA-PB and PAA-L@PVA-PB were compared, PAA-L@PVA-PB showed much higher cesium adsorption capacity compared to Pure-L@PVA-PB. The experimental data were fitted with Langmuir and Freundlich isotherms, and the obtained constants are listed in Table S4.

The obtained isotherm parameters are given in Table S4. The maximum adsorption capacities obtained with the Langmuir isotherms (q_m) of Pure-L@PVA-PB and PAA-L@PVA-PB were 0.713 and 4.082 mg/g, respectively. Therefore, it could be concluded that overall adsorption capacity was increased around 5.7 times by surface functionalization. Surface functionalization by AA provided higher stability of PB immobilization, which led to higher PB content in the composite, and finally higher adsorption capacity could be obtained due to the higher amount of PB. From the PB contents obtained from TGA analysis, the q_m could be normalized to the mass of the PB. The normalized q_m of PAA-L@PVA-PB was 26.17 mg/g PB. The normalized q_m seems to be lower than recent reports on Prussian blue based composites (Basu et al., 2018; Yang et al., 2018), however, these results cannot be compared directly because the previous reports comparably high aqueous cesium concentration in the range of few hundreds mg/L. We investigated adsorption capacity and kinetic in the lower concentration range (<15 mg/L), therefore, overall q_m is calculated lower than the previous studies. However, the comparably higher K_L value indicates higher affinity of cesium toward adsorbent, which is an advantage of immobilizing PB on the supporting materials not imbedding inside of supporting materials.

It has been commonly accepted that cesium adsorption on PB was driven by both of physisorption and chemisorption. Ishizaki et al. (2013) explained that the exclusive abilities of PB to adsorb hydrated cesium ions are caused by regular lattice spaces surrounded by cyanide-bridged metals. On the other hand, chemisorption was also considered for cesium adsorption by PB. A common PB with a formula of $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$ have many defect sites (vacant spaces) of $[\text{Fe}(\text{CN})_6]^{4-}$ filled with coordination and crystallization water molecules due to a high value of the number of waters of crystallization. The similar approach and explanation could be found in literature (Vipin et al., 2013; Takahashi et al., 2018).

The adsorption data were fitted with Langmuir isotherm as well as Freundlich isotherm in order to distinguish dominant adsorption isotherm, however, the R^2 value for both model are similar. Also, the trend was not consistent. For example, PAA-L@PVA-PB showed higher R^2 value for Freundlich while higher R^2 value was observed for Langmuir isotherm in case of Pure-L@PVA-PB. As discussed earlier, the adsorption test was performed in a low concentration range. Isotherm test under high cesium concentration will provide a more accurate result for discussion, but we can conclude that physisorption and chemisorption can occur simultaneously in our test condition.

3.4.3. Effect of initial pH

The influence of pH on cesium adsorption was investigated by changing the initial pH between 4 and 10. Fig. 5 (a) presents the initial pH and final pH after 24 h of adsorption experiments as well as the amount of adsorbed cesium for each pH condition. The final pH was lower in all cases, and the pH decrease was more significant when the initial pH was high. For example, when the initial pH was adjusted to 10, it decreased to 6.3 after 24 h. The decrease in pH was due to cation exchange, as explained earlier (Ishizaki et al., 2013).

The initial and final pH was closely linked to cesium ion adsorption capacity. The cesium adsorption capacity was around 2.3 mg/g at pH 4, but it gradually increased with increasing pH. Under alkaline conditions, at pH 8 and 10, cesium adsorption capacity was around 9.6 mg/g, which is 4.2 times higher than the adsorption at pH 4. It was reported that the Cs^+ is the predominant species at all pH range (Hamed et al., 2016), therefore, the speciation of Cs^+ in different pH range is not the main reason for the effect of pH. The lower performance under acidic conditions resulted from competition between protons (H^+) and cesium (Cs^+),

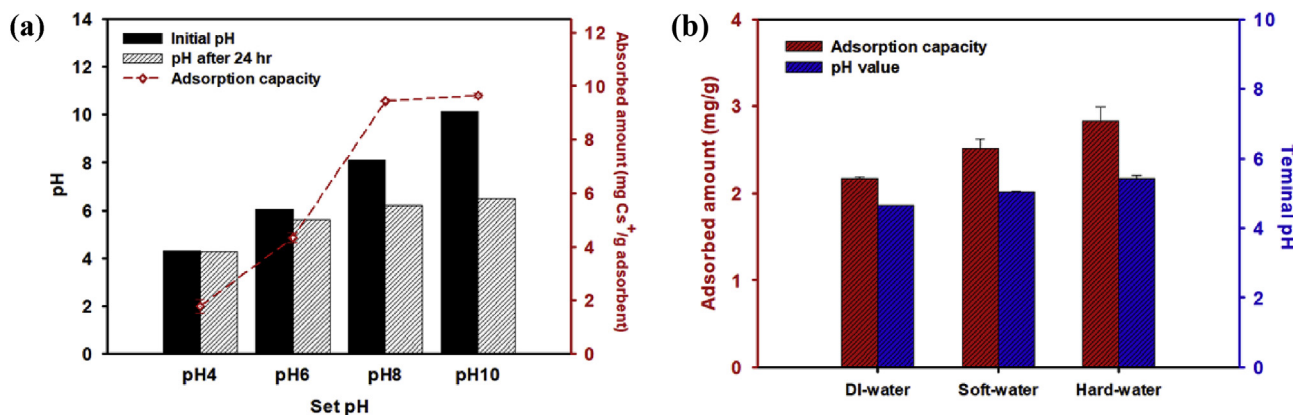


Fig. 5. (a) Cesium adsorption of PAA-L@PVA-PB in range of pH 4–10 and pH change during the adsorption experiment (b) Effect of water matrix on cesium adsorption by PAA-L@PVA-PB (initial cesium concentration 10 mg/L, PAA-L@PVA-PB dosage 2 g/L).

resulting in low adsorption capacity, as reported earlier (Feng et al., 2016; Yang et al., 2018). The influence of pH is high in the case of ion-exchange processes, especially for monovalent cations because of the ion-exchange competition. At low pH, ion exchange sites are mainly protonated, making them less available for cation. Low distribution coefficient (K_d) in low pH condition was reported in the above-mentioned study, which was explained that the presence of excess protons complete with the Cs^+ in the solution and preferably occupy the binding sites available (Hamed et al., 2016). When pH values increase, the sites become available for cation, leading to higher adsorption. (Vipin et al., 2013).

3.4.4. Effect of water matrix

The effect of the water matrix was investigated to evaluate the practical feasibility of the system when exposed to environmental media containing interfering substances. We used three types of water matrix for this study, deionized water, soft-water, and hard-water. Soft- and hard-water was a synthetic water matrix used to represent common surface water and groundwater. Both synthetic waters contained various cations including Ca^{2+} , Na^+ , and K^+ which can be competitors with Cs^+ , because they can be exchanged toward the PB.

The measured cesium adsorption capacity, as well as terminal pH, are presented in Fig. 5 (b). The amount of adsorbed cesium was around 2.1 mg/g under DI water condition, and this value increased to 2.5 mg/g and 2.9 mg/g for soft-water and hard-water, respectively. It is very interesting that adsorption capacity was not decreased even when competing cations were present in the water matrix.

It was reported that Cs-adsorption by PB was governed by three mechanisms, (a) mainly ion-exchange between Cs^+ and K^+ , (b) percolation of Cs^+ cations through vacancy sites from the surface, and (c) proton-exchange with Cs^+ . The excellent selectivity of Cs was mainly due to the complete dehydration of alkali cations in the K^+ exchange. Additionally, the energy difference in the hydrated states between K^+ (−351.8 kJ/mol) and Cs^+ (−306.4 kJ/mol) is the main driving force for K^+ exchange (Cs^+ adsorption) (Takahashi et al., 2018). The experimental results described above were very consistent with previous reports regarding the issue of selectivity (Jang et al., 2016).

The hard water showed the best performance in terms of cesium adsorption. These results should be carefully discussed in relation to the pH change observed during adsorption. As described earlier, pH was decreased by H^+ ions excreted into the solution during cesium adsorption via ion exchange, and lower pH is not favorable

to further cesium adsorption. The hard-water contains the highest amount of alkalinity, 2010 $\mu\text{eq/L}$, compared to DI water or soft-water (385 $\mu\text{eq/L}$), therefore, pH change was minimized. As shown in Fig. 5 (b), the final pH for hard water was 5.4 while the final pH for DI water and soft water were 4.6 and 5.0, respectively. The overall results indicate that the PAA-L@PVA-PB has high selectivity toward cesium, therefore, it has strong potential for practical application in a real water stream.

3.5. Column test

A continuous column test was conducted to demonstrate the feasibility of PAA-L@PVA-PB as a cesium adsorbent for a water treatment system. The column was constructed with 0.9 g of PAA-L@PVA-PB and a solution of 200 $\mu\text{g/L}$ cesium was added into the column at a flow rate of 2 mL/min. The first sample was collected right after the treated cesium solution came out of the upper outlet of the column. The cesium concentration in this initial sampling was 18 $\mu\text{g/L}$, indicating the given contact time (5 min) was not enough to adsorb all the cesium in the solution (Fig. 6). The effluent concentration increased gradually, then a linear increase in effluent concentration could be observed after the first 3 h of operation.

The column was operated for 42.5 h and a breakthrough was not fully monitored during this time of operation. The area above the concentration profile was used to calculate the overall amount of cesium during the experimental periods. The total removed amount of cesium was calculated to be 589.8 μg , which is 57.8% of the cesium added to the column, 1020 μg (0.002 L/min $\times$ 200 $\mu\text{g/L}$).

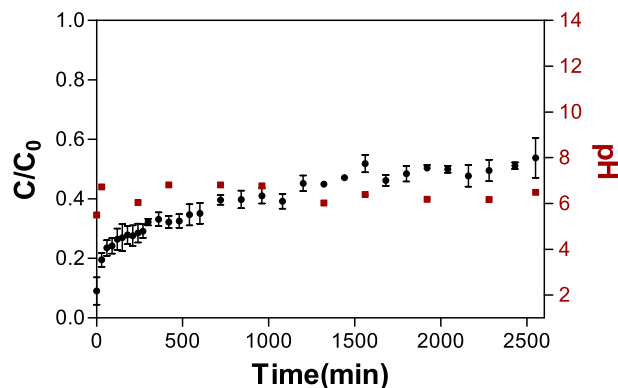


Fig. 6. Cesium concentration and pH in effluent of column operation (initial cesium concentration 40 $\mu\text{g/L}$, PAA-L@PVA-PB dosage 0.9 g; flow rate 2 mL/min).

L × 2550 min). The calculated cesium adsorption on PAA-L@PVA-PB was then calculated to be 0.655 mg/g, which is much lower than $q_{\max}$ obtained with the batch isotherm experiments. This is due to the nature of the column experiment, where the contact time was much shorter than in the batch test. Therefore, column performance can be expected to improve by controlling the flow rate and initial concentration of cesium. The effluent pH was stable during all of the experimental time periods. Overall, the column experimental results indicate the potential use of PAA-L@PVA-PB as a countermeasure for removing radioactive cesium from a contaminated water stream.

4. Conclusion

The focus of this study was to develop a method of preparing a filter type cesium adsorbent containing PB as the active adsorption material. The commercially available PVA sponge was selected as a supporting material to be a cost-effective methodology for preparing cesium adsorbent. PVA sponge was functionalized by reaction with acrylic acid to convert –OH functional groups to –COOH to enhance the immobilization and stability of the PB. The effect of functionalization on PB immobilization was demonstrated by washing experiments, FTIR and SEM-EDS analysis. Use of the LBL assembly method as a strategy for PB synthesis contributed to better stability, and the resulting material showed no PB release during washing. The adsorption kinetics and isotherms of the PAA-L@PVA-PB were further investigated. AA treatment enhanced adsorption capacity of PAA-L@PVA-PB. Its maximum cesium adsorption capacity was 4.082 mg/g, which was 5.7 times higher than Pure-L@PVA-PB, fitted by the Langmuir model. The adsorption behavior was sensitive to the initial pH and buffering. The adsorption capacity increased to 9.6 mg/g when it was tested in a slightly alkaline condition. The PB was highly selective toward cesium in experiments with different water matrices. Finally, the prepared PAA-L@PVA-PB was used to build a column for continuous adsorption testing. During 42.5 h of running time, an overall removal efficiency of 57.8% was obtained, corresponding to a calculated cesium adsorption capacity of 0.655 mg/g. The PAA-L@PVA-PB prepared in this study demonstrated the potential for practical application as a filter-type adsorbent for the remediation of radioactive cesium. The developed PAA-L@PVA-PB can be used to concentrate radioactive cesium in small volume and weight from the contaminated water, which makes it easy to handle for further radioactive waste disposal.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2019.03.101>.

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